DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

EFFECT OF SONICATION ON THE TREATMENT OF TOXIC AND REFRACTORY INDUSTRIAL WASTEWATERS

by
Rukiye ÖZTEKİN

January, 2011
İZMİR

EFFECT OF SONICATION ON THE TREATMENT OF TOXIC AND REFRACTORY INDUSTRIAL WASTEWATERS

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"EFFECT OF SONICATION ON THE TREATMENT OF TOXIC AND REFRACTORY INDUSTRIAL WASTEWATERS"** completed by **RUKİYE ÖZTEKİN** under supervision of **PROF. DR. DELİA TERESA SPONZA** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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Rukiye ÖZTEKİN

EFFECT OF SONICATION ON THE TREATMENT OF TOXIC AND REFRACTORY INDUSTRIAL WASTEWATERS

ABSTRACT

In the framework of this Ph.D. thesis, the treatability of toxic and refractory compounds in petrochemical (PCI), in olive mill (OMI) and in textile (TI) industry real wastewaters (wws) were investigated with sonication alone and with some additives. Sonication alone provided 96.90% PAHs, 92.48% COD_{dis}, 94.23% TOC in PCI ww after 150 min, at 60^{o}C, at 640 W, at 35 kHz, at 90.54 W/cm^2, respectively. With only sonication 83.77% color, 61.24% phenol and 70.52% TAAs yields were observed in OMI ww while 84.92% COD_{dis}, 83.22% TOC, 87.66% color removals were detected in TI ww for the operational conditions given above. The maximum removal efficiencies for PAHs, COD_{dis} were 99.68%, 99.68% at NaCl=15.00 g/l, respectively, in PCI ww. The maximum removals for COD_{dis}, color, phenol, TAAs, TFAs were 93.93%, 96.09%, 94.44%, 91.58%, 90.30% at TiO_2=20.00 mg/l, at NaCl=15.00 g/l, at TiO_2=20.00 mg/l, at DO=10.00 mg/l and at H_2O_2=2000 mg/l, respectively, in OMI ww. The maximum yields for COD_{dis}, color, TAAs were 99.37%, 97.65%, 80.16%, at Fe^{+3}=50.00 mg/l, at DO=10.00 mg/l, at H_2O_2=2000 mg/l, respectively, in TI ww.

The kinetic studies results showed that all the pollutant parameters in PCI, OMI, TI wws are sonodegraded according to the pseudo first order reaction kinetic both with only sonication and with some additives. Higher than 90.00% acute toxicity removals in PCI, OMI, TI wws were measured with Microtox (*Photobacterium phosphoreum*) and *Daphnia magna* (water flea) test organisms for the same operational conditions mentioned above. 201555.82 TL/year total cost, 0.03, 3.12 and 3.32 kWh / kg COD_{dis} specific energies are required for sonodegradation of OMI, PCI, TI wws, respectively, with only sonication. Total costs and specific energy values were lower than other AOPs. The results of this study showed that sonication can be used effectively to treat the toxic and refractory compounds in PCI, OMI, TI wws.

Keywords: Acute toxicity, ANOVA statistical analysis, color, cost analysis, olive mill, petrochemical, phenol, polycyclic aromatic hydrocarbons (PAHs), pseudo first order reaction kinetic, sonication, specific energy, textile, total aromatic amines (TAAs), total fatty acids (TFAs).

SES DALGALARININ TOKSİK VE ZOR AYRIŞABİLEN ENDÜSTRİYEL ATIKSULARIN ARITIMINA ETKİSİ

ÖZ

Bu doktora tezi kapsamında, petrokimya (PEA), zeytin altı (ZEA) ve tekstil endüstrisi (TEA) gerçek atıksularındaki toksik ve zor ayrışabilen bileşiklerin arıtılabilirliği tek başına sonikasyon prosesi ve bazı kimyasal maddelerin ilavesiyle incelenmiştir. Tek başına sonikasyon prosesi ile PEA'da 150 dakika sonikasyon süresi sonunda, 60^oC'de, 640 W'lık bir güçte, 35 kHz'lik bir frekansta ve 90.54 W/cm^2 'lik bir sonikasyon şiddetinde %96.90 poliaromatik hidrokarbon (PAH), %92.48 $KOİ_{çözünmüş}$ ve %94.23 TOK giderme verimleri elde edilmiştir. Aynı işletme koşullarında tek başına sonikasyonla ZEA'da %83.77 renk, %61.24 fenol, %70.52 toplam aromatik aminler (TAA) giderimleri elde edilmiş, TEA'da ise %84.92 $KOİ_{çözünmüş}$, %83.22 TOK, %87.66 renk giderim verimleri bulunmuştur. PEA'da, maksimum PAH ve $KOİ_{çözünmüş}$ giderim verimleri 15.00 g/l NaCl'de, sırasıyla, %99.68 ve %99.68 olarak bulunmuştur. ZEA'da maksimum $KOİ_{çözünmüş}$, renk, fenol, TAA, toplam yağ asitleri (TYA) giderimleri, sırasıyla, %93.93, %96.09, %94.44, %91.58, %90.30 olarak 20.00 mg/l TiO_2'de, 15.00 g/l NaCl'de, 20.00 mg/l TiO_2'de, 10.00 mg/l çözünmüş oksijen'de ve 2000 mg/l H_2O_2 konsantrasyonunda bulunmuştur. TEA'da maksimum $KOİ_{çözünmüş}$, renk, TAA giderimleri, sırasıyla, %99.37, %97.65, %80.16 olup Fe^{+3}=50.00 mg/l'de, çözünmüş oksijen=10.00 mg/l'de ve H_2O_2=2000 mg/l'de bulunmuştur.

Kinetik çalışmalar PEA, ZEA, TEA atıksularındaki bütün kirletici parametrelerin tek başına sonikasyon prosesi kullanıldığında ve ilave bazı kimyasal maddeler olduğunda yalancı birinci derece reaksiyon kinetiğine göre parçalandığını göstermiştir. %90.00 üzerinde akut toksisite giderimleri, PEA, ZEA, TEA atıksularında Mikrotox (*Photobacterium phosphoreum*) ve *Daphnia magna* (su piresi) test organizmalarıyla yukarıda belirtilen aynı işletme koşullarında ölçülmüştür. 201555.82 TL/yıl toplam maliyet, 0.03, 3.12 ve 3.33 kWh / kg KOİ$_{\text{çözünmüş}}$ özgül enerjileri sırasıyla, ZEA, PEA, TEA'da tek başına sonikasyonla hesaplanmıştır. Toplam maliyetler ve özgül enerji değerleri diğer ileri arıtım yöntemlerinden (İAY) daha düşüktür. Bu çalışma sonuçları, sonikasyonun, PEA, ZEA, TEA atıksularındaki toksik ve zor ayrışabilen bileşiklerin arıtımında etkili bir şekilde kullanılabileceğini göstermektedir.

Anahtar Kelimeler: Akut toksisite, ANOVA istatistiksel analizi, renk, maliyet analizi, zeytin işleme, petrokimya, fenol, poliaromatik hidrokarbonlar (PAH), yalancı birinci mertebe reaksiyon kinetiği, ses dalgalarıyla arıtım, özgül enerji, tekstil, toplam aromatik aminler (TAA), toplam yağ asitleri (TYA).

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CHAPTER ONE
INTRODUCTION

1.1 Introduction

The chemical and biological effects of ultrasound were first reported by Alfred Lee Loomis as early as 1927 (Suslick, 1989). In recent years, ultrasound irradiation has received increasing attention for the destruction of organic pollutants in waters and wastewaters (Thompson & Doraiswamy, 1999). The process comprises cyclic formation, growth and subsequent collapse of microbubbles occurring in extremely small intervals of time, and release of large quantities of energy over a small location. Sonochemical degradation in aqueous phase involves several reaction pathways and zones such as pyrolysis inside the bubble and/or at the bubble–liquid interface and hydroxyl radical-mediated reactions at the bubble–liquid interface and/or in the liquid bulk (Thompson & Doraiswamy, 1999, 2000). The relative importance of the various mechanisms involved primarily depends on the physicochemical properties of the pollutants in question; the process is more selective towards hydrophobic and volatile species that can be degraded easily via pyrolytic reactions, while hydrophilic and less volatile compounds are degraded slowly via hydroxyl radical-induced reactions (Suslick, 1989).

Numerous works have demonstrated the efficiency of ultrasounds toward the degradation of a wide variety of organic compounds including estrogens [for instance, 17b-estradiol (b-E2), estrone (E1), 17a-ethynylestradiol (EE2)], endocrine-disrupting chemicals (EDCs) (such as bisphenol A), pharmaceuticals, vegetable oils, nitroorganics (NOCs), trihalomethanes (THMs), aliphatic hydrocarbons, naphthenic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) organochlorine pesticides (OCPs), sugars, tannins, pectin, lipids, polyphenols and polyalcohols, etc. present in relatively dilute aqueous solution and it appears that the applications of this novel means of reaction in environmental remediation and pollution prevention is unlimited (Adewuyi, 2001; Beens et al., 2000; Colussi et al., 1996, 1999; David et al., 1998; Drijvers et al., 1999; Kotronarou et al., 1991; Mason, 1998; Mason et al., 2003; Okuno et al., 2000; Pétrier et al., 1994, 1998; Psillakis et al., 2004; Sanchez-Prado et al., 2008; Serpone et al. 1994; Torres et al., 2007, 2008a, 2008b; Vassilakis et al., 2004).

The intensification of the organic matter solubilization induced by the ultrasonic action, can lead to an increase of the bioavailability of some micropollutants to the degrader consortium (Tiehm & Neis, 1999, 2005; Tiehm, 2001). Nevertheless, it is of great interest to study such ubiquitous compounds (PAHs, THMs, OCPs, EDCs, NOCs, etc.), because they are widespread in all parts of the environment; air, water, soils and sediments (Beens et al., 2000; Broman et al., 1991; Colussi et al., 1999; Jones et al., 1989; Marvin et al., 2000; Menzie et al., 1992).

An important refractory family compounds in petrochemical industry wastewater (PCI ww) are the PAHs, which have a hydrophobic character, a low water solubility and less volatile with increasing molecular weight that limit their biodegradation, their hazard potential can be relatively high, thus making their presence in the water cycle both an acute and a chronic risk to human health and environmental quality (Suslick et al., 1986; Wheat & Tumeo, 1997). Most of the time, compounds studied are hydroxylated and/or halogenated substituted aromatics or hydrocarbons, having a water solubility in a mg/l range. Only a few works concern the degradation of compounds such as PAHs [anthracene (ANT), benzo[k]fluoranthene (BkF), pyrene (PY), benzo[a]pyrene (BaP), etc.] in PCI ww for which solubilities are in the ng/ml range (Cataldo, 2000; David & Riguier, 2009; Laughrey et al., 2001; Little et al., 2002; Meckes et al., 1996; Psillakis et al., 2003, 2004; Taylor Jr. et al., 1999; Wheat & Tumeo, 1997). These compounds have been listed by the United States Environmental Protection Agency (US. EPA) and the European Unions European Economic Community (EU EEC) since 1979 and 1980, respectively, as priority pollutants (Banjoo & Nelson, 2005; Callahan et al., 1979; EU EEC, 1994; Taylor Jr. et al., 1999; US EPA Pollution Control Agency, 2006; Wheat & Tumeo, 1997). Due to associated health concerns, some PAHs are possible or probable human carcinogen such as BaP and all PAHs having four condensed rings (Kim Oanh et al., 2002). The distribution, fate and destruction of these pollutants are then of special significance, especially in water. PAHs are ubiquitous environmental pollutants with mutagenic properties, which have not been included in the Turkish guidelines for treated waste monitoring programmes (Papadaki et al., 2004).

As a consequence of their strongly hydrophobic properties and their resistance to biodegradation, PAHs are not always quantitatively removed from wastewaters by activated sludge treatments, which very efficiently relocate them into treated effluents. In recent years, considerable interest has been shown in the application of ultrasound as an AOPs for the treatment of hazardous contaminants, such as PAHs in water (Huang et al., 2002; Laughrey et al., 2001; Suslick, 2000). The sonication process is capable of effectively degrading PAHs present in dilute solutions, typically in the micro and nano ranges. PAHs were degradated to less toxic and less carcinogenic products and by-products with addition some catalysts during ultrasonic treatment. However, it is notable that none of the studies report the use of ultrasound for the removal of more hydrophobic PAHs compounds typically found in effluents of PCI ww.

In Izmir-Turkey, the petrochemical industry treatment plant wastewaters are treated with conventional activated sludge systems and approximately seventeen hydrophilic, less and more hydrophobic PAHs [naphthalene (NAP), acenaphthylene (ACL), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), ANT, carbazole (CRB), fluoranthene (FL), PY, benz[*a*]anthracene (BaA), chrysene (CHR), benz[b]fluoranthene (BbF), BkF, BaP, indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA) and benzo[*g,h,i*]perylene (BghiP)]are released into receiving bodies, since low COD (56.00%) and PAHs (39.00–42.00%) removal efficiencies are observed. Aerobic activated treatment systems are not equipped for PAHs removal efficiently. PAHs residues have been frequently detected in rivers and lakes that receive sewage and industrial effluents supplied by those surface waters (Psillakis et al., 2004).

Olive mill industry wastewater (OMI ww) is becoming a serious environmental problem, due to its high organic chemical oxygen demand (COD) and biochemical oxygen demand (BOD) concentrations, phytotoxic properties and because of its resistance to biodegradation due to its high molecular–weight polyphenols (tannins, antocyanins, and catechins) and organic contents (including sugars, tannins, pectin, lipids, polyphenols and polyalcohols) (Borja et al., 1997; Ergüder et al., 2000; Hamdi & Ellouz, 1993). On the other hand, monomeric phenols exhibit phytotoxic (Capasso et al., 1992) and antimicrobial activities (Borja et al., 1997; Hamdi & Ellouz, 1993; Perez et al., 1992) while polymeric phenols have a lignin-like structure as their most recalcitrant fraction and are mainly responsible for the typical color of OMI ww and odor nuisance (Hamdi & Ellouz, 1993; Perez et al., 1987). Due to the current lack of appropriate alternative technologies to treat OMI ww, much of the OMI ww in the Mediterranean area is discharged directly into rivers and sea (Borja et al., 2006). OMI ww were stored in evaporation ponds, where anaerobic conditions are quickly established in the evaporation ponds. Evaporation ponds were caused to malodours, the breading of insects and the risks of surface and groundwater contamination (Borja et al., 1997, 2006; Greco Jr. et al., 1999; Tardioli et al., 1997).

Because of the associated environmental problems and potential hazards, several OMI ww treatment technologies such as mechanical, physical, chemical, biological and thermal methods have been developed aiming at the removal of the main toxic organic compounds prior to discharge (Atanassova et al., 2005a, 2005b). An advisable single treatment method that is economically viable has not been suggested yet for the treatment of OMI ww. OMI ww treatment usually comprises a physico-chemical method aiming at the removal of organic matter from the liquid phase (Chemat et al., 2004a, 2004b). However, these processes suffer from serious drawbacks such as high cost, low efficiency and sludge disposal problems. Therefore, research efforts have been directed towards the development of efficient treatment technologies including various advanced oxidation processes (AOPs) (such as, sonication process) and biological processes. In addition to this, the presence of some classes of inhibitory and/or toxic compounds such as polyphenols and lipids makes OMI ww inappropriate for direct biological treatment. However, some bacteria (for example, methanogens) are particularly sensitive to the excess of inhibitory and/or toxic compounds such as the phenolic ones, thus limiting the performance of anaerobic digestion (Benitez et al., 1997; Capasso et al., 1992, 1994; Ince et al., 2009; Priego-Capote et al., 2004). Consequently, several other treatment methods have been investigated for OMI ww treatment. Given the specific treatment objectives, AOPs such as sonication process may be used either for the complete mineralization of all pollutants to CO_2, H_2O and mineral salts, or for the selective removal of the more bioresistant pollutants and their conversion to biodegradable intermediates.

Excess use of various dyes in the TI ww has led to the severe surface water and groundwater contamination by releasing the toxic and colored effluents (Salem & El-Maazawi, 2000). The increasing amount of colored compounds are resistant to the biological destruction (Fung et al., 1999, 2000a, 2000b; Sohrabi & Ghavamia, 2008). Most textile dyes are photolytically stable and refractory towards chemical oxidation (Arslan & Balcioglu, 2001) and these characteristics render them resistant towards decomposition by conventional biochemical and physico-chemical methods. Degradation of dye effluents has therefore received increasing attention. Due to the large numbers of aromatic compounds present in many dye molecules and stability of modern dye, sometimes the conventional treatment methods are ineffective for decolorization and mineralization the TI ww (Entezari & Soltani, 2008). Sonolysis has been used for the decolourization and degradation of dyes effectively (Priego-Capote et al., 2006). The mechanism proposed for the sonochemical processes is usually based on the formation of short-lived radical species generated in violent cavitation events (Entezari & Soltani, 2008).

The potential of ultrasound to destroy organic matter is based not only on thermolytic cleavage of water to yield OH and H radicals ($OH^{\bullet}$ and $H^{\bullet}$), but also on that of dissolved gases and volatile solutes to lead to a variety of other reactive species that facilitate oxidation reactions (Suslick, 1990; Velegraki et al., 2006). In addition, ultrasound enhances mass transfer of chemical reagents in water, improves surface properties of solid particles and accelerates the rate of chemical reactions, thus reducing the consumption of chemicals and generation of waste sludge (Ince et al., 2001; Mason, 1998). The addition of soluble and insoluble reagents to an ultrasonic reactor promotes the formation of cavitation nuclei and radical species and thus the rate of sonochemical reactions (Hung et al., 2000; Mahamuni & Pandit, 2006; Wang, L. et al., 2007).

1.2 The Reasons of this Ph. D. Study

The studies performed until now contained only the removals of some hydrophylic PAHs such as PHE, NAP, ACT, ACL, PY, ANT, FL with sonication assisted by air, N_2(g), O_2(g), TiO_2, HCO_3^{-1}, NaCl, Fe^{+2}, Fe^{+3}, pH, H_2O_2, $S_2O_8^{-2}$, 1-butanol (C_4H_9OH) in synthetic wastewaters (Huang et al., 2002; Busetti et al., 2006; Pathak et al., 2008; David, 2009). In other words, the removal of PAHs by sonication has only been performed in synthetic wastewaters until now. No study was found investigating the removal of less hydrophobic PAHs (for example, BaA, CHR and BbF) and more hydrophobic PAHs (such as, BkF, BaP, IcdP, DahA and BghiP) in a real PCI ww with only sonication and with the addition of some additives [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH, $S_2O_8^{-2}$] throuhout sonication process. The effects of sonication on the removal of the individual hydrophylic (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL and PY], less hydrophobic (BaA, CHR and BbF) and more hydrophobic (BkF, BaP, IcdP, DahA and BghiP) PAHs have not been investigated for a real PCI ww before. No study was found investigating the removals of the sonodegradation by-products of more hydrophobic PAHs in a synthetic or in a real PCI ww with only sonication and with the addition of some additives [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH, $S_2O_8^{-2}$].

1. The removal kinetics of more hydrophobic PAHs with sonication in a synthetic or in a real PCI ww with only sonication and with the addition of some additives were not investigated in recent literature. The kinetic studies performed with less hydrophobic PAHs were limited with only sonication, air, N_2(g), O_2(g), H_2O_2, TiO_2, Fe^{+2}, Fe^{+3}.

2. No study was found investigating the toxicity responses of less and more hydrophobic PAHs in a synthetic or in a real PCI ww to bacteria (*Photobacterium phosphoreum*) in Microtox test and to water flea (*Daphnia magna*) in *Daphnia magna* acute toxicity tests with only sonication and with the addition of some additives mentioned above.

3. No study was found evaluating the cost analysis, specific energy estimation in a synthetic or in a real PCI ww with only sonication and with the addition of some additives [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH, $S_2O_8^{-2}$] throughout sonication process.

4. No study was found investigating the removals of TAAs, TFAs, color, total phenol in a real OMI ww with only sonication and with the addition of some additives mentioned above.

5. No study was found investigating the toxicity responses of a real OMI ww to bacteria (*Photobacterium phosphoreum*) in Microtox test and to water flea (*Daphnia magna*) in *Daphnia magna* acute toxicity tests with only sonication and with the addition of some additives mentioned above.

6. No study was found evaluating the cost analysis and the specific energy estimations in a real OMI ww with only sonication and with the addition of some additives [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] before and after sonication process.

7. No study was found investigating the removal of TAAs, the removal kinetics of COD_{dis}, TOC, color and TAAs in a synthetic or in a real TI ww with only sonication and with the addition of some additives mentioned above.

8. No study was found investigating the toxicity responses and the specific energy estimations of a synthetic or a real TI ww to bacteria (*Photobacterium phosphoreum*) in Microtox test and to water flea (*Daphnia magna*) in *Daphnia*

magna acute toxicity tests with only sonication and with the addition of some additives.

The lacks in the literature mentioned above were performed in the framework of this Ph.D. study.

1.3 The Objectives of this Ph.D. Study

The general objective of this Ph.D. thesis was to evaluate the performance of the sonication process on the treatment efficiencies of a real PCI ww, a real OMI ww and a real TI ww. The specific objectives of this study are as follows:

1. To determine the removal efficiencies in a real PCI ww, based on PAHs, $COD_{dissolved}$ and total organic carbon (TOC), with only sonication and with the addition of some additives [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] throughout sonication process;

    1.a. To determine the sonodegradation by-products of PAHs in a real PCI ww with only sonication and with the addition of some chemicals [O_2(g), H_2O_2 and TiO_2] after sonication process.

    1.b. To determine the PAH removal kinetics in a real PCI ww with only sonication and with the addition of some additives [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] during sonication process.

    1.c. To determine the acute responces of a real PCI ww to bacteria (*Photobacterium phosphoreum*) in Microtox test and to water flea (*Daphnia magna*) in *Daphnia magna* acute toxicity tests with only sonication and with the addition of some chemicals [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH]. To investigate the acute toxicity effects of only additives [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] to the *Daphnia magna* and Microtox acute toxicity tests without sonication.

1.d. To evaluate the cost analysis and estimate the specific energy in a real PCI ww with only sonication and with the addition of some chemicals [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH].

2. To determine the removal efficiencies in a real OMI ww, based on COD_{dis}, TOC, color, total phenol, total aromatic amines (TAAs) and total fatty acids (TFAs), with only sonication and with the addition of some chemicals [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] by sonication process;

2.a. To determine the COD_{dis}, TOC, color, total phenol, TAAs and TFAs removal kinetics in a real OMI ww with only sonication and with the addition of some chemicals [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH]; to determine the sonodegradation metabolites of phenol in a real OMI ww with only sonication.

2.b. To determine the acute responces of real OMI ww to bacteria (*Photobacterium phosphoreum*) in Microtox test and to water flea (*Daphnia magna*) in *Daphnia magna* acute toxicity tests with only sonication and with the addition of some chemicals [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH]. To investigate the acute toxicity effects of only additives [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] to the *Daphnia magna* and Microtox acute toxicity tests without sonication.

2.c. To evaluate the cost analysis and estimate the specific energy in real OMI ww with only sonication and with the addition of some chemicals [air, N_2(g),

O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] .

3. To determine the removal efficiencies in real TI ww, based on COD_{dis}, TOC, color and TAAs with only sonication and with the addition of some chemicals [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] through sonication process; to determine the COD_{dis}, TOC, color and TAAs removal kinetics with only sonication and with the addition of some chemicals [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH].

3.a. To determine the acute responces of real TI ww to bacteria (*Photobacterium phosphoreum*) in Microtox test and to water flea (*Daphnia magna*) in *Daphnia magna* acute toxicity tests with only sonication and with the addition of some chemicals [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH]. To investigate the acute toxicity effects of only additives [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] to the *Daphnia magna* and Microtox acute toxicity tests without sonication.

3.b. To evaluate the cost analysis and estimate the specific energy in a real OMI ww with only sonication and with the addition of some chemicals [air, N_2(g), O_2(g), acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH].

This Ph.D. thesis consisted of seven Chapters. An overview, the reasons of this Ph.D. study and the objectives of this Ph.D. study were presented in Chapter 1. Chapter 2 was summarized the properties of wastewaters in this study. Chapter 3 was reviewed the concepts and previous studies related to this work. The experimental works and the data analysis procedures were explained in Chapter 4. Results and discussions were presented in Chapter 5. Chapter 5 was summarized as follows:

1. The treatabilities of PAHs, COD_{dis} and TOC compounds in a real PCI ww; COD_{dis}, TOC, color, total phenol, TAAs and TFAs compounds in a real OMI ww; and COD_{dis}, TOC, color and TAAs compounds in a real TI ww were investigated with only sonication and with the addition of some chemicals [air, $N_2(g)$, $O_2(g)$, acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH].

2. The sonodegradation by-products of PAHs in a real PCI ww were determined with only sonication and the addition of some chemicals [$O_2(g)$, H_2O_2 and TiO_2] before and after sonication process. Also, the phenolic metabolites in a real OMI ww were determined throughout sonication.

3. Three different kinetic models (pseudo zero order, pseudo first order and pseudo second order) were applied to the experimental data for PAH removals in a real PCI ww; for COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals in a real OMI ww; for COD_{dis}, TOC, color and TAAs yields in a real TI ww with only sonication and with the addition of some chemicals [air, $N_2(g)$, $O_2(g)$, acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH].

4. The acute responces of real PCI ww, real OMI ww and real TI ww to bacteria (*Photobacterium phosphoreum*) in Microtox test and to water flea (*Daphnia magna*) in *Daphnia magna* acute toxicity tests were determined with only sonication and with the addition of some chemicals [air, $N_2(g)$, $O_2(g)$, acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] before and after sonication process..

5. The evaluation of cost analysis and the specific energy estimations in a real PCI ww, in a real OMI ww and in a real TI ww were investigated with only sonication and with the addition of some chemicals [air, $N_2(g)$, $O_2(g)$, acids or alkaline chemicals, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH] after sonication process. Chapter 6 included the conclusions and recommendations while Chapter 7 contained the appendices of the Ph.D. thesis.

CHAPTER TWO
PROPERTIES OF THE WASTEWATER

2.1 Properties of Petrochemical Industry Wastewater (PCI ww)

The properties of petrochemical industry wastewaters are given in Table 2.1 (Benito-Alcázar et al., 2010; Demirci et al., 1998; Khaing, T.-H. et al., 2010; Ravanchi et al., 2009).

Table 2.1 The properties of petrochemical industry wastewaters from literature (Benito-Alcázar et al., 2010; Demirci et al., 1998; Khaing, T.-H. et al., 2010; Ravanchi et al., 2009).

Parameters	Values	Parameters	Values
pH	6.40–10.40	PO_4–P	8.50–10.10 mg/l
DO	1.50–2.18 mg/l	SO_4	15.00–20.00 mg/l
ORP	24.00–40.00 mV	phenols	8.00–15.00 mg/l
COD_{total}	150–1600 mg/l	S_2	50.00–100 mg/l
COD_{dis}	100–1300 mg/l	Cd	3.00–4.00 mg/l
TOC	24.80–800 mg/l	Cr	4.00–5.50 mg/l
Influent PAHs	1000–3000 ng/ml	Ni	20.00–30.00 mg/l
TSS	30.00–1200 mg/l	Pb	10.00–15.00 mg/l
TDS	636–2084 mg/l	Zn	300–450 mg/l
TVSS	200–780 mg/l	Fe	2000–3000 mg/l
BOD_5	350–750 mg/l	Mn	1.00–2.00 mg/l
BOD_5/COD_{dis}	0.40–0.80	Co	0.50–1.50 mg/l
COD/ BOD_5	1.20–2.50	Mg	40.00–50.00 mg/l
Total N	4.10–33.40 mg/l	K	70.00–150 mg/l
NH_4-N	1.50–132 mg/l	oil–grease	40.00–3000 mg/l
NO_2-N	0.04–0.06 mg/l	turbidity	3.88–159.4 NTU
NO_3-N	1.50–2.50 mg/l	conductivity	4.50–5.50 mS/cm
Total P	0.10–14.00 mg/l	hardness	121–154 $CaCO_3$ mg/l

Petrochemicals are chemical products derived from petroleum. Some chemical compounds made from petroleum are also obtained from other fossil fuels such as coal or natural gas, or renewable sources such as corn or sugar cane.

Two petrochemical classes are olefins including ethylene and propylene, and aromatics including benzene, toluene and xylene isomers. Oil refineries produce olefins and aromatics by fluid catalytic cracking of petroleum fractions. Chemical plants produce olefins by steam cracking of natural gas liquids like ethane and propane. Aromatics are produced by catalytic reforming of naphtha. Olefins and aromatics are the building blocks for a wide range of materials such as solvents, detergents and adhesives. Olefins are the basis for polymers and oligomers used in plastics, resins, fibers, elastomers, lubricants and gels (Matar & Hatch, 2001).

Global ethylene and propylene production are ≈ 110 million tonnes and ≈ 65 million tonnes per annum respectively. Aromatics production is ≈ 70 million tonnes. The largest petrochemical industries are located in the USA and Western Europe; however, major growth in new production capacity is in the Middle East and Asia. There is substantial inter-regional petrochemical trade (Matar & Hatch, 2001).

Primary petrochemicals are divided into three groups depending on their chemical structure (Matar & Hatch, 2001):

- Olefins includes ethylene, propylene and butadiene. Ethylene and propylene are important sources of industrial chemicals and plastics products. Butadiene is used in making synthetic rubber.

- Aromatics includes benzene, toluene and xylenes. Benzene is a raw material for dyes and synthetic detergents, and benzene and toluene for isocyanates MDI and TDI used in making polyurethanes. Manufacturers use xylenes to produce plastics and synthetic fibers.

- Synthesis gas is a mixture of carbon monoxide and hydrogen used to make ammonia and methanol. Ammonia is used to make the fertilizer urea and methanol is used as a solvent and chemical intermediate.

2.1.1 List of Significant Petrochemicals and their Derivatives

The following is a partial list of the major commercial petrochemicals (such as ethylene, propylene, benzene, toluene and xylene) and their derivatives reported by Matar & Hatch (2001) are shown in Tables (2.2), (2.3), (2.4), (2.5) and (2.6).

Table 2.2 Chemicals and their derivatives produced from ethylene (Matar & Hatch, 2001).

Ethylene is the simplest olefin; uses as a chemical feedstock and ripening hormone			
	polyethylene; polymerized ethylene		
	ethanol; via ethylene hydration (chemical reaction adding water) of ethylene		
	ethylene oxide; via ethylene oxidation		
		ethylene glycol; via ethylene oxide hydration	
			engine coolant; ethylene glycol, water and inhibitor mixture
			polyesters; any of several polymers with ester linkages in the backbone chain
		glycol ethers; via glycol condensation	
		ethoxylates	
	vinyl acetate		
	1,2–dichloroethane		
		trichloroethylene	
		Tetrachloroethylene (perchloroethylene) uses as a dry cleaning solvent and degreaser	
		vinyl chloride; monomer for polyvinyl chloride (PVC)	
			PVC is type of plastic uses for piping, tubing, other things

The chemicals and their derivatives produced from ethylene are given in Figure 2.1.

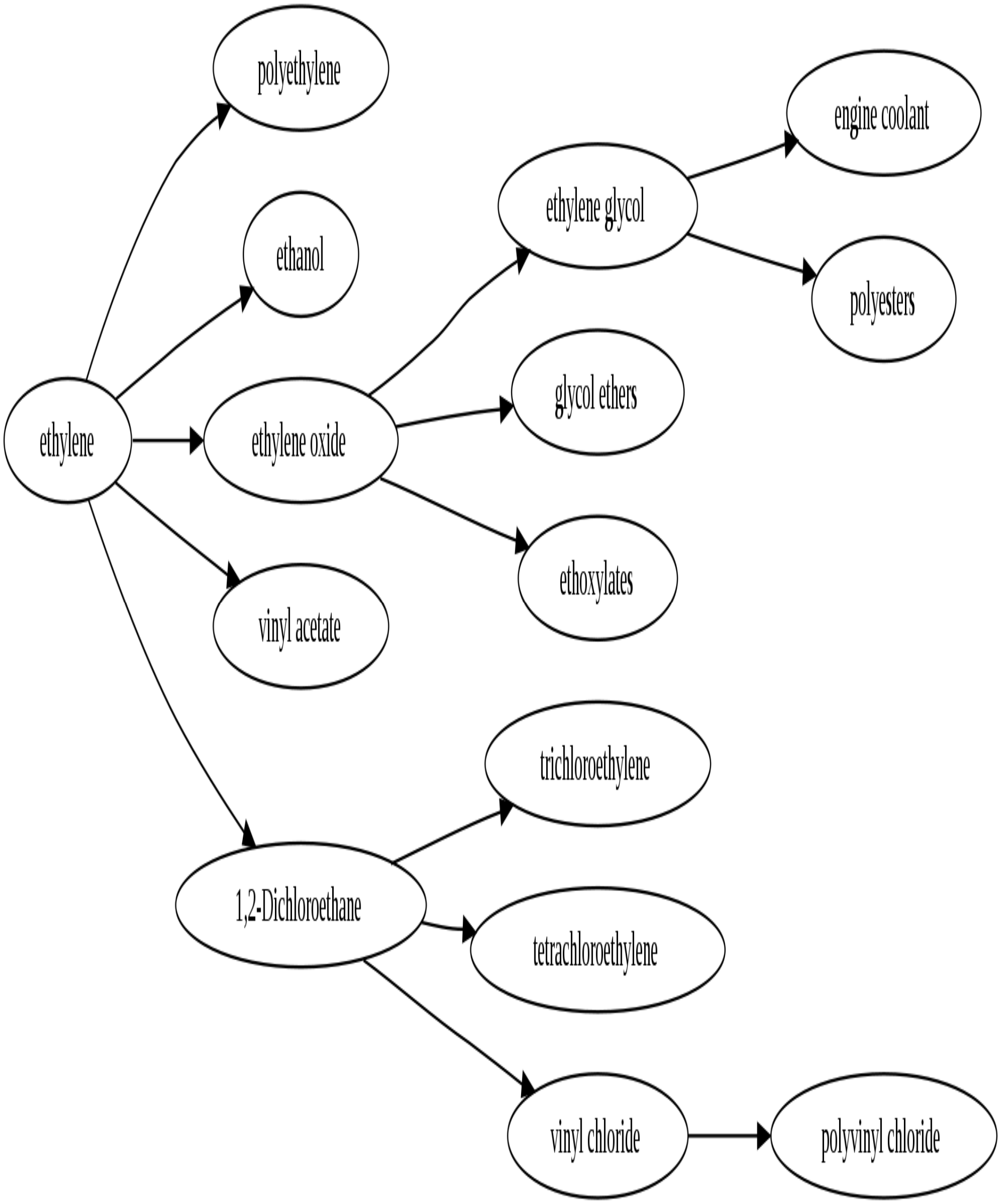


Figure 2.1 Chemicals and their derivatives produced from ethylene (Matar & Hatch, 2001).

The chemicals and their derivatives produced from propylene are tabulated in Table 2.3.

Table 2.3 Chemicals and their derivatives produced from propylene (Matar & Hatch, 2001).

	propylene; uses as a monomer and a chemical feedstock			
		isopropyl alcohol–2–propanol; often uses as a solvent or rubbing alcohol		
		acrylonitrile; useful as a monomer in forming orlon, ABS (acrylonitrile-butadiene-styrene)		
		polypropylene; polymerized propylene		
		propylene oxide		
			polyol; used in the production of polyurethanes	
			propylene glycol; used in engine coolant and aircraft deicer fluid	
			glycol ethers; from condensation of glycols	
		acrylic acid		
			acrylic polymers	
		allyl chloride		
			epichlorohydrin–chloro–oxirane; used in epoxy resin formation	
				epoxy resins; a type of polymerizing glue from bisphenol A, epichlorohydrin and some amine
C_4 hydrocarbons; a mixture consisting of butanes, butylenes and butadienes				
	isomers of butylene; useful as monomers or co-monomers			
		isobutylene; feed for making methyl *tert*-butyl ether (MTBE) or monomer for copolymerization with a low percentage of isoprene to make butyl rubber		
	1,3–butadiene (or buta–1,3–diene); a diene often used as a monomer or co-monomer for polymerization to elastomers (polybutadiene, styrene-butadiene rubber) or a plastic (ABS)			
		synthetic rubbers; synthetic elastomers made of any one or more of several petrochemical (usually) monomers (1,3–butadiene, styrene, isobutylene, isoprene, chloroprene); Elastomeric polymers are often made with a high percentage of conjugated diene monomers (1,3–butadiene, isoprene, chloroprene		
higher olefins				
	polyolefins such poly-alpha-olefins which are used as lubricants			
	alpha-olefins; used as monomers, co-monomers and other chemical precursors. For example, a small amount of 1–hexane can be copolymerized with ethylene into a more flexible form of polyethylene.			
	other higher olefins			
	detergent alcohols			

The chemicals and their derivatives produced from propylene are shown in Figure 2.2.

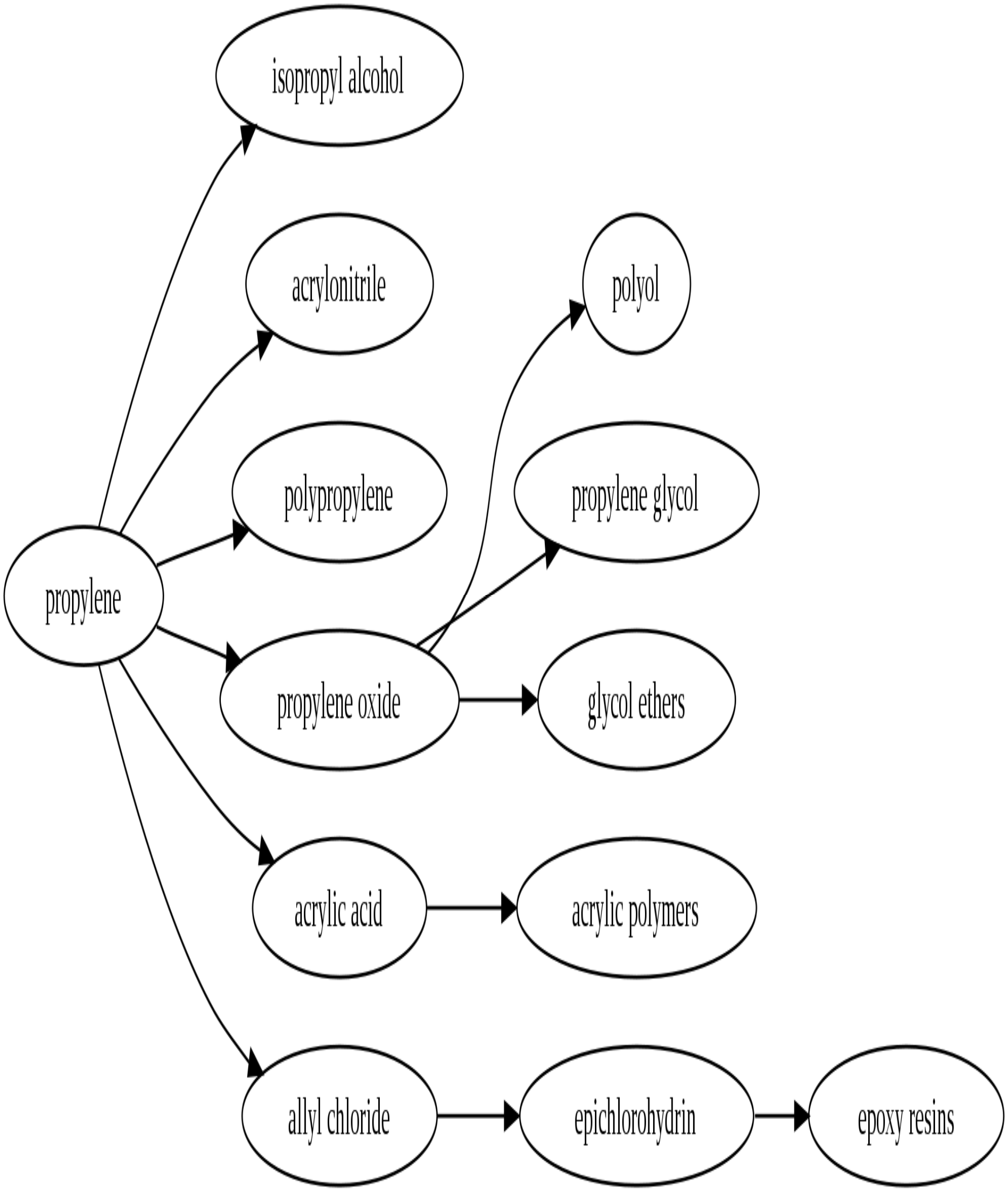


Figure 2.2 Chemicals and their derivatives produced from propylene (Matar & Hatch, 2001).

The chemicals and their derivatives produced from benzene are seen in Table 2.4.

Table 2.4 Chemicals and their derivatives produced from benzene (Matar & Hatch, 2001).

benzene; the simplest aromatic hydrocarbon				
	Ethylbenzene made from benzene and ethylene			
		Styrene made by dehydrogenation of ethylbenzene; used as a monomer		
			polystyrenes; polymers with styrene as a monomer	
	cumene (Isopropylbenzene); a feedstock in the cumene process			
		phenol (hydroxybenzene); often made by the cumene process		
		acetone (dimethyl ketone); also often made by the cumene process		
		bisphenol A; a type of "double" phenol used in polymerization in epoxy resins and making a common type of polycarbonate		
			epoxy resins; a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine	
			polycarbonate; a plastic polymer made from bisphenol A and phosgene (carbonyl dichloride)	
		solvents; liquids used for dissolving materials; examples often made from petrochemicals include ethanol, isopropyl alcohol, acetone, benzene, toluene, xylenes		
	cyclohexane; a 6-carbon aliphatic cyclic hydrocarbon sometimes used as a non-polar solvent			
		adipic acid; a 6-carbon dicarboxylic acid which can be a precursor used as a co-monomer together with a diamine to form an alternating copolymer form of nylon.		
			nylons; types of polyamides, some are alternating copolymers formed from copolymerizing dicarboxylic acid or derivatives with diamines	
		caprolactam; a 6-Carbon cyclic amide		
			nylons; types of polyamides, some are from polymerizing caprolactam	
	Nitrobenzene can be made by single nitration of Benzene			
		aniline (aminobenzene)		
			Methylene diphenyl diisocyanate (MDI) used as a co-monomer with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas	
				Polyurethanes
	alkylbenzene; a general type of aromatic hydrocarbon which can be used as a presursor for a sulfonate surfactant (detergent)			
		Detergents often include surfactants types such as alkylbenzenesulfonates and nonylphenol ethoxylates		
	chlorobenzene			

The chemicals and their derivatives produced from benzene are shown in Figure 2.3.

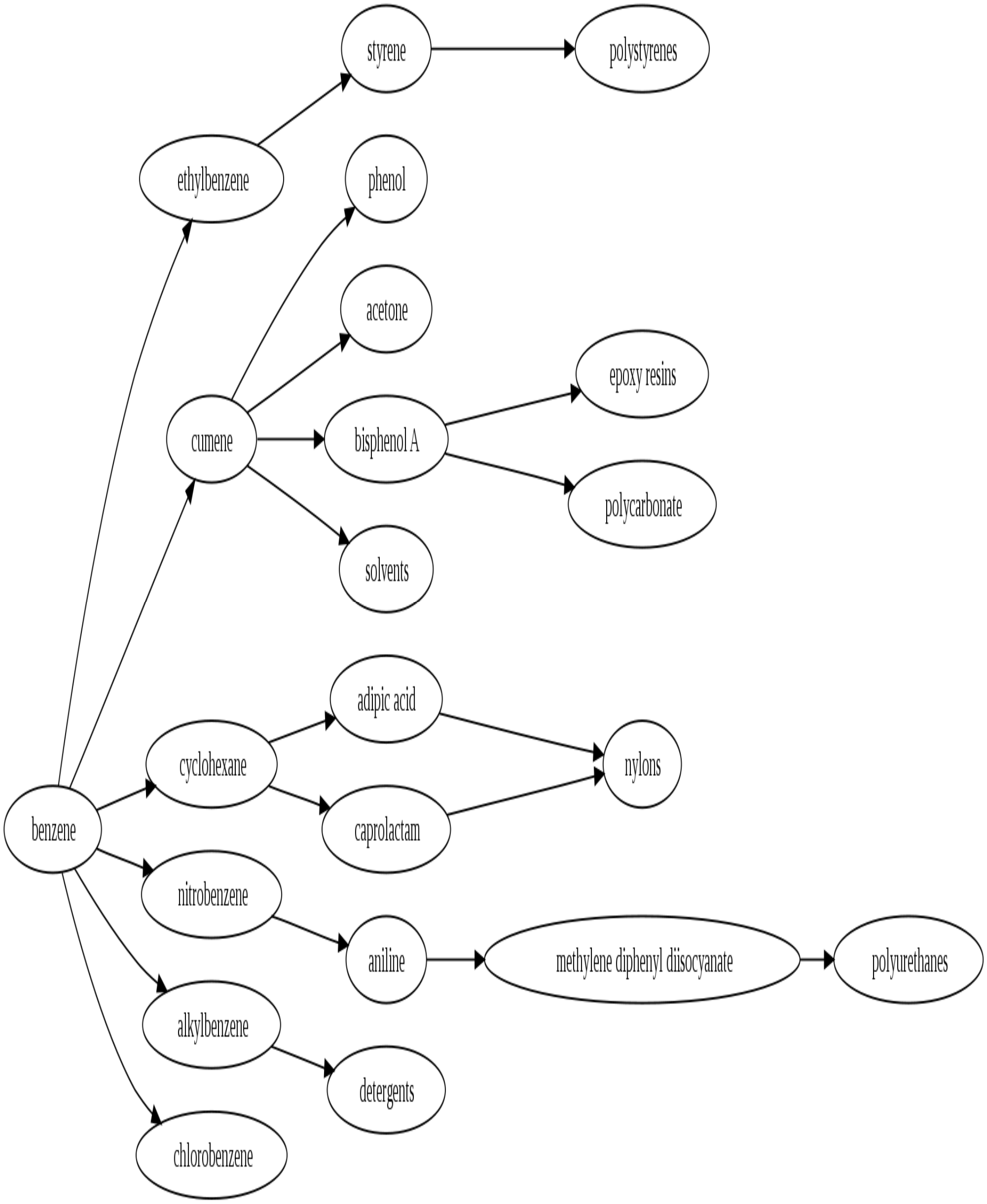


Figure 2.3 Chemicals and their derivatives produced from benzene (Matar & Hatch, 2001).

The chemicals and their derivatives produced from toluene are given in Table 2.5.

Table 2.5 Chemicals and their derivatives produced from toluene (Matar & Hatch, 2001).

Toluene (methylbenzene) can be a solvent or precursor for other chemicals			
	benzene		
	Toluene diisocyanate (TDI) used as co-monomers with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas		
		polyurethanes; a polymer formed from diisocyanates and diols or polyols	
	benzoic acid (carboxybenzene)		
		caprolactam	
			nylon

The chemicals and their derivatives produced from toluene are shown in Figure 2.4.

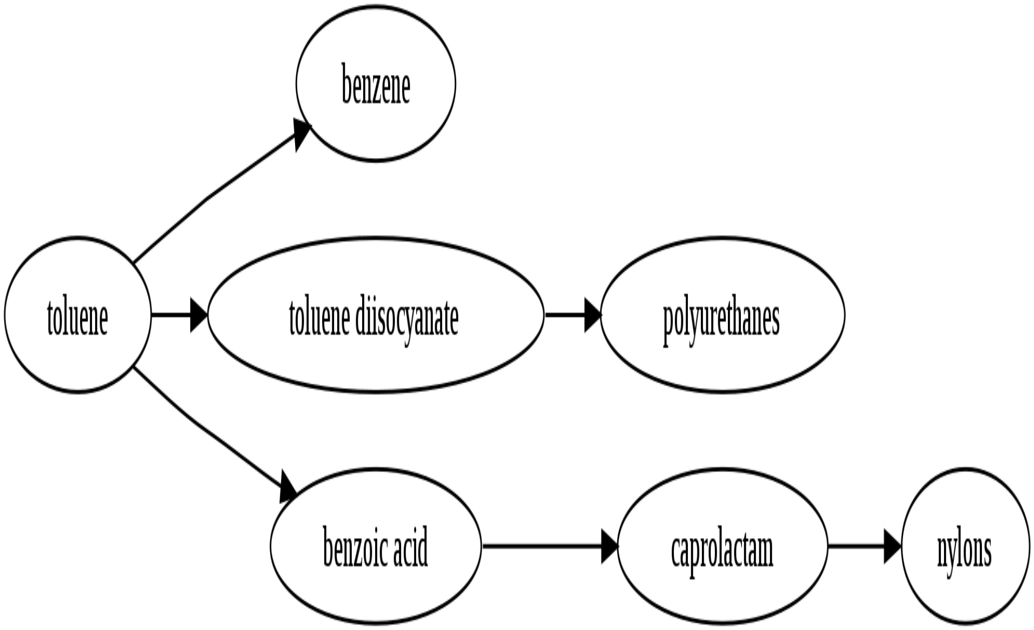


Figure 2.4 Chemicals and their derivatives produced from toluene (Matar & Hatch, 2001).

The chemicals and their derivatives produced from xylene are given in Table 2.6.

Table 2.6 Chemicals and their derivatives produced from xylenes (Matar & Hatch, 2001).

mixed xylenes; any of three dimethylbenzene isomers, could be a solvent but more often precursor chemicals			
	ortho-xylene; both methyl groups can be oxidized to form (*ortho*-) phthalic acid		
		phthalic anhydride	
	para-xylene; both methyl groups can be oxidized to form terephthalic acid		
		Dimethyl terephthalate can be copolymerized to form certain polyesters	
			polyesters; although, there can be many types, polyethylene terephthalate is made from petrochemical products and is very widely used.
		purified terephthalic acid; often copolymerized to form polyethylene terephthalate	
			polyesters
	meta-xylene		
		isophthalic acid	
			alkyd resins
			polyamide resins
			unsaturated polyesters

The chemicals and their derivatives produced from xylene are shown in Figure 2.5.

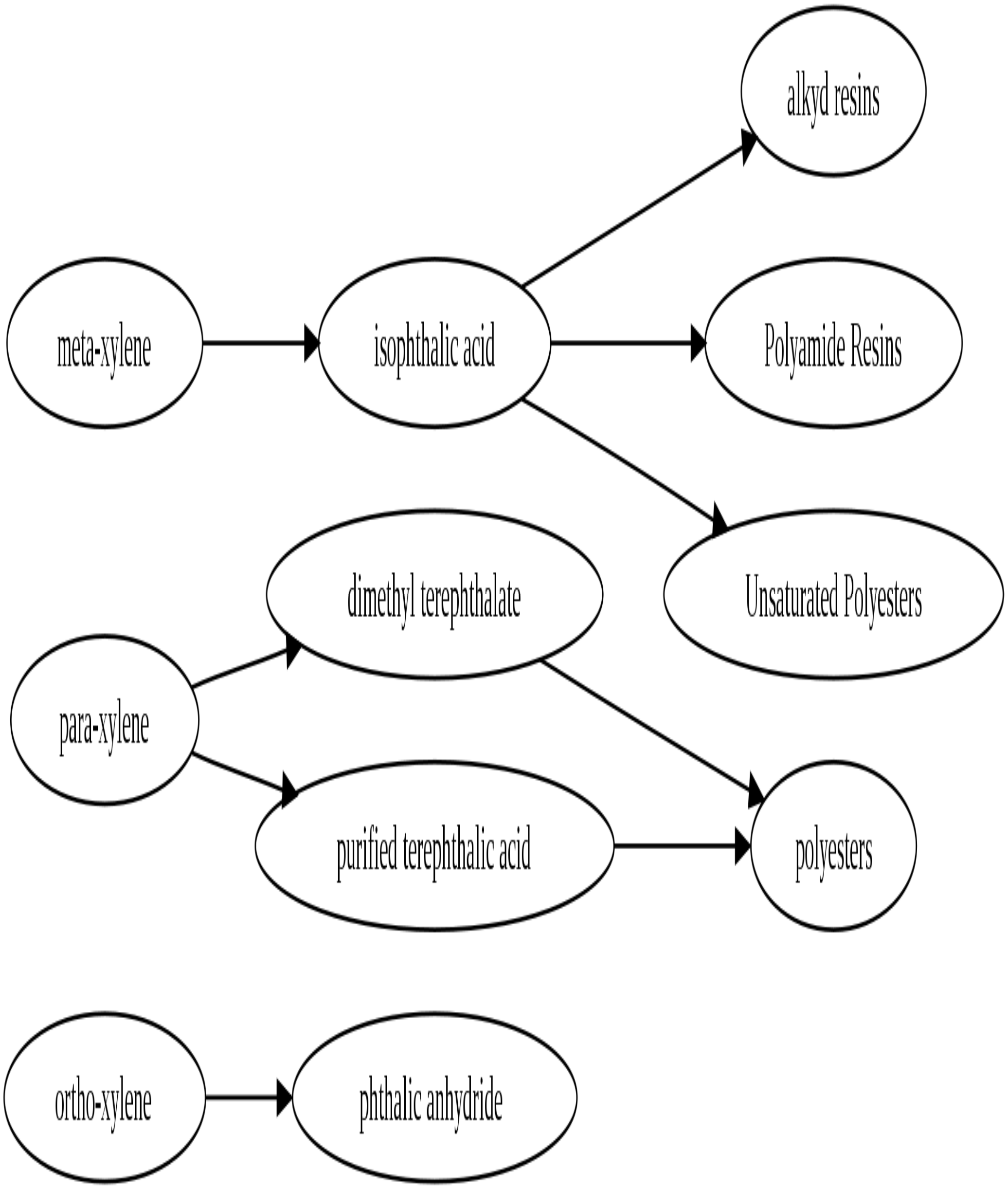


Figure 2.5 Chemicals and their derivatives produced from xylenes (Matar & Hatch, 2001).

Petrochemical products determined by Matar & Hatch (2001) are given in Table 2.7.

Table 2.7 Petrochemicals products (Matar & Hatch, 2001).

Petrochemicals **Basic Feedstock**	**Polymers &Fibers**	**Petroleum**	**Chemicals**	**Healthcare**
butadiene	acrylic fiber	lubricants	adhesives and sealants	healthcare pharm
ethylene	acrylonitrile butadiene styrene (ABS)	additives	agrochemicals	
para-xylene	acrylonitrile styrene (AS)	catalysts	construction chemicals	
propylene	polybutadiene (PBR)	marine fuel oil	corrosion control chemicals	
	polyvinyl chloride (PVC)	petroleum refining	cosmetics raw materials	
Intermediates	polyethylene (PE)		electronic chemicals and materials	
2-ethylhexanol (2-EH)	polyethylene terephthalate (PET)		flavourings, fragrances, food additives	
acetic acid	polyol polypropylene (PP)		specialty and industrial chemicals	
acrylonitrile (AN)	polystyrene (PS)		specialty and industrial gases	
ammonia	styrene butadiene (SBR)		inks, dyes and printing supplies	

Table 2.7 Petrochemicals products (Matar & Hatch, 2001) (cont.).

Petrochemicals Intermediates	Polymers &Fibers	Petroleum	Chemicals	Healthcare
bis(2-ethylhexyl) phthalate (dioctyl phthalate)	urea-formaldehyde (UF)		packaging, bottles, and containers	
n-butane			paint, coatings, and resins	
cyclohexane			polymer additives	
dimethyl terephthalate (DMT)			specialty and life sciences chemicals	
dodecylbenzene			surfactants and cleaning agents	
ethanol				
ethanolamine				
ethoxylate				
1,2-dichloroethane (ethylene dichloride or EDC)				
ethylene glycol (EG)				
ethylene oxide (EO)				
formaldehyde				
n-hexane				

Table 2.7 Petrochemicals products (Matar & Hatch, 2001) (cont.).

Petrochemicals	**Polymers & Fibers**	**Petroleum**	**Chemicals**	**Healthcare**
Intermediates				
linear alkyl benzene (LAB)				
methanol				
methyl tert-butyl ether (MTBE)				
phenol				
propylene oxide				
purified terephthalic acid (PTA)				
styrene monomer (SM)				
urea vinyl acetate monomer (VAM)				
vinyl chloride monomer (VCM)				

2.1.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs, known as polycyclic aromatic hydrocarbons or polyaromatic hydrocarbons or polynuclear aromatic hydrocarbons are a group of organic compounds that are generated primarily during the incomplete combustion of organic materials including wood and fossil fuels such as coal, oil and gasoline (Vallack et al., 1998). There are hundreds of PAHs compounds in the environment, but only seventeen of them are included in the priority pollutants list of United States Environmental Protection Agency (U.S. EPA, 2002) is given in Table 2.8.

The priority pollutants list of U.S. EPA based on a number of factors including toxicity, extent of information available, source specificity, frequency of occurrence at hazardous waste sites, and potential for human exposure (Agency for Toxic Substances and Disease Registry, ATSDR, 1995; International Agency for Research on Cancer, IARC, 2003)

PAHs can be divided into two groups based on their physicochemical and biological characteristics: i) the low molecular weight PAHs with 2- to 3-rings, and ii) the high molecular weight PAHs with 4- to 7-rings (Nagpal, 1993). PAHs are organic compounds widely distributed in the environment, formed by the incomplete combustion of organic materials during natural or anthropogenic processes. They comprise a large group of compounds with two or more fused benzene rings that are less soluble in H_2O and less volatile with increasing molecular weight. PAHs are highly hydrophobic, with a low H_2O solubility, biodegradability and readily adsorbed onto the particles of sludge in wastewater treatment plants (Badin et al., 2008; Banjoo & Nelson, 2005; Benabdallah El-Hadj et al., 2007; Cataldo, 2000; Grishchenkov et al., 2000; Hua, I. et al., 1995; Hua, L. et al., 2008; Huang et al., 2002; Sanchez-Brunete et al., 2007; Suslick, 2000; Suslick et al., 1986; Tchobanoglous & Burton, 1991; Wheat & Tumeo, 1997; Zhang, H. et al., 2009a, 2009b).

Table 2.8 The priority pollutants list of U.S. EPA (ATSDR, 1995; IARC, 2003; Manoli & Samara, 1996, 1999; U.S. EPA, 2002).

No	**Parameters**	**Symbol**	**Health Risk, (IARC)**	**Carcinogenic Effect**	**Health Risk, (U.S. EPA)**	**Carcinogenic Effect**
1	acenaphthene	ACT	NT	Not tested	NT	Not tested
2	acenaphthylene	ACL	NT	Not tested	NT	Not tested
3	antracene	ANT	3	Not classicable	3	Not classicable
4	benz[*a*]antracene	BaA	2A	Possibly	B2	Probably
5	benzo[*a*]pyrene	BaP	B2	Probably	B2	Probably
6	benzo[*e*]pyrene	BeP	NT	Not tested	NT	Not tested
7	benzo[*b*]fluoranthene	BbF	2B	Possibly	B2	Probably
8	benzo[*g,h,i*]perylene	BghiP	NT	Not tested	B2	Probably
9	benzo[*j*]fluoranthene	BjF	NT	Not tested	NT	Not tested
10	benzo[*k*]fluoranthene	BkF	B2	Probably	B2	Probably
11	chrysene	CHR	3	Not classicable	B2	Probably
12	dibenz[*a,h*]anthracene	DahA	2A	Possibly	B2	Probably
13	fluoranthene	FL	3	Not classicable	3	Not classicable
14	fluorene	FLN	NT	Not tested	NT	Not tested
15	indeno[*1,2,3–cd*]pyrene	IcdP	2A	Possibly	B2	Probably
16	phenanthrene	PHE	3	Not classicable	3	Not classicable
17	pyrene	PY	3	Not classicable	3	Not classicable

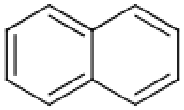
2A and 2B: Possibly carcinogenic; B2: Probably carcinogenic; 3: Not classi¢able as to human carcinogenicity; NT: Not tested for human carcinogenicity.

2.1.2.1 Chemical Structures, Properties and Health Effects of PAHs

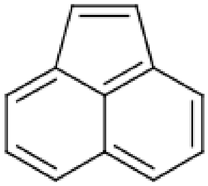
Chemical structures of the studied seventeen PAH compounds in U.S. EPA are illustrated in Figure 2.6. PAHs are composed of two or more aromatic (benzene) rings which are fused together when a pair of carbon atoms is shared between them. The resulting structure is a molecule where the benzenoid rings are fused together in a linear fashion (e.g. ANT) or in an angular arrangement (e.g. ACL) (Dabestani & Ivanov, 1999). In some PAHs, named as heterocyclic aromatic hydrocarbons, one carbon atom is substituted by an atom of another element, such as nitrogen, oxygen, sulfur or chlorine (Amoore & Hautala, 1983; Toxic Organic Compounds in the Environment, TOCOEN, 2007).

The environmentally significant PAHs are the compounds which contain two (e.g., NAP) with a chemical formula of $C_{10}H_8$) to seven benzene rings (e.g. coronene with a chemical formula of $C_{24}H_{12}$). Within this range, there is a large number of PAHs which differ in number of aromatic rings; position at which aromatic rings are fused to each other; and number, chemistry, and position of substituents on the basic ring system (Nagpal, 1993). Trivial names are used for some of the simple PAHs such as ANT, PHE, PY, FL and perylene. More complicated compounds are named by their substitution on their basic structure, such as by benzo– , dibenzo– or naptho– groups (Odabasi, 1998).

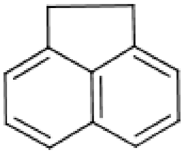
The distribution and partitioning of organic pollutants in various compartments of the environment (e.g. air, water, soil/sediment and biota) is determined by their physical-chemical properties such as water solubility, vapor pressure, Henry's law constant, octanol-water partition coefficient (K_{OW}), and organic carbon partition coefficient (K_{OC}) (ATSDR, 1995). Table 2.9 shows the some important properties of the studied PAHs compounds. The physical-chemical properties of PAHs vary with molecular weight. For instance, PAHs resistance to oxidation, reduction and vaporization increases with increasing molecular weight, whereas the aqueous solubility of these compounds decreases (Nagpal, 1993). Pure PAHs generally exist as colorless, white or pale yellow–green solids at room temperature and most of them have high melting and boiling points (ATSDR, 1995).



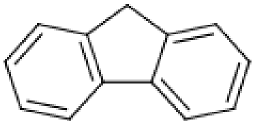
naphthalene (NAP)



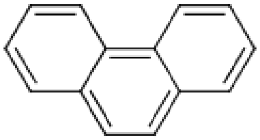
acenaphthylene (ACL)



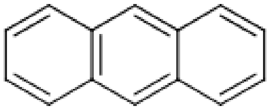
acenaphthene (ACT)



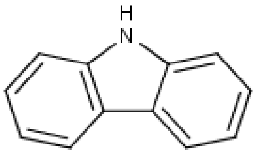
fuorene (FLN)



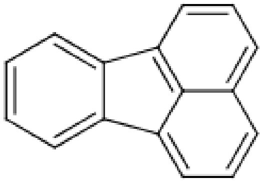
phenanthrene (PHE)



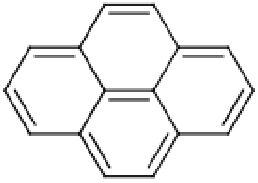
anthracene (ANT)



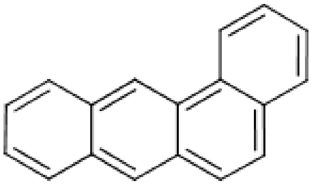
carbazole (CRB)



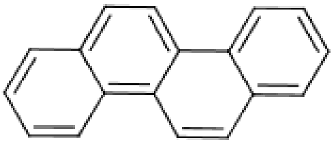
fluoranthene (FL)



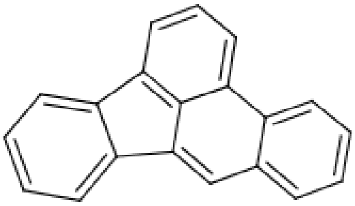
pyrene (PY)



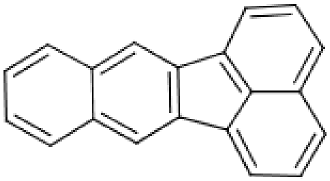
benz[*a*]anthracene (BaA)



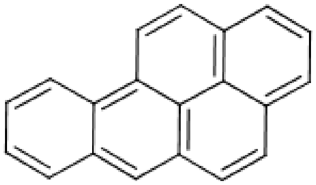
chrysene (CHR)



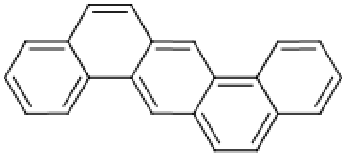
benzo[*b*]fluoranthene (BbF)



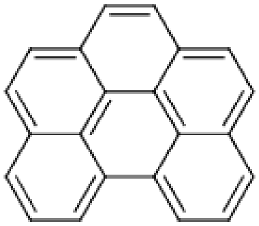
benzo[*k*]fluoranthene (BkF)



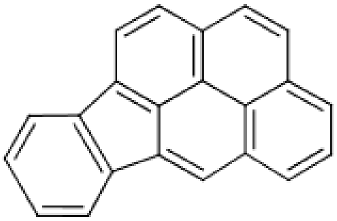
benzo[*a*]pyrene (BaP)



dibenz[*a,h*]antracene (DahA)



benzo[*ghi*]perylene (BghiP)



indeno[*1,2,3–cd*]pyrene (IcdP)

Figure 2.6 Chemical structures of PAHs used in this study (National Library of Medicine, NLM, 2008a).

Table 2.9 Selected physical-chemical properties of individual PAHs compounds used in this study.

PAHs	**Cas-No**[a]	**MF** [a]	**Benzene Ring No**	**MW** [a] **(g/mol)**	T_M [a] **(°C)**	T_B [a] **(°C)**	S_W [a] **(25°C) (mg/l)**	V_P [a] **(25°C) (mm Hg)**	**H** [a] **(25°C) (atm m^3/mol)**	**log** K_{OA} [c] **(25°C)**	**log** K_{OW} [a]
NAP	91-20-3	$C_{10}H_8$	2	128	80	218	31.00	8.50×10^{-2}	4.40×10^{-4}	-	3.36
ACL	208-96-8	$C_{12}H_8$	3	152	93	280	16.10	6.68×10^{-3}	1.14×10^{-4}	6.34	3.94
ACT	83-32-9	$C_{12}H_{10}$	3	154	93	279	3.90	2.15×10^{-3}	1.84×10^{-4}	6.52	3.92
FLN	86-73-7	$C_{13}H_{10}$	3	166	115	295	1.69	6.00×10^{-4}	9.62×10^{-5}	6.90	4.18
PHE	85-01-8	$C_{14}H_{10}$	3	178	99	340	1.15	1.21×10^{-4}	3.35×10^{-5} [b]	7.68 [b]	4.46
ANT	120-12-7	$C_{14}H_{10}$	3	178	215	340	4.34×10^{-2} *	2.67×10^{-6} [d]	5.56×10^{-5}	7.71	4.45
CRB	86-74-8	$C_{12}H_9N$	3	167	246	355	1.80	7.50×10^{-7} [e]	1.16×10^{-7} [b]	8.03 [b]	3.72
FL	206-44-0	$C_{16}H_{10}$	4	202	108	384	0.26	9.22×10^{-6}	8.86×10^{-6}	8.76	5.16
PY	129-00-0	$C_{16}H_{10}$	4	202	151	404	0.135	4.50×10^{-6}	1.19×10^{-5}	8.81	4.88
BaA	56-55-3	$C_{18}H_{12}$	4	228	84	438	9.40×10^{-3}	2.10×10^{-7}	1.20×10^{-5}	10.28	5.76
CHR	218-01-9	$C_{18}H_{12}$	4	228	258	448	2.00×10^{-3}	6.23×10^{-9}	5.23×10^{-6}	10.30	5.81
BbF	205-99-2	$C_{20}H_{12}$	5	252	168	-	1.50×10^{-3}	5.00×10^{-7}	6.57×10^{-7}	11.34	5.78
BkF	207-08-9	$C_{20}H_{12}$	5	252	217	480	8.00×10^{-4}	9.70×10^{-10} [d]	5.84×10^{-7}	11.37	6.11
BaP	50-32-8	$C_{20}H_{12}$	5	252	177	495 [f]	1.62×10^{-3}	5.49×10^{-9} [d]	4.57×10^{-7}	11.56	6.13
DahA	53-70-3	$C_{22}H_{14}$	5	278	270	524	2.49×10^{-3}	1.00×10^{-10}	1.23×10^{-7}	12.59	6.75
BghiP	191-24-2	$C_{22}H_{12}$	6	276	278	> 500	2.60×10^{-4}	1.00×10^{-10}	3.31×10^{-7}	12.55	6.63
IcdP	193-39-5	$C_{22}H_{12}$	6	276	164	536	1.90×10^{-4}	1.25×10^{-10}	3.48×10^{-7}	12.43	6.70

naphthalene (NAP), acenaphthylene (ACL), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[*a*]anthracene (BaA), chrysene (CHR), benz[*b*]fluoranthene (BbF), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight, T_M: Melting point, T_B: Boiling point, S_W: Solubility in water, V_P: Vapor pressure, H: Henry's law constant, log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient, * at 24°C.

[a] NLM, (2008a), [b] Odabasi et al., (2006a), [c] Odabasi et al., (2006b), [d] NLM, (2008b), [e] Virtual Computational Chemistry Laboratory, VCCL, (2007), [f] Estimation Program Interface, EPI, (2007).

Since PAHs are non-polar and hydrophobic compounds, they are poorly soluble in aqueous environments, but are soluble in organic solvents or organic acids. This means that they are generally found adsorbed on particulates and on humic matter in aqueous environments, or solubilized in any oily matter which may co-exist in water, sediments and soil as contaminants (Dabestani & Ivanov, 1999). Temperature and dissolved/colloidal organic fractions of water enhance the solubility of the PAH compound in water (Nagpal, 1993), and solubility decreases as the molecular weight and number of rings increases. Thus, the high molecular weight PAHs are almost exclusively bound to particulate matter, while the lower molecular weight ones can also be found dissolved in water (ATSDR, 1995).

PAHs tend to have low vapor pressures. As molecular weight and the number of rings increase, their vapor pressure decreases. At a given temperature, substances with higher vapor pressures vaporize more readily than substances with a lower vapor pressure. As a result, the high molecular weight PAHs are found predominantly in particle-phase, while the lower molecular weight ones are present predominantly in gas-phase in the air (Dabestani & Ivanov, 1999).

The ratio of a chemical's concentration in air and water at equilibrium can be expressed by Henry's law constant. This partition coefficient is used as a measure of a compound's volatilization. Henry's law constants for low molecular weight PAHs are in the range of 10^{-3} - 10^{-5} atm m^3/mol and for the high molecular weight PAHs they are in the range of 10^{-5} - 10^{-8} atm m^3/mol. Thus, significant volatilization can take place for compounds with Henry's law constant values ranging from 10^{-3} - 10^{-5} while PAHs with values $< 10^{-5}$ do not volatilize much (ATSDR, 1995; Dabestani & Ivanov, 1999).

The K_{OW} is used to estimate the potential for an organic chemical to move from water into lipid, and has been correlated with bio-concentration in aquatic organisms. For PAHs compounds, the values of log K_{OW} increase with increasing number of rings. K_{OW} values for PAHs are relatively high indicating a relatively high potential for adsorption to suspended particulates in air and water and for bio-concentration in organisms (ATSDR, 1995).

The K_{OC} indicates the chemical's potential to bind to organic carbon in soil and sediment. The log K_{OC} values for PAHs increase with increasing number of rings. The low molecular weight PAHs have K_{OC} values in the range of 10^3 - 10^4 indicating a moderate potential to be adsorbed to organic carbon in the soil and sediments. High molecular weight PAHs have K_{OC} values in the range of 10^5 - 10^6 indicating stronger tendencies to adsorb to organic carbon (ATSDR, 1995). Persistence of the PAHs also varies with their molecular weight. The low molecular weight PAHs are most easily degraded. The reported half-lives of NAP, ANT and BaP in sediment are 9 h, 43 and 83 h, respectively, while for higher molecular weight PAHs, their half-lives are up to several years in soils/sediments (United Nations Environment Programme, UNEP, 2002).

In human beings, systemic, immunological, neurological, reproductive, developmental, genotoxic and carcinogenic adverse health effects have been linked to several PAHs (ATSDR, 1995). The International Agency for Research on Cancer (IARC) has reported that BaA and BaP are probably carcinogenic to human (Group B2); BbF, BkF and IcdP are possibly carcinogenic to human (Group 2A). In the U.S. EPA list, BaA, BaP, BbF, BkF, CHR, DahA and IcdP are classified as Group B2, probable human carcinogens (ATSDR, 1995) (Table 2.8).

2.1.2.2 Production and Uses of PAHs

As pure chemicals, PAHs generally exist as colorless, white or pale yellow-green solids. They can have a faint, pleasant odor. Among a large number of compounds, only a few PAHs (e.g. ACT, ANT, FLN, FL, NAP and PHE) are produced for commercial use. They are mostly used as intermediaries in pharmaceutical, photographic and chemical industries (dyes, plastics, etc). Limited uses in the production of pesticides, fungicides, insecticides, moth repellent and surfactants have been also reported (ATSDR, 1995; Nagpal, 1993).

2.1.2.2.1 Naphthalene (NAP). NAP also known as naphthalin, bicyclo[4.4.0]deca–1,3,5,7,9–pentene (International Union of Pure and Applied Chemistry, IUPAC name) or antimite and not to be confused with naphtha, is a crystalline, aromatic, white, solid hydrocarbon with formula $C_{10}H_8$ and the structure of two fused benzene rings. It is best known as the traditional, primary ingredient of mothballs (Amoore & Hautala, 1983). NAP is the most abundant distillate of coal tar. Its most common use is as a household fumigant against moths. In the past, it was used in the manufacture of carbaryl insecticide and vermicide. NAP is also an important hydrocarbon raw material used in the manufacture of phthalic anhydride (intermediate for polyvinyl chloride, PVC, plasticizers), celluloid and hydronapthalenes (used in lubricants), and motor fuels. NAP is also used in the production of beta–naphthol, synthetic tanning agents, leather, resins, dyes, surfactants and dispersants. Some uses as an antiseptic and as a soil fumigant have been reported as well (ATSDR, 1995; Nagpal, 1993; Spectrum, 2003e; U.S. EPA, 2002b).

2.1.2.2.2 Acenaphthylene (ACL). ACL (acenaphthylene, IUPAC name) also known as cycopenta(de)naphthalene. ACL is a consisting of NAP with an ethylene bridge connecting positions 1 and 8. It is a constituent of coal tar. Reduction of the Ethylene group gives the related compound ACT. Unlike most PAHs, it has no fluorescence (ATSDR, 1995; Spectrum 2003c).

2.1.2.2.3 Acenaphthene (ACT). ACT also known as 1,2–dihydroacenaphthylene (IUPAC name), 1,8–ethylenenaphthalene, *peri*–ethylenenaphthalene, naphthyleneethylene, acenaphthene. ACT is a consisting of NAP with an ethylene bridge connecting positions 1 and 8. An alternative name, 1,2–dihydroacenaphthylene emphasizes that it is a hydrogenated form of ACL. It is a constituent of coal tar. ACT is used as a chemical intermediary in pharmaceutical and photographic industries, and to a limited extent, in the production of soaps, pigments and dyes, insecticides, fungicides, plastics and processing of certain foods (ATSDR, 1995; Nagpal, 1993; Spectrum, 2003a).

2.1.2.2.4 Fluorene (FLN). FLN (9*H*–fluorene, IUPAC name) is a precursor to other FLN compounds; the parent species has few applications. Fluorene–9–carboxylic acid is a precursor to pharmaceuticals. 2–aminofluorene, 3,6–bis–(dimethylaminofluorene), and 2,7–diiodofluorene are precursors to dyes. Oxidation of FLN gives fluorenone, which is nitrated to give commerically useful derivatives. 9–fluorenylmethyl chloroformate (Fmoc chloride) is used to introduce the 9–fluorenylmethyl carbamate (Fmoc) protecting group on amines in peptide synthesis. Polyfluorene polymers (where carbon 7 of one unit is linked to carbon 2 of the next one, displacing two hydrogens) are electrically conductive and electroluminescent, and have been much investigated for use as a luminophore in organic light-emitting diodes. FLN is used as a chemical intermediate in many chemical processes, in the formation of poly-radicals for resins, and in the manufacture of resinous products and dyestuffs. Derivatives of FLN show activity as herbicides and growth regulators (ATSDR, 1995; Spectrum, 2003d).

2.1.2.2.5 Phenanthrene (PHE). PHE (phenanthrene, IUPAC name) is used in the manufacture of dyestuffs, explosives and phenanthrenequinone which is an intermediate for pesticides. It is also an important starting material for PHE based drugs. This leads directly to use in biochemical research for the pharmaceutical industry. A mixture of PHE and ANT tar is used to coat water storage tanks to keep them from rusting (ATSDR, 1995; Spectrum, 2003f).

2.1.2.2.6 Antracene (ANT). ANT (antracene, IUPAC name) is used as a raw material for the manufacture of fast dyes, pigments and coating materials; as a chemical intermediary for dyes; and as a diluent for wood preservatives. It is used in the manufacture of synthetic fibers, plastics, mono-crystals and scintillation counter crystals. Its uses in insecticides, fungicides, smoke screens and organic semiconductor researches have been also reported (ATSDR, 1995; Nagpal, 1993; Spectrum, 2003b).

2.1.2.2.7 Carbazole (CRB). CRB also known as (9*H*–carbazole, IUPAC name) 9–azafluorene, dibenzopyrrole, diphenylenimine, diphenyleneimide, USAF EK–600. A classic laboratory organic synthesis for CRB is the Borsche–Drechsel Cyclization. In the first step phenylhydrazine is condensed with cyclohexanone to the corresponding Imine. The second step is a HCl catalyzed rearrangement reaction and ring–closing reaction to tetrahydrocarbazole. In one modification both steps are rolled into one by carrying out the reaction in acetic acid. In the third step this compound is oxidized by red lead to CRB itself. Another classic is the Bucherer CRB synthesis. A second method for the synthesis of CRB is the Graebe–Ullmann Reaction. In a first step a N–phenyl–1,2–diaminobenzene (N–phenyl–o–phenylenediamine) is converted into a diazonium salt which instantaneously forms a 1,2,3–triazole. The Triazole is unstable and at elevated temperatures nitrogen is set free and the CRB is formed (ATSDR, 1995).

2.1.2.2.8 Fluoranthene (FL). FL (fluoranthene, IUPAC name) also known as benzo[*j, k*]fluorene. FL is a consisting of a NAP and a benzene unit connected by a five-membered ring. It is a member of the class of PAHs known as non-alternant PAHs because it has rings other than those with six carbon atoms. It is a structural isomer of the alternant PY. It is not as thermodynamically stable as PY because its electrons cannot resonate throughout the complete structure as the corresponding ones in PY. Its name is derived from its fluorescence under UV light. FL is a constituent of coal tar and petroleum derived asphalt. This compound is used as a lining material to protect the interior of steel and ductile-iron drinking water pipes and storage tanks (ATSDR, 1995; Spectrum 2003c).

2.1.2.2.9 Pyrene (PY). PY (pyrene, IUPAC name) is a consisting of four fused benzene rings, resulting in a flat aromatic system. This colorless solid is the smallest peri–fused PAH (one where the rings are fused through more than one face). PY forms during incomplete combustion of organic compounds. PY and its derivatives are used commercially to make dyes and dye precursors, for example pyranine and naphthalene–1,4,5,8–tetracarboxylic acid (ATSDR, 1995; Spectrum 2003c).

2.1.2.2.10 Chrysene (CHR). CHR (chrysene, IUPAC name) also known as benzo[*a*]phenanthrene and 1,2–benzphenanthrene. High purity CHR is colorless, the yellow-blue being due to the traces of its yellow-orange isomer tetracene, which cannot be separated easily. CHR is a natural constituent of coal tar, from which it was first isolated and characterized. CHR is formed in small amounts during the burning or distillation of coal, crude oil and plant material. It is also found in creosote, a chemical used to preserve wood. CHR is used in the manufacture of some dyes (ATSDR, 1995; Spectrum 2003c).

2.1.2.2.11 Benzo[a]pyrene (BaP). BaP (benzo[*a*]pyrene, IUPAC name) is found in coal tar, in automobile exhaust fumes (especially from diesel engines), in all smoke resulting from the combustion of organic material, and in charbroiled food (ATSDR, 1995; Spectrum 2003c).

There are no known commercial uses for ACL, BaA, BbF, BaP, BjF, BkF, BghiP, CHR, DahA, IcdP and PY except as research chemicals (ATSDR, 1995)

2.1.2.3 Sources of PAHs

The sources of PAHs can be divided into two categories:

(1) Natural sources and
(2) Anthropogenic sources.

Anthropogenic activities predominate, but some PAHs in the environment originate from Natural sources.

2.1.2.3.1 Natural Sources

In nature, PAHs may be formed by three ways: (i) High temperature pyrolysis of organic materials (such as, agricultural burning, forest and prairie fires), (ii) low to moderate temperature diagenesis of sedimentary organic material to form fossil fuel (for example, coal, crude oil) and (iii) direct biosynthesis by microbes and plants (for instance, algae/phytoplankton and microorganisms) (Nagpal, 1993).

PAHs also form as significant components of petroleum products such as some paints, creosote (used in wood preservation) and asphalt (used for road paving) (U.S. EPA, 2002a).

2.1.2.3.2 Anthropogenic Sources

Anthropogenic sources include combustion and industrial production. Incomplete combustion of organic matter at high temperature is one of the major anthropogenic sources of environmental PAHs (ATSDR, 1995).

Anthropogenic sources fall into two groups:
(1) Stationary sources and
(2) Non-stationary sources.

Stationary sources include coal and gas-fired boilers; coal gasification and liquefaction plants; carbon black, coal tar pitch and asphalt production; aluminum production; coke-ovens; the iron-steel industries; catalytic cracking towers; petroleum refineries and related activities; electrical generating plants; industrial and municipal incinerators (waste burning); residential heating; and any other industry that entails the use of wood, petroleum or coal to generate heat and power (Dabestani & Ivanov, 1999; Nagpal, 1993).

Non-stationary sources of PAHs refer to automobiles or other vehicles which use petroleum derived fuels. Temperatures within an internal combustion engine are often sufficient enough to convert a fraction of the fuel or oil into PAHs via incomplete combustion (Nagpal, 1993).

2.2 Properties of Olive Mill Industry Wastewater (OMI ww)

Olive mill effluent (OME) arises from the production of olive oil in olive mills (Table 2.10). It is produced seasonally by a large number of small olive mills scattered throughout the olive oil-producing countries. Mediterranean countries alone produce 97.00% of the total olive oil production, while European Union (EU) countries produce 80.00–84.00%. The largest olive oil-producing countries are Spain, Italy, Greece and Turkey, followed by Tunisia, Portugal, Morocco and Algeria (Paraskeva & Diamadopoulos, 2006). The main olive oil producing and consuming countries in 2009 reported by California and World Olive Oil Statistics (2009) and by International Olive Oil Council (2009) are given in Table 2.11.

Table 2.10 Olive oil properties (International Olive Oil Council, 2009).

Parameters	Values
Food energy per 100g	3,700 kJ (880 kcal)
Melting point	– 6°C
Boiling point	300°C
Smoke point	190°C (virgin) 210°C (refined)
Specific gravity at 20°C	0.9150–0.9180 (@ 15.5 °C)
Viscosity at 20°C	0.84 g/cm.second
Refractive index	1.4677–1.4705 (virgin and refined) 1.4680–1.4707 (pomace)
Iodine value [a]	75.00–94.00 (virgin and refined) 75.00–92.00 (pomace)
Acid value	maximum: 6.60 (refined and pomace) 0.60 (extra-virgin)
Saponification value [b]	184–196 (virgin and refined) 182–193 (pomace)
Peroxide value [c]	20.00 (virgin) 10.00 (refined and pomace)

a: Iodine value: (or "iodine adsorption value" or "iodine number" or "iodine index") in chemistry is the mass of iodine in grams that is consumed by 100 g of a chemical substance. The amount of iodine solution thus required to keep the solution yellow/brown is a measure of the amount of iodine sensitive reactive groups. One application of the iodine number is the determination of the amount of unsaturation contained in fatty acids.

b: Saponification value (or "saponification number", also referred to as "sap" in short) represents the number of milligrams of KOH or NaOH required to saponify 1g of fat under the conditions specified. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. If more moles of base are required to saponify N grams of fat then there are more moles of the fat the chain lengths are relatively small, given the following relation:

Number of moles = mass of oil / relative atomic mass

c: Peroxide value of an oil or fat is used as a measurement of the extent to which rancidity reactions have occurred during storage. Other methods are available but peroxide value is the most widely used.

Table 2.11 The main olive oil producing and consuming countries (California and World Olive Oil Statistics, 2009; International Olive Oil Council, 2009).

Country	**Production in Tons (2009)**	**Production in 2009 (%)**	**Consumption in 2005 (%)**	**Annual per Capita Consumption (kg)**
World	2 907 985	100	100	0.43
Spain	1 199 200	41.20	20.00	13.62
Italy	587 700	20.20	30.00	12.35
Greece	332 600	11.40	9.00	23.70
Syria	168 163	5.80	3.00	7.00
Tunisia	150 000	5.20	2.00	11.10
Turkey	143 600	4.90	2.00	1.20
Morocco	95 300	3.30	2.00	1.80
Portugal	53 300	1.80	2.00	7.10
USA	2 700	0.10	8.00	0.56
France	6 300	0.20	4.00	1.34
Others	169 122	5.80	18.00	1.18

The composition of OME is quite variable and is composed of many complex substances that are toxic and not easily degradable (e.g. polyphenols, tannins, polyalcohols, pectins and lipids etc.). Typical OME composition by weight is: 83.00–94.00% H_2O, 4.00–16.00% organic compounds and 0.40–2.50% mineral salts. The mineral fraction typically contains 47.00% potassium salts and 7.00% sodium salts. The organic fraction contains 2.00–15.00% of phenolic compounds corresponding to a concentration of 3.00–10.00 g/l (Azbar et al., 2002; Capasso et al., 1992; Garcia et al., 1990; Tuncel & Nergiz, 1993; Zouari, 1998) given in Table 2.12.

Table 2.12 Typical OME composition by weight (Azbar et al., 2002; Capasso et al., 1992; Garcia et al., 1990; Tuncel & Nergiz, 1993; Zouari, 1998).

Parameters		**Values (%)**
a) H_2O		83.00–94.00
b) Organic compounds		4.00–16.00
	1. phenolic compounds	2.00–15.00
c) Mineral salts		0.40–2.50
	1. potassium salts	47.00
	2. sodium salts	7.00

When disposed into the environment, OME can create serious deteriorations such as coloring of natural waters, a serious threat to aquatic life, pollution in surface and ground waters, alterations in soil quality, phytotoxicity and odor nuisance. In this manner, significant numbers of studies were focused on the efficient treatment of OME including various chemical, physical, physicochemical and biological treatments or their combinations (Aktas et al., 2001; Al-Malah et al., 2000; Andreozzi et al., 1998; Azbar et al., 2002, 2004, 2008a, 2008b, 2009; Azbar & Yonar, 2004; Azzam et al., 2004; Boari et al., 1984; Ceccon et al., 2001; Mantzavinos & Kalogerakis, 2005; Kestioglu et al., 2005; Sabbah et al., 2004).

The COD is also high, ranging from 45.00 to 220.00 g/l, as is the BOD_5 that ranges from 35.00 to 100.00 g/l. The pH of OME is acidic around 4.0–5.0 and the concentration of TSS could go up to 50.00 g/l depending on the olive mill (Azbar et al., 2002; Davies et al., 2004). The traditional three-phase continuous centrifugation process generally yields an oily phase (20.00% [w/v]), a solid residue phase (30.00% [w/v]), and an aqueous phase (50.00% [w/v]), the latter originating from the water content of the fruit (Borja et al., 2006).

Many volatile compounds responsible for this flavor originate from the degradation of triacylglycerols, polyunsaturated fatty acids or phospholipids. Other compounds are derived from autoxidation of fatty acids. In fact, a large number of volatiles can be formed during autoxidation of unsaturated acyl lipids and many of them are causing off-flavours. This phenomenon, which concerns oils rich with unsaturated bonds, has limited the use of ultrasound as a commercial technique for the production of edible fats (Jahouach-Rabai et al., 2008). The major by-products in OMI ww after sonication process reported by Jahouach-Rabai et al. (2008) given in Table 2.13. Volatile and semi-volatile materials are present in the crude oil as natural fragrances and oxidation by-products. Deterioration products such as alcohols, aldehydes, ketones, alkanes, esters and short chain acids are formed as secondary metabolites from the hydroperoxides of unsaturated fatty acids, under the influence of the high temperature, O_2, metals or other pro-oxidants. The sonochemistry is directly related to cavitation. The collapse of the ultrasound-induced cavities can produce very high local temperatures and pressures, which have been suggested to produce oxidation of fats and oils resulting in the breakup of pre-existing lipo(hydro)peroxides. Especially, oils having more unsaturated C=C bonds are more susceptible to off-flavours when sonicated (Jahouach-Rabai et al., 2008).

The presence of phenolic derivatives (methylcatechol, catechol, acetylcatechol, *o*–quinone and guaiacol) depends on the ripeness of the olives, the environment of the olive cultivations, the storage time and the extraction procedures. Tyrosol and hydroxytyrosol are common components found in OMI ww. Also, 2–(5–ethylidene–2–oxotetrahydro–2*H*–pyran–4–yl) acetic acid in OMI ww is derived from cleavage of the aglycon part of oleuropein (Capasso et al., 1995; Della Greca et al., 2001). Raw (untreated) OMI ww has broad spectrum toxicity against bacteria (Capasso et al., 1995), fungi, algae (Della Greca et al., 2001), plants (Casa et al., 2003), insects (Capasso et al., 1994; Delgado-Moreno et al., 2009), animals and human cells (Capasso et al., 1995). However, fractionated OMI ww extracts and isolated biophenols demonstrate selective or minimal toxicity (Capasso et al., 1995; Martinez-Nieto et al., 1993; Mulinacci et al., 2001). Nevertheless, European research identifies OMI ww as a potential source for the recovery of antioxidant (Aldini et al., 2006), anti–atherogenic (Leger et al., 2000) and anti-inflammatory biophenols (Visioli et al., 1999).

Table 2.13 The major by-products in OMI ww after sonication process (Jahouach-Rabai et al., 2008).

No	by-Products Names	No	by-Products Names
1	oleic acid	31	hydroxyphenyl ethanol
2	linoleic acid	32	p–hydroxyphenylacetic acid
3	linolenic acid	33	di–hydroxyphenyl ethanol
4	1,3–octadiene	34	vanilic acid
5	styrene	35	3,4,5–trimetoxibenzoic acid
6	1–nonene	36	syringic acid
7	heptanal	37	gallic acid
8	1,3–nonadiene	38	caffeic acid
9	2(Z)–heptenal	39	4–ethyl, 2–methoxyphenol
10	6–methyl–5–hepten–2–one	40	1–tridecene
11	1–decene	41	2(E), 4(E)–decadienal
12	octanal	42	n–pentadecane
13	D–limonene	43	n–hexadecane
14	1,3–hexadiene	44	n–heptadecane
15	1,3,7–octatriene	45	hexanal
16	2(E)–octenal	46	linoleate 13–OOH
17	sterols	47	3–hydroxyphenylacetic acid
18	1–undecene	48	p–hydroxybenzoic acid
19	undecane	49	p–hydroxy–benzaldehyde
20	nonanal	50	p–hydroxyphenylpropionic acid
21	5–undecene	51	protocatetic acid
22	ethyl cyclohexane carboxylate	52	syringic aldehyde
23	2(E)–nonenal	53	p–coumaric acid
24	4–ethylphenol	54	ferulic acid
25	1–dodecene	55	methylcatechol
26	decanal	56	catechol
27	o–quinone	57	tyrosol
28	guaiacol	58	butanal
29	hyroxytyrosol	59	toluene
30	9–OOhydroperoxide	60	2–(5–ethylidene–2–oxotetrahyro–2H–pyran–4–yl) Acetic acid

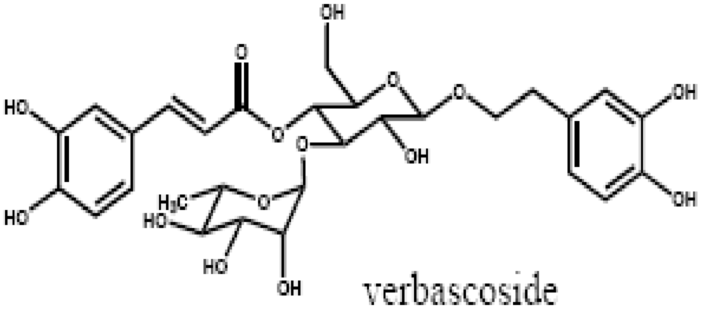
2.2.1 Phenolic Compounds

Pyrolysis differs from other high-temperature processes like combustion and hydrolysis in that it does not involve reactions with O_2, H_2O or any other reagents. Pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content.

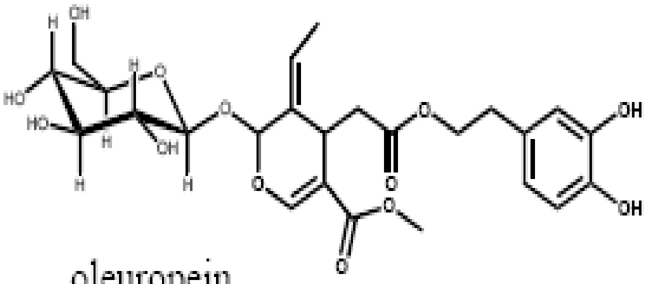
Pyrolytic destruction of phenol in the gas phase is negligible; the degradation occurs mainly in the bulk solution. A possible explanation for this is that a considerable increase in the concentration results in the formation of a complex H-bonding network between the phenolic compounds. It is well known that molecules containing COOH or CHO groups exist as dimers in solution due to the formation of H-bonds between two neighbouring molecules. This results in a more robust and stable configuration, thus leading to reduced degradation (Vassilakis et al., 2004). The major phenolic compounds in OMI ww after sonication process reported by Juarez et al. (2008) and Priego-Capote et al. (2004, 2006) as shown in Table 2.14. Some phenolic compounds in OMI ww after sonication process (Ceccon et al., 2001; Inoue, K. et al., 2006; Juarez et al., 2008; Priego-Capote et al., 2004, 2006) given in Figure 2.7.

Table 2.14 The major phenolic compounds in OMI ww after sonication process (Ceccon et al., 2001; Inoue , K. et al., 2006; Juarez et al., 2008; Priego-Capote et al., 2004, 2006).

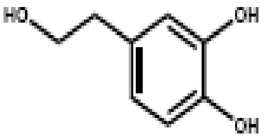
No	**Phenolic Compounds Names**	**No**	**Phenolic Compounds Names**
1	luteolin	17	apigenin
2	hydroxytyrosol	18	rutin
3	tyrosol	19	glucoside
4	oleuropein	20	metylcatechol
5	caffeic acid	21	catechol
6	p–hydroxybenzoic acid	22	acetylcatechol
7	verbascoside	23	o–quinone
8	quercetin	24	guaiacol
9	ferulic acid	25	p–coumaric acid
10	protocatechuic acid	26	p–hydroxybenzaldehyde
11	p–hydroxyphenylacetic acid	27	syringic acid
12	vanillic acid	28	3–hydroxyphenylacetic acid
13	p–hydroxyphenylpropionic acid	29	hydroxyphenyl ethanol
14	syringic aldehyde	30	di–hydroxyphenyl ethanol
15	3,4,5–trimetoxibenzoic acid	31	gallic acid
16	proanthocyanidin	32	flavone



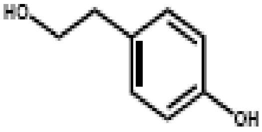
verbascoside



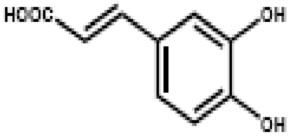
oleuropein



hydroxytyrosol



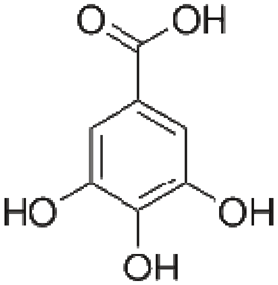
tyrosol

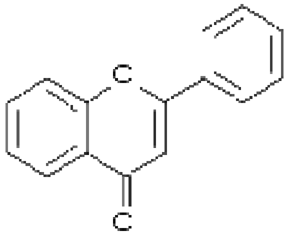


caffeic acid

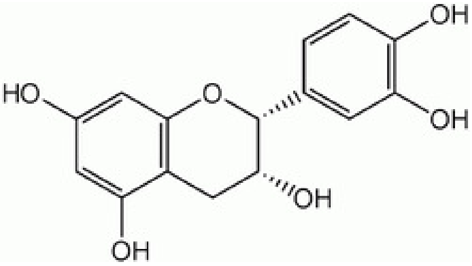
Figure 2.7 Some phenolic compounds in OMI ww after sonication process (Juarez et al., 2008; Priego-Capote et al., 2004, 2006).

Base unit:





	gallic acid	flavone
Class/polymer:	hydrolyzable tannins	condensed tannins



Proanthocyanidin (condensed tannins)

Figure 2.7 Some phenolic compounds in OMI ww after sonication process (Juarez et al., 2008; Priego-Capote et al., 2004, 2006) (cont.).

2.2.2 Aromatic Amines

Aromatic amines have the N_2 atom connected to an aromatic ring as in anilines (Figure 2.8). The aromatic ring decreases the alkalinity of the amine, depending on its substituents. The presence of an amine group strongly increases the reactivity of the aromatic ring, due to an electron-donating effect.

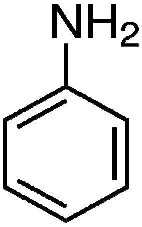
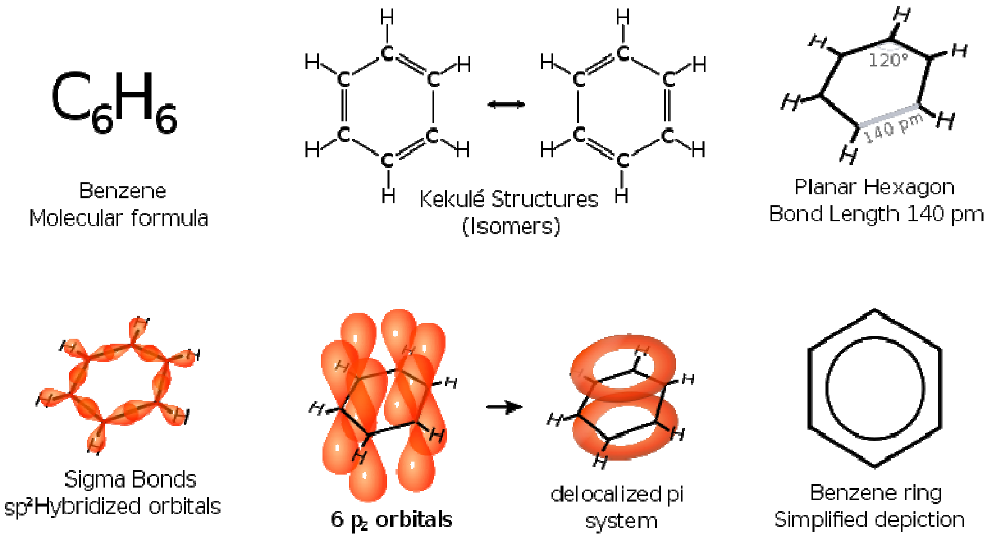


Figure 2.8 Aniline, C_6H_7N (Other names; phenylamine and aminobenzene or benzenamine) (Rehorek et al., 2004).

Hydrolysis and pyrolysis are main degradation mechanisms for aromatic amines with ultrasound. The attack of non-volatile compounds in the ‘‘bulk’’ water by $OH^\bullet$ that destroy the chromophoric system through azo bond cleavage. $OH^\bullet$ attack leads to hydroxyl amines followed by subsequent oxidation forming aromatic nitroso and nitro compounds. The attack at the carbon atom adjacent to the azo bond, leading to phenyl derivative radicals. Further degradation pathways are difficult to predict since the fate of the fragments depends on their physical and chemical properties. Further reactions may occur inside the cavity (pyrolysis), in the hypercritical water layer or in the ‘‘bulk’’ water (Rehorek et al., 2004). The major aromatic amines in OMI ww after sonication process reported by Rehorek et al. (2004) as seen in Table 2.15. Benzene (major aromatic amines) in OMI ww (Rehorek et al., 2004) as shown in Figure 2.9.

Table 2.15 The major aromatic amines in OMI ww after sonication process (Rehorek et al., 2004).

No	Aromatic Amines Names	No	Aromatic Amines Names
1	aniline	10	p–xylene
2	4–nitroaniline	11	m–xylene
3	o–toluidine	12	mesitylene
4	4,4–oxydianiline	13	durene
5	2,4,6–trimetlyaniline	14	benzidine
6	anisidine	15	3,3,5,5–tetrametlylbenzidine
7	benzene	16	dimethylaniline
8	nitrobenzene	17	3,3–dichlorobenzidine
9	ethylbenzene		



Benzene
Molecular formula

Kekulé Structures
(Isomers)

Planar Hexagon
Bond Length 140 pm

Sigma Bonds
sp^2Hybridized orbitals

6 p_z orbitals

delocalized pi
system

Benzene ring
Simplified depiction

Figure 2.9 Benzene, C_6H_6 (cther names; benzol and cyclohexa-1,3,5-triene) (Rehorek et al., 2004).

2.2.3 Fatty Acids

Rancidification is the chemical decomposition of fats, oils and other lipids (This may also occur in mechanical cutting fluids). There are 3 basic types of Rancidity:

- Hydrolytic rancidity occurs when H_2O splits fatty acid chains away from the glycerol backbone in glycerides. Triacylglycerols may be hydrolysed into free fatty acids).

- Oxidative rancidity occurs when the double bonds of an unsaturated fatty acid react chemically with O_2.

- Microbial rancidity refers to a process in which micro-organisms such as bacteria use their enzymes, including lipases, to break down chemical structures in the fat. In each case, these chemical reactions result in undesirable odors and flavors.

Free fatty acids produced by hydrolysis can undergo auto-oxidation. Oxidation primarily occurs with unsaturated fats by free radical-mediated processes. These chemical processes can generate highly reactive molecules in rancid foods and oils that are responsible for producing unpleasant and noxious odors and flavors (Richardson & Montgomery, 2005).

Rancidification can be decreased, but not completely eliminated, by storing fats and oils in a cool, dark place with little exposure to O_2 or free-radicals, since heat and light accelerate the rate of reaction of fats with O_2 (Richardson & Montgomery, 2005). The fat composition in olive as seen in Table 2.16. The major fatty acids in OMI ww after sonication process reported by Richardson & Montgomery (2005) in Table 2.17. Some fatty acids in OMI ww after sonication process (Richardson & Montgomery, 2005) as shown in Figure 2.10.

Table 2.16 The fat composition in olive (Food Standards Agency, 1991; Richardson & Montgomery, 2005).

Fat Composition of Olive		
Saturated fats		palmitic acid: 7.50–20.00% stearic acid: 0.50–5.00% arachidic acid: < 0.80% behenic acid: < 0.30% myristic acid: < 0.10% lignoceric acid: < 1.00%
Unsaturated fats	monounsaturated fats	oleic acid: 55.00–83.00% palmitoleic acid: 0.30–3.50%
	polyunsaturated fats	linoleic acid: 3.50–21.00 % linolenic acid: < 1.50%

Table 2.17 The major fatty acids in OMI ww after sonication process (Richardson & Montgomery, 2005).

No	Fatty Acids Names	No	Fatty Acids Names
1	oleic acid	13	lactic acid
2	linoleic acid	14	acetate
3	linolenic acid	15	propionate
4	sinapic acid	16	butyrate
5	vanillin	17	iso–butyrate
6	iso–captionate	18	iso–valerate
7	captionate	19	valerate
8	heptanoic acid	20	acetic acid
9	palmitic acid	21	myristic acid
10	stearic acid	22	lignoceric acid
11	arachidic acid	23	palmitoleic acid
12	behenic acid		

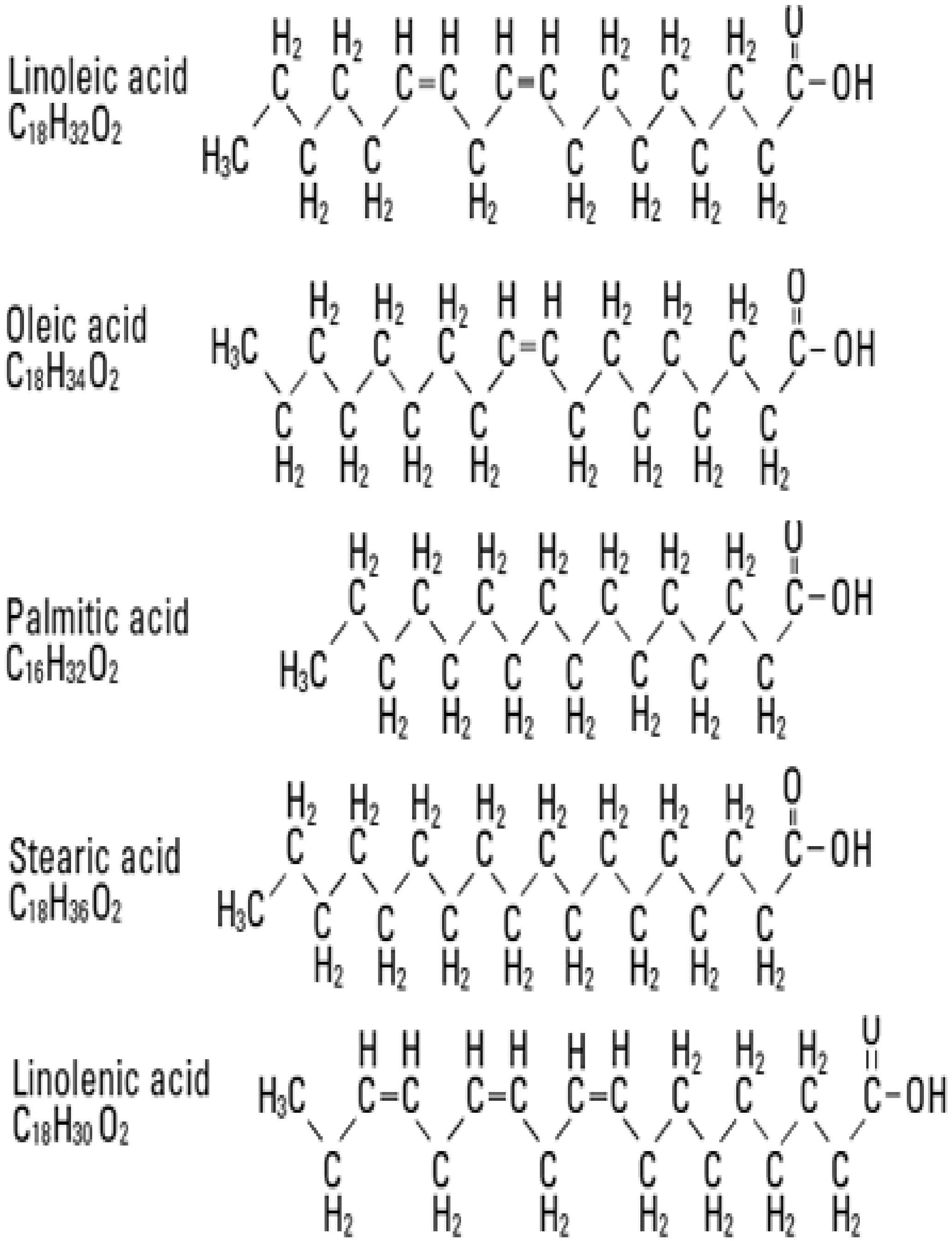


Figure 2.10 The major fatty acids in OMI ww (Richardson & Montgomery, 2005).

2.2.4 Color

Oxidation and pyrolysis are main degradation mechanisms for decolorization with ultrasound.

Reactions in the bulk are facilitated by increasing the temperature due to the higher mass transfer of different species at higher temperatures and this leads to an enhancement of the reaction rate of radicals ($H^{\bullet}$, $OH^{\bullet}$, $O_2H^{\bullet}$) with dye molecules (Ghodbane & Hamdaoui, 2009a, 2009b). On the other hand, any increase in temperature will raise the vapor pressure of a medium and so lead to easier cavitation but less violent collapse (Behnajady et al., 2008a, 2008b).

Under extreme alkaline conditions ($pH > 7.0$), $OH^{\bullet}$ scavenging effects become more significant (Vajnhandl et al., 2005, 2007). The enhancement of degradation rate at basic conditions ($pH > 7.0$) may be caused by the change of hydrophobic property of dye. The hydrophilic property of the dye which is mostly degraded outside the cavitation process by the $OH^{\bullet}$ produced by ultrasound (Ghodbane & Hamdaoui, 2009b).

2.3 Properties of Textile Industry Wastewater (TI ww)

Overall at present there are more than 100000 commercial dyes with a rough estimated production of $7.00x10^5$–$1.00x10^6$ tons/year (Christie, 2007; Hunger, 2003; Husain, 2006; Meyer, 1981; Zollinger, 1987, 1998). Of such a huge production the exact data on the quantity of dyes discharged in environment is not available. However, it is reported that 10.00–15.00% of the used dyes enter the environment through wastes (Hai et al., 2007; Husain, 2006). The big consumers of dyes are textile, dyeing, paper and pulp, tannery and paint industries, and hence the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities. Dyes are considered an objectionable type of pollutant because they are toxic (Bae & Freeman, 2007; Christie, 2007; Combes & Havelandsmith, 1982; Nemerow & Doby, 1958) generally due to oral ingestion and inhalation, skin and eye irritation, and skin sensitization leading to problems like skin irritation and skin sensitization and also due to carcinogenicity (Christie, 2007; Hatch & Maibach, 1999; Rai et al., 2005). They impart color to water which is visible to human eye and therefore, highly objectionable on aesthetic grounds. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem (Kuo, 1992; Walsh et al., 1980). Further, the dyes have a tendency to sequester metal and may cause microtoxicity to fish and other organisms (Walsh et al.,1980). As such it is important to treat colored effluents for the removal of dyes.

Some properties of dyes classified on their usage (Christie, 2007; Hunger, 2003) are discussed in brief here.

2.3.1 Acid Dyes

Acid dyes used for nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink-jet printing, food and cosmetics. They are generally water soluble. The principal chemical classes of these dyes are azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso (Christie, 2007; Hunger, 2003).

2.3.2 Cationic (Basic) Dyes

Cationic (basic) dyes used for paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene, terephthalate and to some extent in medicine too. Originally they were used for silk, wool and tannin-mordanted cotton. These water-soluble dyes yield coloured cations in solution and that's why are called as cationic dyes. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine (Christie, 2007; Hunger, 2003).

2.3.3 Disperse Dyes

Disperse dyes used mainly on polyester and to some extent on nylon, cellulose, cellulose acetate and acrylic fibers. These are substantially water-insoluble nonionic dyes used for hydrophobic fibers from aqueous dispersion. They generally contain azo, anthraquinone, styryl, nitro and benzodifuranone groups (Christie, 2007; Hunger, 2003).

2.3.4 Direct Dyes

Direct dyes used in the dyeing of cotton and rayon, paper, leather and, to some extent to nylon. They are water-soluble anionic dyes and, when dyed from aqueous solution in the presence of electrolytes have high affinity for cellulosic fibers. Generally the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines and oxazines (Christie, 2007; Hunger, 2003).

2.3.5 Reactive Dyes

Reactive dyes generally used for cotton and other cellulosics, but are also used to a small extent on wool and nylon. These dyes form a covalent bond with the fiber and contain chromophoric groups such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. Their chemical structures are simpler, absorption spectra show narrower absorption bands and the dyeings are brighter making them advantageous over direct dyes (Christie, 2007; Hunger, 2003).

2.3.6 Solvent Dyes

Solvent dyes used for plastics, gasoline, lubricants, oils and waxes. These dyes are solvent soluble (water-insoluble) and generally nonpolar or little polar, i.e., lacking polar solubilizing groups such as acid, carboxylic acid or quaternary ammonium. The principal chemical classes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane are also used (Christie, 2007; Hunger, 2003).

2.3.7 Sulfur Dyes

Sulfur dyes used for cotton and rayon and have limited use with polyamide fibers, silk, leather, paper and wood. They have intermediate structures and though they form a relatively small group of dyes the low cost and goodwash fastness properties make this class important from an economic point of view (Christie, 2007; Hunger, 2003).

2.3.8 Vat Dyes

Vat dyes used for cotton mainly to cellulosic fibers as soluble leuco salts and for rayon and wool too. These water-insoluble dyes are with principal chemical class containing anthraquinone (including polycyclic quinones) and indigoids (Christie, 2007; Hunger, 2003).

Besides these, there are some other classes too like azoic having azo groups used for cotton and other cellulosic materials; fluorescent brighteners having stilbene, pyrazoles, coumarin and naphthalimides used for soaps and detergents, fibers, oils, paints, plastics, mordant having azo and anthraquinone used for wool, leather, natural fibers after pretreating with metals and anodized aluminium (Christie, 2007; Hunger, 2003).

In this study, TI ww was used during sonication and these TI ww was including Methylene Blue (MB) dyestuff. MB properties summarized as following pages.

2.3.9 Metylene Blue (MB) Dyestuff

Methylene Blue (MB), (IUPAC name is 7–(dimethylamino)–N,N–dimethyl–3H–phenothiazin–3–iminium chloride) is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$ (Environmental Health & Safety, EHS, 2011). It has many uses in a range of different fields, such as biology (as a bacteriologic stain) and chemistry (as an indicator). At room temperature it appears as a solid, odorless, dark green crystals or crystalline powder, having a bronze-like luster, that yields a deep blue color solution when dissolved in water or alcohol. The hydrated form has 3 molecules of water per molecule of MB; Methylene blue trihydrate ($C_{16}H_{24}ClN_3O_3S$) (Adams et al., 2007). Methylene blue should not be confused with methyl blue, another histology stain, new MB, nor with the methyl violets often used as pH indicators. The International Nonproprietary Name (INN) of MB is methylthioninium chloride (Linz et al., 2006).

CHAPTER THREE
LITERATURE REVIEW

3.1 Sonolysis

3.1.1 Theory

The hydroxyl radicals ($OH^\bullet$) are formed by H_2O sonolysis, and the generation rate of the products depends on; the nature and concentration of the gases dissolved in the solution, ultrasonic wave frequency and power, pressure and temperature of the medium (Lauterborn & Vogel, 1984; Suslick, 2000). Applying ultrasound to an aqueous system initiates the cavitation process (the formation, growth, and collapse of gas and vapor-filled bubbles in a liquid). If organic species are present in the H_2O, it is expected that degradation will occur and to complete mineralization. The extreme conditions created by acoustic cavitation initiate 3 distinct destruction pathways for organic contaminants oxidation by $OH^\bullet$, supercritical water oxidation (SCWO) and pyrolysis. Pyrolytic mechanisms dominate at high solute concentrations while $OH^\bullet$ attack dominates at low solute concentrations (Lauterborn & Vogel, 1984; Suslick, 2000).

3.1.2 First Mechanism

The primary mechanism is $OH^\bullet$ oxidation. The severe conditions are enough to break down H_2O vapor within the bubble into H_2 radicals ($H^\bullet$) and $OH^\bullet$. But the highly reactive nature of these radicals prevents a long travel path length into the solution. Only organic molecules present within the bubble or very near the bubble surface will be destroyed in this fashion. Not the simultaneous production of the $OH^\bullet$ indicates that reductive pathways may be available for organic breakdown. (Lauterborn & Vogel, 1984; Suslick, 2000).

3.1.3 Second Mechanism

Supercritical water (SCW) is a phase of H_2O exists above its critical temperature and pressure, 374ºC and 221 atm (Lauterborn & Vogel, 1984; Suslick, 2000). This unique state of H_2O has different density, viscosity and ionic strength properties than H_2O under ambient conditions. Supercritical water oxidation (SCWO) is one technique studied for the treatment of contaminants in wastewater. Since the organic contaminant has an increased solubility within SCW, these organic species are brought into close proximity with the oxidant, O_2 from dissolved air. Oxidation is accelerated. During sonolysis, it is proposed that SCW is present in a small thin shell around the bubble. This mode of destruction is expected to be secondary in importance because the fraction of H_2O in the supercritical state is estimated to be on the order of $1.50x10^{-3}$ parts out of 100 parts of H_2O. The volume of the gaseous bubble is estimated to be $2.00x10^{4}$ times greater than the volume of the thin SCW shell surrounding the bubble. The value of SCW may be limited to increasing the solubility of the organic contaminant near the bubble interface for radical attack. The possible occurrence of SCWO in the sonochemical reactor may be one reason to justify the use of an O_2 containing purge gas (Lauterborn & Vogel, 1984; Suslick, 2000).

3.1.4 Third Mechanism

A third mechanism is pyrolytic breakdown of organic contaminants. Pyrolysis is defined as the thermal destruction of a compound in the absence of O_2. The high temperatures attained within the bubbles are well above the temperatures required to destroy organic materials (Figure 3.1). This mechanism requires the compound to be present in the vapor phase within the bubble. Compounds with higher vapor pressures will have a higher vapor concentration inside the bubble (Lauterborn & Vogel, 1984; Leighton, 1994; Suslick, 1988, 2000). In the bubble during collapse would degrade organic species present within the bubble interior. Since bubble implosion occurs by the influx of a jet stream of the surrounding liquid, it may not be necessary for the organic contaminants to be initially present in the bubble interior for degradation to occur. This implosion scenario is analogous to the injection of contaminated liquid directly into the hot reaction zone (Lauterborn & Vogel, 1984; Suslick, 2000).

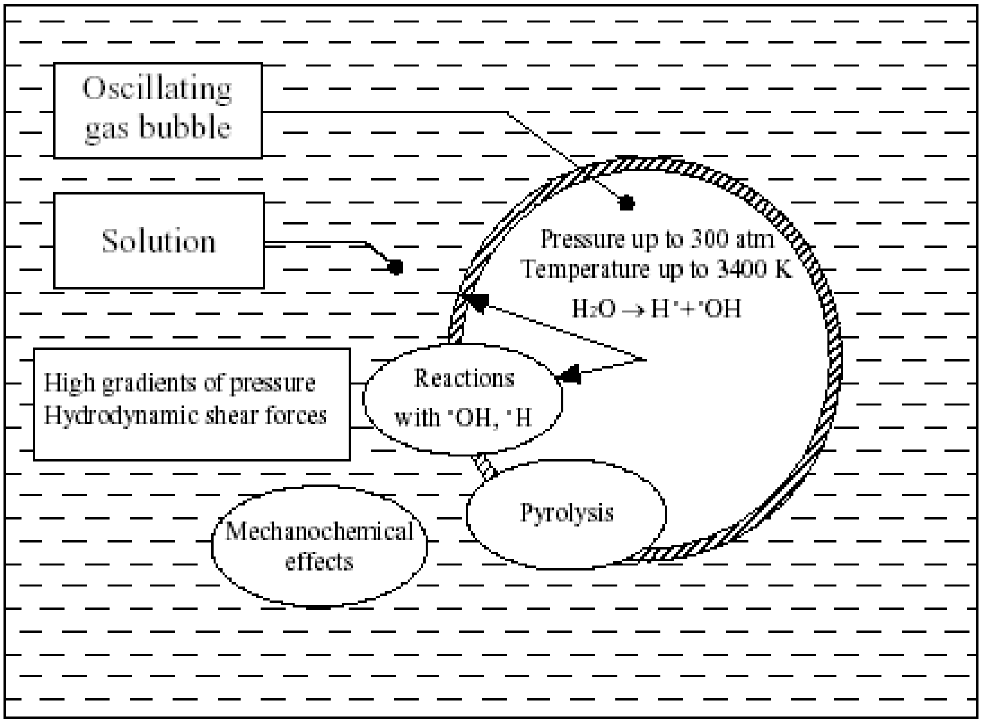


Figure 3.1 Compression of a cavitations bubble in aqueous solutions (T $_{\text{Oscillating gas bubble}}$ = 3127ºC) (Flannigan & Suslick, 2005; Lauterborn & Vogel, 1984; Suslick, 2000).

The principal result of these conditions in an aqueous solution is the breakdown of H_2O vapor in the bubble into $H^\bullet$ and $OH^\bullet$. This essentially transforms the bubble into a micro reactor where interesting chemistry can occur (Minnaert, 1933; Rae et al., 2005). Cavitation is the formation, growth and implosive collapse of bubbles in a liquid. Cavitational collapse produces intense local heating (≈ 4730ºC), high pressures (≈ 1000 atm) and enormous heating and cooling rates (> - 164°C/s) and liquid jet streams (≈ 400 km/h). The size, life time and fate of a cavitation bubble depend on the following parameters: frequency, intensity (acoustic pressure), bubbled gas, external parameter (temperature, pressure) and solvent (Gogate, 2006, 2007, 2008a, 2008b; Suslick, 2000).

3.1.5 Wastewater Treatment by Sonication

Chemical activation for the occurrence of the reaction can be achieved by thermal, photochemical, electrochemical and sonochemical activation. These techniques supply energy to make an active oxidizable species of the pollutants (Suslick, 1986).

3.1.5.1 Recent Advances

3.1.5.1.1 Catalytic Sonicative Degradation of Wastewater. Since sonolysis is a very slow process, catalytic modifications have been tried out to enhance the rates along with sonication. Solid catalysts can be separated by filtration are used for this purpose. Catalysts like Ni, V_2O_5, Pt, AgO and fenton reagent help the oxidation reactions are applicable in these cases (Suslick et al., 1986).

3.1.5.1.2 Chemi-sonication of the Wastewater (CAVOX). Radical attack degrades and oxidises a number of organic contaminants. This homogeneous destruction of compounds (CCl_4, CH_2Cl_2, $C_2H_2Cl_4$) at 100-1000 ppm is possible in conjunction with the strongly oxidising chemicals i.e, H_2O_2 and ultrasound. Depending upon the quantity of the entrained gas and concentration of H_2O_2 used along with intensive cavitation, the destruction process takes 1 - 4 h for 100-1000 ppm (Suslick et al., 1986).

3.1.5.1.3 Synergism of Sonication with Conventional Methods. Coupling of ultrasound with UV radiation or electrostatic forces or with wet air oxidation (WAO between 100 to 372°C) gives synergetic improvements in the treatment efficiency as (Suslick et al., 1986):

3.1.5.1.3.1 Photocatalytic. Photocatlaytic action with the ultrasound has resulted in higher degradation rates of the contaminants. The mechanical effects of cavitation involving photocatalyst surface cleaning and increased mass transfer of the polluting species to the powdered catalyst surface (Arrojo et al., 2008; Suslick et al., 1986).

3.1.5.1.3.2 Electrochemical Effects. Electrochemical effects effective oxidation rate of aromatics is increased when employed with ultrasound. When a salt solution is present with aromatic compound, the reaction becomes faster via formation of intermediate such as, chlorinated hydrocarbons (Suslick et al., 1986).

3.1.5.1.3.3 Sonication-Wet Air Oxidation (SONIWO). Sonication followed by WAO gives an economic hybrid model and an efficient process. Sonication in the presence of the catalytic WAO including catalysts like $CuSO_4$ and $NiSO_4$ is more effective than without a catalyst. Sonication can breakdown large molecular weight compounds are then easily oxidized by WAO. The effluent treatment by sonication is an excellent polishing step. The process looks simple, rather slow and for scale-up, extra energy cost is the major drawback (Applications of sonication process in environmental engineering, 2009; Levec & Pintar 2007; Recent sonication combined with other treatment processes, 2009; Suslick et al., 1986).

3.2 Sonochemistry

In chemistry, the study of sonochemistry is concerned with understanding the effect of sonic waves and wave properties on chemical systems (Suslick et al., 1986; Suslick, 1988; Thompson & Doraiswamy, 1999; 2000). Since acoustic waves have unique physical properties, the corresponding atomic and molecular chemistry is unique as well. Often these effects are most apparent in ultrasonic systems. This is demonstrated in phenomenon i.e, ultrasound, sonication, sonoluminescence and sonic cavitation. e.g, in chemical kinetics, ultrasound can greatly enhance chemical reactivity in a number of systems; effectively acting as a catalyst by exciting the atomic and molecular modes of the system (i.e, the vibrational, rotational, and translational modes). In reactions use solids ultrasound breaks up the solid pieces from the energy released from the bubbles created by cavitation collapsing through them. This gives the solid reactant a larger surface is for the reaction to proceed over, increasing the observed rate of reaction. Ultrasound produces radicals in liquids due to the high temperatures and pressures experienced locally when a bubble collapses. Sonochemistry can be performed by using a bath for ultrasonic cleaning or with a high power probe (Suslick et al., 1986; Suslick, 1988).

Sonochemistry that the use of high-intensity sound (ultrasound) to alter chemical reactions. Types of sonochemistry are:

3.2.1 Heterogeneous Sonochemistry

The use of ultrasound to alter chemical reactions in a 2-phase system, usually a liquid and a solid.

3.2.2 Homogeneous Sonochemistry

The use of ultrasound to alter chemical reactions in a single liquid.

3.3 Cavitation

The formation, growth, and collapse of gas and vapor-filled bubbles in a liquid. Irradiation of liquids with sound or ultrasound can create acoustic cavitation; turbulent flow of liquids can create hydrodynamic cavitation.

3.3.1 Acoustic Cavitation

Ultrasound, with frequencies between 15 kHz and 10 MHz, has a drastic effect on chemical reactions [low frequency or conventional power ultrasound (20-100 kHz), medium frequency ultrasound (300-1000 kHz) and diagnostic or high frequency ultrasound (2-10 MHz)] (Cum et al., 1992; Vajnhandl & Majcen Le Marechal, 2005) (Table 3.1). The mechanism that causes this effect is known as acoustic cavitation. With typical sound velocities in liquids of ≈ 1500 m/s, acoustic wavelengths range from ≈ 10 to 10^{-4} cm. This phenomenon proceeds as follows:

A sound wave impinging on a solution is merely a cyclic succession of compression and expansion phases imparted by mechanical vibration (Vajnhandl & Majcen Le Marechal, 2005). During the solution expansion phase, small vapor-filled bubbles are formed due to weak points in the solution, primarily at trapped gas pockets on particulate surfaces. These bubbles grow and contract in response to the expansion and compression phases of the cycle, respectively. Because, the surface area of the bubble is greater during the expansion phase than during the compression phase, growth of the bubble is greater than the contraction, resulting in an increase in the average bubble size over many cycles. Over time, the bubble reaches a critical size depending on the ultrasonic frequency, where upon the pressure of the vapor within the bubble cannot withstand the external pressure of the surrounding solution. The result is a catastrophic collapse of the bubble with high velocity jets of solution shooting into the interior. This implosion process is acoustic cavitation. Extreme environments are produced in and near the bubble as a result. It is estimated that 4.00×10^4 bubbles/s/m^3 are produced. The bubbles are on the order of 10 to 200 μm in diameter, and they are short lived, with a life time ≈ 10 μs. So, the bulk solution conditions remain relatively unaffected. But the implosion of the bubble causes enormous local effects. The temperature of the vapor within the bubble has been estimated to reach as high as 4730ºC with a pressure ≈ 1000 atm (Cum et al., 1992; Vajnhandl & Majcen Le Marechal, 2005).

Table 3.1 Range of parameters that make cavitations easier or implosion more violent (Vajnhandl & Majcen Le Marechal, 2005).

	Characteristic of			
	Reaction Medium	**Sound Wave**	**Gas**	**Other Parameters**
Positive effect on cavitation	high vapor pressure	low frequency (power US)	high solubility	high external temperature
	low viscosity	greater intensity		low external pressure
	low surface tension			
Positive effect on implosion	low vapor pressure	low frequency (kHz region)	low solubility	low external temperature
			larger ratio of specific heat	high external pressure
			low thermal conductivity	
			Monoatomic gases	

3.3.2 Basics of Sonochemistry

Sonochemistry is defined as the chemical effects produced by subjecting a chemical reaction to sound waves (Figure 3.2) (Suslick, 1988, 2000; Suslick & Flannigan, 2005). Transducers are used for the generation of ultrasound and they are liquid driven or magnetostrictive or piezoelectric transducers. It is only ultrasound is useful for chemical reactions. Similar to the transmission of the normal sound waves, in ultrasound (> 16 kHz) during the rare faction stage of the wave, the liquid molecules are torn apart causing cavitation to occur i.e., formation of voids. These spots or cavities violently collapse during the next compression cycle. Propagation of ultrasonic waves in the liquid promotes the formation of cavitation bubbles can grow and implode under the periodic variation of the pressure fields (Suslick, 1988, 2000; Suslick & Flannigan, 2005) in Figure 3.2.

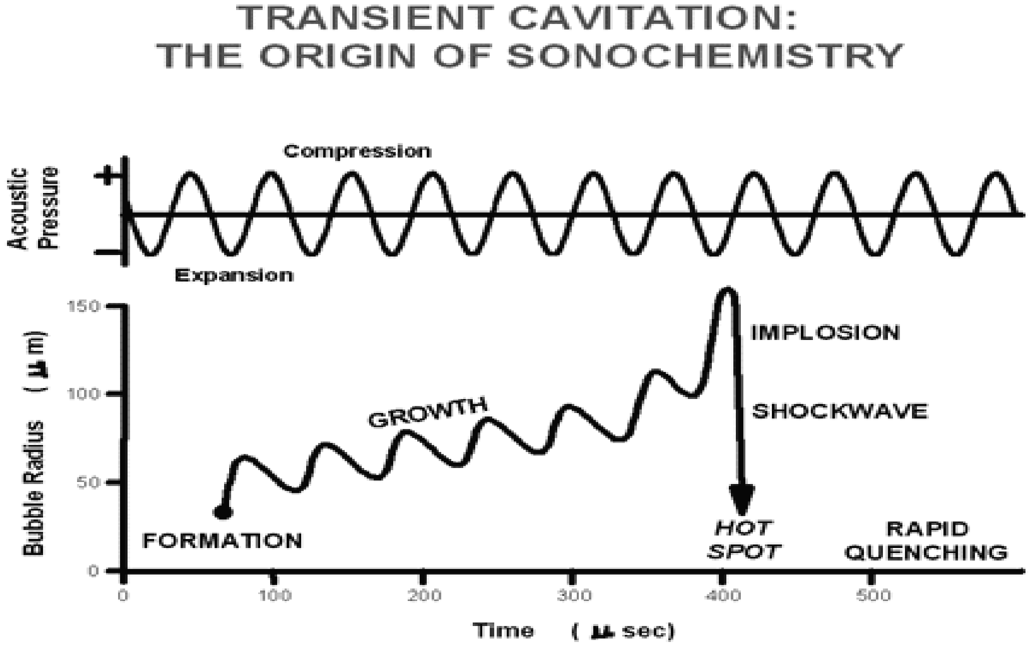


Figure 3.2 Transient acoustic cavitation: the origin of sonochemistry & sonoluminescence (Beckett & Hua, 2001; Generation of an acoustic bubble, 2011; Suslick, 2000; Suslick & Flannigan, 2005).

3.3.2.1 Forms of Cavitation

Two forms of cavitation are;

3.3.3.1.1 Transient Cavitation. The bubbles grow over one (2 or 3) acoustic cycles to double their initial size and finally collapse violently.

3.3.3.1.2 Stable Cavitation. The bubbles oscillate around their equilibrium position over several refraction/compression cycles.

3.3.2.2 Characteristics of the Ultrasonic Wave

Ultrasound travels through a liquid as a longitudinal wave, the molecules of the liquid oscillate about their equilibrium positions in the direction of the motion of the wave (Figure 3.3). The effective pressure in any given region of liquid is showed by the Eq. (3.1):

$$P_t = P_h + P_a \tag{3.1}$$

where;

P_t : Total pressure in a specific region in the liquid (atm),

P_h : Hydrostatic pressure (atm),

P_a : Acoustic pressure in a particular region and time (atm).

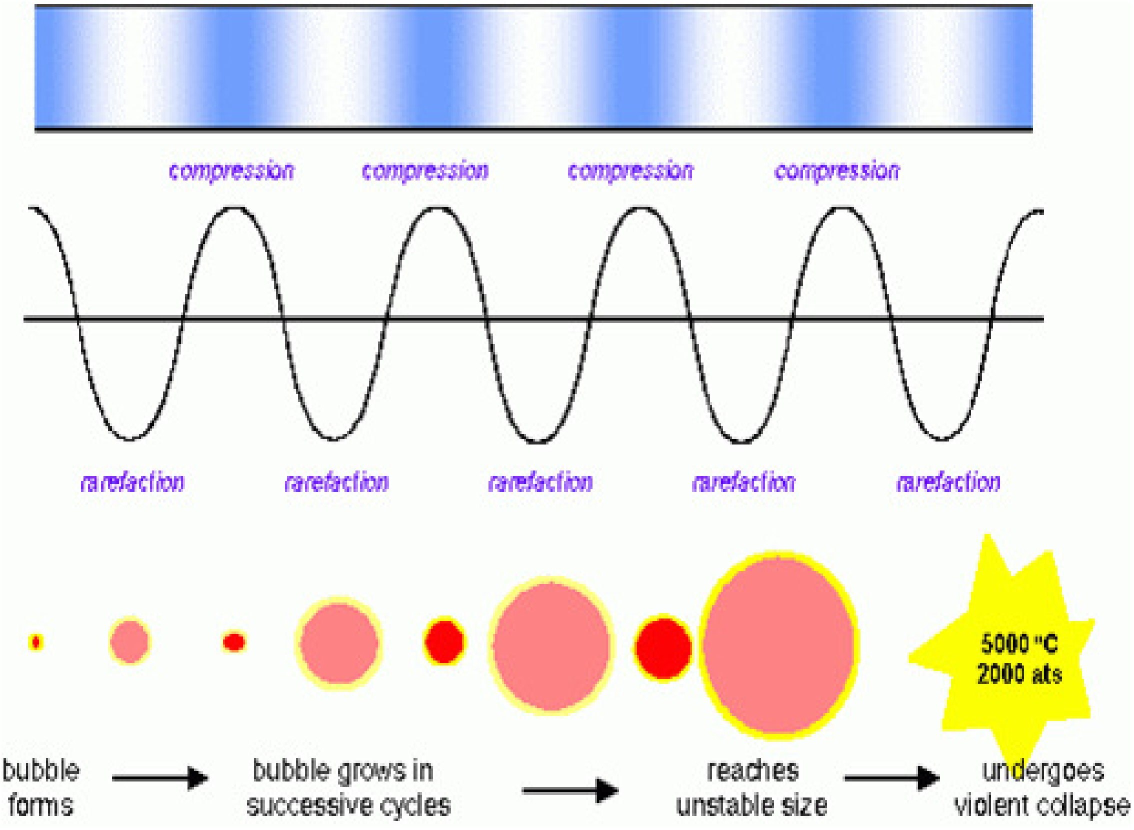


Figure 3.3 Generation of an acoustic bubble (Suslick, 2000).

3.3.2.3 Nucleation, Growth and Collapse of Micro Bubbles

Pockets of gas are trapped on microscopic impurities (dust particles), inherently present in any liquid or in imperfections on the wall of the vessel (Suslick, 2000). The gas nuclei expand under the influence of the ultrasonic wave and detach to form free micro bubbles in the liquid. The micro bubbles continue to adsorb energy from the wave and grow isothermally. When the micro bubbles reach a critical size (≈ 2 to 3 times the resonance radius) they implode violently. Assuming adiabatic collapse, the temperature of the hot spot can be estimated using the equation below. This equation demonstrates the importance of g in determining the collapse temperature (the collapse is not completely adiabatic, so the thermal conductivity will affect T_f in a real system) in Eq. (3.2):

$$T_f = \left[T_i \left(\frac{R_{\max}}{R_{\min}} \right)^{(3g-1)} \right] \tag{3.2}$$

where;

T_f : Temperature of the core (^oC),

T_i : Ambient temperature (^oC),

R_{max} and R_{min} : Maximum and minimum bubble radius,

G: The ratio of specific heats,

C_p/C_v of the gas inside the bubble (g=1.67 for monoatomic gases and 1.40 for diatomic gases).

3.3.3 Ultrasonic Irradiation

Ultrasonic irradiation differs from traditional energy sources (i.e, heat, light, or ionizing radiation) in duration, pressure and energy/molecule (Suslick, 2000). The immense local temperatures and pressures, the extraordinary heating and cooling rates generated by cavitation bubble collapse mean that ultrasound provides an unusual mechanism for generating high energy chemistry. Like photochemistry, very large amounts of energy are introduced in a short period of time, but it is thermal. As in flash pyrolysis, high thermal temperatures are reached, but the duration is very much shorter (> 10^{-4} s) and the temperatures are even higher (by 5- to 10-fold). Similar to shock-tube chemistry or multiphoton infrared laser photolysis, cavitation heating is very short lived, but occurs within condensed phases. Sonochemistry has a high-pressure component suggests that one might be able to produce on a microscopic scale the same macroscopic conditions of high temperature pressure bomb reactions or explosive shockwave synthesis in solids. The most intense and reliable source of ultrasound used in the chemical laboratory is the direct immersion ultrasonic horn (50 to 500 W/cm²) can be used for work under either inert or reactive atmospheres or at moderate pressures (< 10 atm). Ultrasound can be easily introduced into a chemical reaction with good control of temperature and ambient atmosphere (Suslick, 2000).

3.3.4 Sonoluminescence

Sonoluminescence is the emission of light during ultrasonic irradiation of liquids (Suslick, 2000). There are two types of sonoluminescence as follows:

3.3.4.1 Multi-bubble Sonoluminescence

The emission of light from a cloud of cavitating bubbles formed during ultrasonic irradiation of a liquid (Suslick, 2000).

3.3.4.2 Single-bubble Sonoluminescence

The emission of light from a single cavitating bubble in a liquid, usually H_2O (Suslick, 2000).

3.4 Ultrasonic Degradation

The use of ultrasound are applied for degradation of organic contaminants. Nearly all are performed in aqueous media for relevance to treating contaminated ecosystems (Suslick, 2000). Chlorinated compounds (carbon tetrachloride, pentachlorophenate, trichloroethylene, chloroform, methylene chloride and chlorofluorocarbons) seem to be the most studied class of compounds. Most of these species have a high vapor pressure and tend to concentrate within the bubbles allowing fast degradation down to Cl^{-1}, CO_2 and other inorganic species. The degradation mechanism is pyrolysis rather than $OH^{\bullet}$ attack. Phenolic compounds provide a more opportune system because of their relatively high solubility in H_2O. Volatility is a lesser concern than with other contaminants. Sonolysis of phenol showed mineralization of phenol with benzoquinone, hydroquinone and catechol as the organic intermediates and oxalic, maleic, acetic, formic and propanoic acids as the short chain polar intermediates. All are degraded by $OH^{\bullet}$ attack (Lindsey & Tarr, 2000a). Sonochemical reactions of nitrotoluenes in the presence of $KMnO_4$ oxidize the $-CH_3$ group to –COOH. Nitrophenol degrades primarily by denitration during pyrolysis with radical attack of minor importance to produce NO_2, NO_3, benzoquinone, hydroquinone, nitrocatechol, formate and oxalate (High-output ultrasonic reactor, 2008; Suslick, 2000).

3.5 The Advantages of Sonication Method in Wastewater Treatment

The advantages of sonication method can be summarized as follows:

1. The sonication method is simple to use.

2. There is no hazardous or complicated operation requiring skilled labor.

3. The method can be easily operated with immediate on/off by central control.

4. The equipment necessary to implement the reliable method has a footprint and is modular in desing, such that additional units can be added easily.

5. The implementing equipment does not need much space.
6. It is especially useful when it is not possible to stir the sample.
7. The sonochemical destruction can be achieved at ambient conditions.
8. The sonochemical reduction ca be applied different temperatures.
9. Sonication process can be applied as a physico-chemical method for, and it does not require any transference of the pollutant from an aqueous phase to another phase, as it would be required in combustion or adsorption.
10. It may also be used to provide the energy for certain chemical reactions to proceed.
11. Sonication method provides a high destruction effect on the toxic and refractory compounds in wastewater.
12. Sonication process does not require any, although it may be enhanced by the addition of chemical additives in wastewater.
13. Sonication method does not require the pH adjustment of wastewater.
14. Sonication process does not require the filtration of wastewater.
15. Sonication method to operate the short reaction time and to obtaine higher removal efficiencies compared with other wastewater treatment processes.
16. The method does not produce any waste sludge. Over biological processes which generate sludge that mandates disposal (generally as hazardous waste).
17. Sonication method does not produce any off gases.

18. Those using ozone (O_3) in which the unused O_3 in the off-gas must be destroyed and the residual O_3 in the treated water must be removed.

19. Sonication method is not limited by water and wastewater characteristics such as turbidity, color, odor or suspended solids.

20. Sonication process can be applied as either a pre-treatment or post-treatment in combination with other water purification processes.

21. It is feasible to apply the method to different environmental matrices (water, air, soil and others) and work sites.

22. Sonication is an alternative to the freeze-pump-thaw and sparging methods in wastewater treatment.

23. Sonication method can be provided a naturaly stirring process during wastewater treatment.

24. Sonication can also be used to initiate crystallisation (anti-solvent precipitations) processes and even control polymorphic crystallisations in wastewater treatment.

25. Sonication be used to intervene in anti-solvent precipitations (crystallisation) to aid mixing and isolate small crystals in wastewater.

26. Sonication method is more economical than other wastewater treatment processes.

3.6 Literature Review for Petrochemical Industry Wastewater (PCI ww)

Various technical methods have been applied for PCI ww treatment: (1) Physical, (2) Chemical, (3) Biological and their combinations.

New technologies in the PCI ww treatment were discussed as follows:

- PCI ww treatment by means of clean electrochemical technologies (Valero et al., 2010).

- Enhanced biodegradation of PCI ww using ozonation and biological activated carbon (BAC) advanced treatment processes [treating phenol, benzoic acid, aminobenzoic acid and PCI ww which contain acrylonitrile butadiene styrene (ABS)] (Lin et al., 2001).

- Sulfide removal in PCI ww by autotrophic denitrification (Vaiopoulou et al., 2005).

- Application of anaerobic treatment to chemical and PCI ww (Whang et al., 2009).

- Observer-based time-optimal control of an aerobic SBR (sequencing batch reactor) for chemical and PCI ww treatment (Vargas et al., 2000).

- Transformation of dimethyl phthalate, dimethyl isophthalate and dimethyl terephthalate by *Rhodococcus rubber Sa* [phthalate ester isomers, including dimethyl phthalate (DMP), dimethyl isophthalate (DMI) and dimethyl terephthalate (DMT), were found to be transformed by *Rhodococcus rubber Sa* isolated from a mangrove sediment using DMT as a carbon source initially] and modeling the processes using the modified Gompertz model (Li et al., 2005).

- The use of wetlands for PCI effluents (Knight et al., 1999; New technologies in the PCI ww treatment, 2011).

The removals performed with sonication process in PCI ww were as follows;

In the study by Laughrey et al. (2001) 77.00% total PAHs removal was observed for the sonochemical degradation of 50.00 μg/l of initial PAHs mixture concentration (NAP, ACL and PHE) in PCI ww after 120 min sonication time, at 40°C, at 150 W power and at 24 kHz frequency. In a performed by Psillakis et al. (2004) 74.00% NAP, 72.00% ACL and 76.00% PHE removals were obtained in PCI ww containing 50 ng/ml NAP, 50 ng/ml ACL and 50 ng/ml PHE, at 150 W power, at 80 kHz frequency in the presence of 320 ng/ml of 1-butanol, 100 g/l of NaCl, 75 and 100 g/l of $FeSO_4$, respectively, after 100 min sonication time, at 40°C.

Psillakis et al. (2003) 82.00% NAP, 80.00% ACL, 75.00% ACT, 70.00% FLN, 67.00% PHE, 65.00% ANT, 58.00% FL and 55.00% PY removals were detected in PCI ww containing 10.00 ng/ml NAP, 50.00 ng/ml ACL, 30.00 ng/ml ACT, 15.00 ng/ml FLN, 20.00 ng/ml PHE, 20.00 ng/ml ANT, 15.00 ng/ml FL and 10.00 ng/ml PY, respectively, at 80 kHz frequency, at 130 W power, after 180 min sonication time at pH=7.0 and at 25°C.

In a study performed by David (2009) it was found 65.00% NAP, 57.00% PHE, 53.00% PY, 50.00% BkF and 55.00% ANT removals in PCI ww containg 227 ng/ml NAP, 97 ng/ml PHE, 118 ng/ml PY, 12 ng/ml BkF and 110 ng/ml ANT, respectively, at 20 and 506 kHz frequencies, at 30 W power, after 120 min sonication time, at 2.4 and 6.1 W/cm^2 power intensities, at 20±1°C. The concentrations of PAHs in aqueous solution appears to be sufficient to detect the gaseous by-products ($CO >> CO_2 > C_2H_2 \approx C_2H_4$), which were analyzed in the headspace of the reactor after 90 min of ultrasonic treatment.

In a study performed by Little et al. (2002) 56.00% PHE yield was found in PCI ww containing 60 ng/ml PHE, at 40°C, at an ultrasound frequency of 30 kHz and at a power of 320 W after 135 min sonication time. Wheat & Tumeo (1997) 75.00% PHE removal was measured in PCI ww containing 390 ng/ml PHE, under air (100 ml/min), at 30 kHz frequency, at 250 W power, after 120 min sonication time, at 24°C. Sun & Weavers (2006) 85.00% PHE removal was observed in PCI ww containing 200 ng/ml PHE, in 10.00 mg/l mixture of acetone, hexane and dichloromethane, at 20 kHz frequency, at 400 W power, after 40 min sonication time, at 20°C.

In a study performed by Park et al. (2002) 59.00% coronene, 68.00%1,12-benzoperylene, 70.00% PY, 73.00% PHE, 79.00% ANT and 85.00% 1-methylnaphthalene removals were found in PCI ww containing coronene, 1,12-benzoperylene, PY, PHE, ANT and 1-methylnaphthalene (between 0 to 40 mg/l concentrations), respectively, in H_2O_2=3.00 g/l, at 20 kHz frequency, at 600 W power, after 120 min sonication time at 25°C. Gogate et al. (2004b) determined 89.00-97.00% less hydrophobic PAHs (NAP, ACL, PHE, FLN and ANT) removals in PCI ww, in H_2O_2=1.00 g/l, at 25 kHz frequency, at 500 W power, after 120 min sonication time at 25°C.

Taylor Jr. et al. (1999) 60.00% PHE, 55.00% ANT and 50.00% PY yields was observed in PCI ww containing 10.00 ng/ml PHE, 30.00 ng/ml ANT and 50.00 ng/ml PY, respectively, at 20 kHz frequency, at 600 W power, in 20 mg/l Fulvic Acid, in 50 and 100 ml sonication volume, after 30 min sonication time, at 20°C.

Kim et al. (2001) observed 72.00% dibenzothiophene removal in PCI ww, in 7.50 mg/l dibenzothiophene, at an ultrasonic frequency of 20 kHz, after 180 min sonication time at pH=7.0 and an energy intensity of 300 W/cm^2, at 25°C.

Psillakis et al. (2004) found 74.00% PHE, 72.00% NAP and 76.00% ACL yields in PCI ww, respectively, at a temperature 40°C, power 450 W and frequency of 28 kHz after 98 min sonication time, at pH=7.0, respectively.

In the study by Laughrey et al. (2001) 77.00% total PAHs removal efficiency in PCI ww was observed for the sonochemical degradation of 50.00 μg/l of initial PAHs mixture concentration (NAP, ACL and PHE) in water after 120 min sonication time, at 40°C, at 150 W and at 24 kHz. In a study performed by Kojima et al. (2005) 99.00% total PAHs removals in PCI ww was measured at 35 kHz frequency, at 800 W power, after 120 min aeration conditions at 25°C.

Benabdallah El-Hadj et al. (2007) found 31.00-34.00% NAP and 44.00-50.00% PY removals in PCI ww, in mesophilic (35°C) and thermophilic (55°C) conditions for 2.0 ng/ml NAP and 1.55 ng/ml PY, respectively, at 20 kHz frequency and at 70 W power, after 110 min sonication time, before anaerobic digestion. Wu & Ondruschka (2005) 0.87% FL and 0.77% BaA and 79.00% BbF yields was found in PCI ww at 30 kHz frequency, at 500 W power after 120 min sonication time, at 25°C and at pH=7.5, respectively.

Laughrey et al. (2001) obtained 80.00% total PAHs removals in PCI ww at 20°C under 30 min of N_2(g) (6.00 mg/l N_2) sparging at 20 kHz frequency, and at 70 W power, after 120 min sonication time, at pH=7.0. The PAHs yields reached higher than that found by Laughrey et al. (2001) under similar operational and sonicational conditions. In the last study, 87.00% total PAHs removal was found for initial 0.90 μg/l total PAHs concentration at 400 W power and at 24 kHz frequency under 25 min N_2(g) (5.00 mg/l N_2) sparging at 60°C after 150 min sonication time, at pH=7.0.

In a study performed by Wen et al. (2003) 85.00% total PAHs removal was obtained in PCI ww containing 10.00 mg/l TiO_2 powder, at frequency and power of 32 kHz and 480 W after 150 min sonication time at 60°C and at pH=7.0.

Lindsey & Tarr (2000b) 72.00% total PAHs yield was observed in PCI ww containing Fe^{+2}=15.00 mg/l, at a 34 kHz frequency, at a power of 450 W after 125 min sonication at 60°C and at pH=7.2. Psillakis et al. (2004) studied the sono-removal of 150 μg/l total initial concentration of PAHs mixture (NAP, ACT, PHE) in an aqueous solution. 92.20% NAP, 96.25% ACT and 89.80% PHE removal efficiencies were found with Fe^{+2}=14.00 mg/l concentration, with a power of 150 W, at a frequency of 80 kHz, a sonication temperature of 20°C, after 150 min irradiation at pH=6.8, respectively. Beckett & Hua (2000, 2003) 40.00% 1,4–dioxane (heterocyclic organic compound) was measured in PCI ww with the addition of 0.02-1.00 ng/l Fe^{+2} concentrations, at a 30 kHz frequency, at a power of 590 W after 115 min sonication time at pH=7.0.

Son et al. (2006) investigated the thermal degradation and chemical oxidation of 1,4–dioxane throughout sonication. These processes contributed approximately 25.00% and 34.00% to the thermal degradation and chemical oxidation of 1,4–dioxane, respectively, according to the result of the sonication process after 100 min sonication time without HCO_3^{-1} and with 10.00 mg/l HCO_3^{-1}, respectively.

Son et al. (2006) reported 78.12% total PAHs removal in PCI ww containing 50.00 ng/ml of mixture of seven PAHs (NAP, ACL, ACT, FLN, PHE, ANT and FL) in the presence of $S_2O_8^{-2}$ =10.00 mg/l after 150 min of sonication time at pH=6.0 and at 30°C.

3.7 Literature Review for Olive Mill Industry Wastewater (OMI ww)

Since the OMI ww contains a great variety of components different treatment processes werew applied to treat the wastewaters of this industry. These are based on:

1. Biological treament such as aerobic (Garrido Hoyos et al., 2002), bioreactors (Dhaouadi & Marrot, 2010), Aerobic Fluidized Bed Fermentor (AFBF) (Hamdi & Ellouz, 1993), anaerobic digester (Anderson & Yang, 1992; Andreozzi et al., 1998; Blika et al., 2009), Up-flow Anaerobic Sludge Blanket reactor (UASB) (El-Gohary et al., 2009; Sabbah et al., 2004), anaerobic filters (AF) (Borja & González, 1994; Martinez Nieto et al., 1993), anaerobic contact process (Borja & González, 1994), etc.

2. Physical and Physico-chemical methods such as thermal (Blika et al., 2009), distillation (El-Abbassi et al., 2009), combustion or incineration (Miranda et al., 2007), flocculation-clarification (Rozzi & Malpei, 1996), membrane technology, (Paraskeva et al., 2007), ultrafiltration (Turano et al., 2002), centrifugation (Turano et al., 2002), reverse osmosis (Coskun et al., 2010), sonolysis (Cravotto et al., 2008; Vassilakis et al., 2004), fenton reaction, (Khoufi et al., 2006, 2009) electrochemical oxidation (Gotsi et al., 2005), electrocoagulation (Adhoum & Monser, 2004; Inan et al., 2004), adsorption (Al-Malah et al., 2000; Azzam et al., 2004), ion exchance (Fiorentino et al., 2004), etc.

3. Natural treatment (land applications) (Kapellakis et al., 2006)**.**

The recent literature studies performed with sonication process in OMI ww were as follows;

Benedito et al. (2004) investigated the treatment of olive oil extraction wws containing alpechin (Olive oil extraction produces a great volume of residue. These olive mill wastes are known as alpechin) and other solids by sonication. 40.00% COD yield was provided in OMI ww containing 10.00 mg/l alpechin at 40 kHz frequency, at 700 W power, after 15 min sonication time, at 50°C.

In a study performed by Jimenez et al. (2007) 40.00%, 27.00% and 53.00% TFAs removals were found in OMI ww in 3 different sonicators with horn probe, cleaning bath and conventional thermal treatment, respectively, at a power of 150 W at a frequency of 25 kHz, in the presence of 100 l/h air, for 20 min sonication time at temperatures varying between 28°C and 30°C.

Zouari (1998) 60.00% COD, 50.00% color and 20.00% phenol removals was found in OMI ww after 180 min sonication time, at 30 kHz frequency, at 350 W power at pH=6.5 and at 30°C.

Nikolopoulos et al. (2004) 60.40% and 98.70% 4-hydroxybenzoic acid (a phenolic compound) removals was found in OMI ww containing 5 mg/l a mixed (Al–Fe) pillared clay, named FAZA, in H_2O_2=500 mg/l, at 20 kHz frequency, at 400 W power, after 240 min sonication time, at 20±2°C.

Silva et al. (2007) 95.00% total phenol yield was obtained in OMI ww containing a concentration of 50 mg/l each one of cinnamic acid, p-hydroxycinnamic acid, o-hydroxycinnamic acid, 3,4-dihydroxycinnamic acid, 4-hydroxy-3-methoxycinnamic acid, 3,5-dimethoxy-4-hydroxybenzoic acid, 4-hydroxy-3-methoxybenzoic acid, 3,4,5-trihydroxybenzoic acid, 4-hydroxybenzoic acid, m-dihydroxybenzene, 1,2-dihydroxybenzene, 3,4-dimethoxybenzoic acid and 3,4-dihydroxybenzoic acid), 0.75 g/l Degussa TiO_2 suspensions, in H_2O_2=400 mg/l, after 180 min sonication time, at 80 kHz frequency, at 120 W power, at 31±1°C and pH=4.8-5.5, respectively.

Atanassova et al. (2005b) 45.00% COD and 28.00% total phenol removals was measured in OMI ww, at 80 kHz frequency, at 150 W power, at 60°C and 240 min irradiation time, in 19.00% NaCl addition.

In a study performed by Priego-Capote et al. (2006) it was found 73.00% color removal after 110 min of sonication time at a power of 400 W and a frequency of 50 kHz at 60°C with 3.00 g/l C_4H_9OH concentration in OMI ww.

Japon-Lujan et al. (2006) 40.00% total phenol yields were observed in OMI ww containing 8.00 ml phenolic compounds (such as, tyrosol, oleuropein, hydroxytyrosol, apigenin-7-glucoside, verbacoside and luteolin-7-glucoside), in 5.00 ml ethanol solvent solution, at 20 kHz frequency, at 450 W power, after 25 min sonication time, at 40°C and pH=8.0-12.0.

In a study performed by Jahouach-Rabai et al. (2008) 89.00% TFAs removal was observed at 20 kHz frequency, at a 750 W ultrasonic power, after 45 min sonication time at 70°C in an OMI ww. By increasing of H_2O_2 concentrations the TFAs concentrations decreased by oxidation of oleic acid and further degradation to hexanal was detected. 61.00% removal efficiencies were obtained for some non-odorous organics (hexanal, hept-2-enal, 2(E)–decadienal, 4(E)-decadienal) and for some phenolic organics.

Vassilakis et al. (2004) investigated the sonochemical degradation of some phenolic by-products namely, *p*-coumaric acid (polyphenolic compound) and *p*-hydroxybenzaldehyde in OMI ww. 90.00% total phenol, 30.00% *p*-coumaric acid 55.00% p-hydroxybenzaldehyde (polyphenolic compounds) yields were found at an initial phenolic compound concentration of 100 mg/l, at 80 kHz frequency, at 150 W power and at 30^{o}C after 120 min sonication time.

Chemat et al. (2004a) investigated the TFAs in an OMI ww composed of palmitic, stearic, oleic and linoleic acids. The removal yields of these TFAs were 61.00% in OMI ww at 20 kHz frequency, at a power of 150 W, after 20 min of sonication time at 50^{o}C. In a study performed by Hachicha, R. et al. (2009) it was found that the TFAs fraction of OMI ww composed of oleic, palmitic and linoleic acids and degraded through sonication with yields varying between 50.40% and 52.00% after 180 min sonication time, at 30 kHz frequency, at 200 W power, at 35^{o}C.

Canizares-Macias et al. (2004) investigated an ultrasound process assisted with Rancimat method for the determination of the phenol yields in OMI effluents. 56.00% phenol removal was found at 20 kHz frequency, at a power of 400 W, after 60 min sonication time at 25^{o}C.

Kallel et al. (2009a, 2009b) 16.55% 4-hydroxyphenylethanol, 30.00% 4-hydroxybenzoic acid, 40.00% 4-hydroxy-3-methoxyphenethylacohol, 50.00% 4-hydroxy-3-methoxybenzoic acid, 70.93% 3,4-dihydroxyphenyl alcohol, 35.00% 3,4-dihydroxybenzoic acid, 43.00% 3,4-dihydroxyphenylglycol, 46.00% 3,4-dihydroxycinnamic acid, 48.00% total phenol and 92.00% COD removals were achieved in OMI ww by fenton oxidation and simultaneous sonication with 100 mg/l Fe^0 and 340 mg/l H_2O_2 solution, 2.00 mg/l 4-hydroxyphenylethanol, 2.00 mg/l 4-

hydroxybenzoic acid, 2.00 mg/l 4-hydroxy-3-methoxyphenethylacohol, 2.00 mg/l 4-hydroxy-3-methoxybenzoic acid, 2.00 mg/l 3,4-dihydroxyphenyl alcohol, 2.00 mg/l 3,4-dihydroxybenzoic acid, 2.00 mg/l 3,4-dihydroxyphenylglycol and 2.00 mg/l 3,4-dihydroxycinnamic acid at pH=2.0-4.0, after 60 min sonication time, at 25^oC, at 650 W power and at 35 kHz frequency, respectively.

3.8 Literature Review for Textile Industry Wastewater (TI ww)

Gupta & Suhas (2009) classified the methodologies adopted to treat the TI ww containing dye-stuffs in four categories:

1. Physical treatment such as; sedimentation (Cheremisinoff, 2002), microfiltration (Marcucci et al., 2001), ultrafiltration (Cheremisinoff, 2002), nanofiltration (Marmagne & Coste, 1996), reverse osmosis (Avlonitis et al., 2008), etc.

2. Chemical treatment such as; coagulation/flocculation (Shi et al., 2007; Wang, J. et al., 2006a, 2006b; Zhou et al., 2008), adsorption (Lee et al., 2006), oxidation (Namboodri et al., 1994a,1994b), electro oxidation (Dogan &Turkdemir, 2005), ozonation (Gahr et al., 1994; Snider & Porter, 1974; Sundrarajan et al., 2007), fenton's reagent oxidation (Arslan-Alaton, 2003; Namboodri et al., 1994a,1994b), UV (Behnajady et al., 2005; Namboodri & Walsh, 1996; Shu & Chang, 2005), photolysis (Aguedach et al., 2005; Bandala et al., 2008; Behnajady et al., 2005), sonolysis (Chowdhury & Viraraghavan, 2009; Hong et al., 1999), wet air oxidation (Perkins et al., 1996), photo-fenton process (Aguedach et al., 2005), photocatalysis (Behnajady et al., 2006; Galindo et al., 2001; Ghorai et al., 2007; Gupta et al., 2007a; Harrelkas et al., 2008; Vinodgopal & Kamat, 1998) and electro-coagulation (Chemical modifications of cotton textiles, 2009; Faouzi et al., 2007; Gupta et al., 2007b; Lin & Peng 1994; Oliveira et al., 2007), etc.

3. Biological treatment such as, aerobic (Brown & Laboureur, 1983a), aerobic with bacteria (Rai et al., 2005), aerobic with fungi (Bumpus & Brock, 1988) and aerobic with other microorganisms (Basto et al., 2007; Ghodake et al., 2009; Nigam et al., 2000; Salony et al., 2006; Zhang, F. M. et al., 1998, 1999),

anaerobic treatment (Delee et al., 1998; Donlon et al., 1997; Dos Santos et al., 2007; Forgacs et al., 2004; Isık & Sponza, 2003; Rai et al., 2005; Zhang, G. et al., 2008, 2009) and combined aerobic-anaerobic treatment (Brown & Laboureur, 1983b; Frijters et al., 2006; Van der Zee & Villaverde, 2005), etc.

4. Acoustical for example, sonolysis (Destaillats et al., 2000a, 2000b, 2001), etc.

5. Radiation for instance, UV (Namboodri & Walsh, 1996), etc.

6. Electrical processes such as, electro-oxidation (Faouzi et al., 2007) and electro-coagulation (Lopes et al., 2004), etc.

The studies performed with sonication to treat the TI ww are summarized as follows:

In a study performed by Vinodgopal et al. (1998) it was reported that 60.00% Remazol Black mineralization was achieved in a TI ww containing 75.00 mg/l Remazol Black after 360 min irradiation under 500 kHz frequency and at 100 W power after 120 min aeration. In a study performed by Ince & Tezcanli (2001) 76.00% COD removal was achieved in a TI ww containing 363 mg/l C.I. Reactive Black 5, at 520 kHz frequency, at 100 W power, 1.63 W/cm^2, after 240 min sonication time at 80^{o}C and at pH=11.0 under 15 min aeration. Jamalluddin & Abdullah (2011) found 96.00% Reactive Blue 4 color yield in a TI ww containing 70.00 mg/l Reactive Blue 4, at 35 kHz frequency, at 50 W power, under 4.00 mg/l.min aeration, after 60 min sonication time at 60^{o}C and at pH=4.0.

Gogate et al. (2004a) observed 25.00% COD and 30.00% Rhodamine B color removal in a TI ww containing 4.50 mg/l Rhodamine B, at 20+30+50 kHz frequencies, at 900 W power, at 0.025-0.10 W/l power density, after 30 min sonication time at 60^{o}C under aeration (1.00 mg/l.min). Guzman-Duque et al. (2011) achieved 80.00% Crystal Violet and 73.00% Orange-G color yields and 90.00% COD$_{dis}$ removal in a TI ww containing 350 mg/l Crystal Violet and 120 mg/l

Orange-G under aeration (3.50 mg/l.min) after 180 min sonication time at 800 kHz frequency, at 80 W power, at pH=3.0-5.0 and at 30°C, respectively.

In a study performed by Singla et al. (2009) 80.00% C.I. Martius Yellow decolorization was obtained in a TI ww containing 15.00 mg/l C.I. Martius Yellow dye at 355 kHz frequency, at 30 W power, at power densities varying between 0.049 and 1.16 W/l, after 240 min sonication time at 25°C uner N_2=4.00 mg/l.min. In a study performed by Kritikos et al. (2007) 75.00% COD and 80.00% C.I. Reactive Black 5 color removals was achieved in a TI ww containing 120 mg/l C.I. Reactive Black 5, at 80 kHz frequency, at 135 W power, under N_2=4.20 mg/l.min, after 60 min sonication time at 30°C and at pH=5.8.

In a study performed by Tangestaninejad et al. (2008) 82.00% Coproxon Navy Blue R1, 86.00% Nylosan Black 2-BI-Acid Black, 75.00% Methyl Orange and 78.00% Congo Red color removals were accomplished in a TI ww containing 60.00 mg/l Coproxon Navy Blue R1 and 200 mg/l Nylosan Black 2-BI-Acid Black, 20.00 mg/l Methyl Orange and 40 mg/l Congo Red at 24 kHz frequency, at 400 W power under O_2=5.00 ml/min, after 20 min sonication time at 30°C and at pH=4.3, respectively. Ge & Qu (2003) obtained 48.12% COD and 90.88% C.I. Acid Red B color removals in a TI ww containing 100 mg/l C.I. Acid Red B under 4.00 and 6.00 mg/l DO concentrations, at 50 kHz frequency, at 150 W power after 240 min sonication time at 60°C with stirring at 150 rpm, respectively.

Entezari et al. (2008) obtained 91.50% C.I. Reactive Black 5 color yield in a TI ww containing 250 mg/l C.I. Reactive Black 5, at 500 kHz frequency, at 1 W/cm^2 power intensity, after 240 and 90 min sonication time at 30°C and at pH=5.5-5.8 with 700 rpm agitation. In a study performed by Behnajady et al. (2008b) 80.00% COD and 94.00% Malachite Oxalate Green color removals was accomplished in a TI ww containing 10.00 mg/l Malachite Oxalate Green, at 35 kHz frequency, at 170 W power, in iso-butanol=1000 mg/l, at 0.049-1.16 W/l power density, after 200 min sonication time at 60°C with 400 rpm mechanical agitation.

In a study performed by He et al. (2007) and He et al. (2008) 93.00% Reactive Yellow 84 and 95.00% C.I. Reactive Blue 19 color and 70.00% COD removals were achieved in a TI ww containing 500 mg/l C.I. Reactive Yellow 84 and 20.00 mg/l C.I. Reactive Blue 19 at a 20 kHz frequency, at 176 W power, at 176 W/l power density after 60 and 30 min sonication times, respectively, at 60^{o}C and at pH=8.0-10.0. Minero et al. (2008) observed 99.00% C.I. Acid Blue 40 decolorization in a TI ww containing 50.00 mg/l C.I. Acid Blue 40 at 35 W power, at 354.5 kHz frequency, at 176 W/l power density after 20 min sonication timeat 60^{o}C at pH=11.0.

In a performed by Destaillats et al. (2000a) 80.00% Methyl Orange color yield was observed in a TI ww containing 10.00 mg/l Methyl Orange at 500 kHz frequency, at 50 W power, at pH=10.0 and at 2 W/cm^2 power intensity after 60 min sonication time at 45^{o}C. Zhang, H. et al. (2006) found 82.80% TAAs removal at combined US/O_3 systems in a TI ww containing 40.00 mg/l Methyl Orange, at 20 kHz frequency, at 250 W power, after 120 min sonication time at 60^{o}C and at pH=9.70.

Mehrdad & Hashemzadeh (2010) accomplished 78.00% COD yield in a TI ww containing 60.00 mg/l Rhodamine B, at 24 kHz frequency, at 400 W power, in H_2O_2=198 mg/l, after 10000 min sonication time at 30^{o}C and at pH=5.0-8.0. Behnajady et al. (2008a) 67.00% COD_{dis} and 75.00% TAAs removals was achieved in a TI ww containing 10.00 mg/l Rhodamine B, at an initial COD_{dis} concentration of 12.00 mg/l at 35 kHz frequency, at 170 W power and at a power density of 0.163 W/ml after 180 min sonication time at 25^{o}C in H_2O_2=1000 mg/l. In a study performed by Inoue, M. et al. (2006) 37.30% TAAs removal was accomplished in a TI ww containing 50.00 mg/l Orange II, at 404 kHz frequency, at 41.50 W power, in H_2O_2=20.00 mg/l, after 240 min sonication time at 30^{o}C.

In a study performed by Arslan et al. (1999) and Balcioglu & Arslan (1999) 93.00% C.I. Acid Orange 7, 85.00% C.I. Acid Blue color, 60.00% COD and 50.00% COD removals were achieved in a TI ww containing 20.00 mg/l C.I. Acid Orange 7 and 30.00 mg/l C.I. Acid Blue in 340 and 250 mg/l H_2O_2, concentrations at 30 and

45 kHz frequencies, at 20 and 285 W powers after 90 and 80 min sonication times at 60^oC at pH=2.8-3.0, respectively. Yavuz et al. (2009) accomplished 98.30% COD and 50.00% TAAs removals in a TI ww containing 20.00 mg/l Basic Red 29 at 40 kHz frequency, at 25 W power and at 0.25 W/ml power density after 30 min sonication time at 40^oC with H_2O_2=1000 mg/l addition.

Mrowetz et al. (2003) and Zhang & Zheng (2009) achieved 45.00% C.I. Acid Orange 8, 90.00% C.I. Acid Orange 7, 96.30% C.I. Acid Green 20 color yields in TI ww containing 10.00 mg/l C.I. Acid Orange 8 and 20.00 mg/l C.I. Acid Orange 7 and 79.50 mg/l C.I. Acid Green 20, at 20 kHz and 40 kHz frequencies, at 250 W power, at 1.08 W/l power density, in 100 and 1700 mg/l H_2O_2 concentrations after 100 and 30 min sonication times at 35^oC and at 60^oC and at pH=3.0, respectively.

In a study performed by Wang, J. et al. (2011) and Wang, X. et al. (2008) 60.00% and 97.20% color removals was accomplished in TI ww containing 10.00 and 20.00 mg/l Reactive Brilliant Red K-BP, at 20 kHz frequency, at 150 W power, in 680 and 300 mg/l H_2O_2 concentrations, after 240 and 120 min sonication times at 30^oC and at 60^oC and at pH=5.5, respectively.

In a study performed by Sundararaman et al. (2009) 82.00% COD and 95.00% Reactive Yellow 16 color removals was achieved with Sono-fenton process in a TI ww containing 50.00 mg/l Reactive Yellow 16, at 34 kHz frequency, at 120 W power, in H_2O_2=900 mg/l, after 30 min sonication time at 60^oC and at pH > 8.00. Zhang, H. et al. (2009a, 2009b) 72.00% COD removal was found in a TI ww containing 79.50 mg/l C.I. Acid Orange 7, at 20 kHz frequency, at 250 W power, in H_2O_2=170 mg/l, after 30 min sonication time at 30^oC and at pH=10.0.

In a study performed by Ghodbane & Hamdaoui (2009b) and Sun et al. (2007) 93.00% Acid Blue 25 and 92.39% Acid Black 1 color removals were achieved in TI ww containing 50 mg/l Acid Blue 25 and 90.00 mg/l Acid Black 1, at 1700 and 40 kHz frequencies, at 14 and 50 W powers, at a 50 W/l power density, in 386 and 150

H_2O_2 concentrations, after 30 min sonication time at 60°C and at 40°C and at pH=5.0-8.0, respectively.

In a study performed by Abbasi & Asl (2008) 90.00% Basic Blue 41 color removal was achieved in a TI ww containing 15.00 mg/l Basic Blue 41, at 35 kHz frequency, at 160 W power, after 180 min sonication time at 30°C with TiO_2=100 mg/l at pH=8.0. Gogate et al. (2004a) observed 25.00% COD and 25.00% Rhodamine B color removals in a TI ww containing 4.50 mg/l Rhodamine B, at 20+30+50 kHz frequencies, at 900 W power, at 0.025-0.10 W/l power density, after 30 min sonication time at 60°C in presence of TiO_2=25.00 mg/l.

Wang, J. et al. (2008) obtained 60.00% Azo Funchsine solution decolorization in a TI ww containing 100 mg/l Azo Funchsine solution at 40 kHz frequency, at 50 W power after 60 min sonication time at 30°C with TiO_2=50.00 mg/l at pH=7.5. In a study performed by Mrowetz et al. (2003) 36.00% COD removal was found in a TI ww containing 75.00 mg/l Acid Orange 8, at 20 kHz frequency, at 250 W power, in TiO_2=100 mg/l after 100 min sonication time at 35°C.

In a study performed by Behnajady et al. (2008a) 60.00% TAAs removal was achieved in a TI ww containing 10.00 mg/l Rhodamine B, at 35 kHz frequency, at 170 W power, 0.163 W/ml power density after 180 min sonication time at 60°C with NaCl=0.625 g/l. In a study performed by Wu, C.-H. (2008) 75.00% COD and 99.00% C.I. Reactive Red 198 color removals were accomplished in a TI ww containing 15.00 mg/l C.I. Reactive Red 198, in NaCl=5.00 g/l, at 40 kHz frequency, at 400 W power after 120 min sonication time at pH=7.0 and at 60°C. Lorimer et al. (2000) observed 97.00% Sandolon Yellow decolorization in a TI ww containing 50.00 mg/l Sandolon Yellow, at 40 kHz frequency, at 100 W power, in NaCl=4.00 g/l, after 80 min sonication time at 60°C.

Zhang, H. et al. (2009a, 2009b) found 50.00% COD removal in a TI ww containing 25.00 mg/l C.I. Acid Orange 7, in NaCl=10.00 g/l, at 20 kHz frequency, at 250 W power, 201 W/l power density after 90 min sonication time at pH=4.1-9.4

and at 60^{o}C. In a study performed by Maezawa et al. (2007) 95.00% Acid Orange 52 color and 95.00% COD removals were obtained in a TI ww containing 25.00 mg/l Acid Orange 52, in 20.00 g/l NaCl concentrations at 200 kHz frequency, at 600 W power, after 240 min sonication time at 60^{o}C and at pH=5.5.

In a study performed by Merouani et al. (2010a, 2010b) 58.00% COD removal was achieved in a TI ww containing 5.00 mg/l Rhodamine B for Fe^{+2}=5.00 mg/l, at a 300 kHz frequency, at a 60 W power after 140 min sonication time at 30^{o}C and at pH=5.3. Gopinath et al. (2010) 90.00% Congo Red decolorization was achieved in a TI ww containing Congo Red with Fe^{+3}=20.00 mg/l, at 30 kHz frequency, at 300 W power after 60 min sonication time at pH=3.0-4.0 and at 60^{o}C.

In a study performed by Sun, J.-H. et al. (2007) 36.94% TAAs removal was accomplished in a TI ww containing 2.00 mg/l Acid Black 1, at 40 kHz frequency, at 50 W power, 50 W/l power density, in Fe^{+2}=10.00 mg/l, after 30 min sonication time at 40^{o}C and at pH=7.0. In a study performed by Ghodbane & Hamdaoui (2009b) 85.00% Acid Blue 25 decolorization was observed in a TI ww containing Acid Blue 25, at 1700 kHz frequency, at 14 W power, in Fe^{+2}=10.00 mg/l, after 30 min sonication time at 55^{o}C and at pH=5.0-8.0.

Yachmenev et al. (2004) found 88.00% COD removal in a TI ww containing 20.00 mg/l C.I. Reactive Blue 9, at 20 kHz frequency, after 60 min sonication time at 25^{o}C and at pH=8.0. In a study performed by Wang, J. et al. (2007) 90.00% TAAs removal was accomplished in a TI ww containing 10.00 mg/l Acid Red B, at 40 kHz frequency, at 50 W power, after 100 min sonication time at 60^{o}C and at pH=7.0. Fung et al. (1999), Fung et al. (2000a) and Fung et al. (2000b) observed 86.00% COD and 80.00% C.I. Reactive Red 20 color removal in a TI ww containing 15.00 mg/l C.I. Reactive Red 20, at 320 kHz frequency, at 66 W power after 90 and 100 min sonication times at 25^{o}C in TI ww at pH=8.5.

In a study performed by Mrowetz et al. (2003) 30.00% Acid Orange 8 decolorization was found in a TI ww containing 75.00 mg/l Acid Orange 8, at 20 kHz frequency, at 250 W power, in Fe^{+3}=50.00 mg/l after 100 min sonication time at 35°C. Wang, J. et al. (2008) obtained 65.00% COD yield in a TI ww containing 100 mg/l Azo Funchsine solution at 40 kHz frequency, at 50 W power after 60 min sonication time at 30°C with Fe^{+3}=50.00 mg/l at pH=7.5.

In a study performed by Wang, J. et al. (2011) 94.20% Brilliant Red K-2BP color removal was accomplished in a TI ww containing 20.00 mg/l Brilliant Red K-2BP, at 20 kHz frequency, at 150 W power, in Fe^{+3}=5.00 mg/l, after 120 min sonication time at 60°C and at pH=5.5. Jamalluddin & Abdullah (2010) 90.00% Reactive Blue 4 color yield obtained in a TI ww containing 70.00 mg/l Reactive Blue 4, at 35 kHz frequency, at 50 W power, in Fe^{+3}=20.00 mg/l, after 60 min sonication time at 30°C and at pH=4.0.

In a study performed by Madhavan et al. (2010) 85.00% Orange-G color and 82.00% COD removals were accomplished in a TI ww containing 90.00 mg/l Orange-G, at 213 kHz frequency, at 450 W power, after 75 min sonication time at 30°C and at pH=5.8-12.0. Sayan (2006) reported 80.62% Rifacion Yellow HE4R color and 85.22% COD removal removals in a TI ww containing 1.00 g/l Rifacion Yellow HE4R with ultrasound and combined ultrasound/activated carbon at 850 kHz frequency, 140 W power, after 120 min sonication at pH=2.0-12.0 and at 60°C.

In a study performed by Merouani et al. (2010b) 55.00% COD and 66.00% Rhodomanie B color removals in TI ww were accomplished in 5.00 mg/l Rhodomanie B, in HCO_3^{-1}=3.00 g/l, at 300 kHz frequency, at 60 W power, after 50 min sonication time at 60°C and at pH=5.3. Guzman-Duque et al. (2011) 90.00% Orange-G decolorization was found in 20.00 mg/l Orange-G, at 800 kHz frequency, at 80 W power, in HCO_3^{-1}=3.00 g/l, after 180 min sonication time at 30°C and at pH=3.0-9.0. In a study performed by Sun, J.-H. et al. (2007) 97.00% Acid Black 1 color removal was accomplished in 20.00 mg/l Acid Black 1, at 40 kHz frequency, at 50 W power, at 50 W/l power density, in HCO_3^{-1}=1.00 g/l, after 30 min sonication time at 40°C and at pH=3.0.

Wu, C.-H. (2008) achieved 92.00% C.I. Reactive Red 198 decolorization in TI ww containing 10.00 mg/l C.I. Reactive Red 198, C_4H_9OH=1.20 g/l, at 40 kHz frequency, at 400 W power after 120 min sonication time at pH=7.0 and at 60°C. Merouani et al. (2010a) found 40.00% COD yield in 5.00 mg/l Rhodamine B, in tert-butyl alcohol=20.00 mg/l, at 300 kHz frequency, at 60 W power after 240 min sonication time at 30°C and at pH=5.3.

Ghodbane & Hamdaoui (2009a) obtained 92.00% Acid Blue 25 color removal in TI ww containing 15.00 mg/l Acid Blue 25, at 1700 kHz frequency, at 14 W power, in tert-butyl alcohol=1570 mg/l, after 35 min sonication time at 50°C and at pH=5.7. In a study performed by Gultekin et al. (2009) 72.00% C.I. Acid Orange 8 color removal was accomplished in 20.00 mg/l C.I. Acid Orange 8, at 300 kHz frequency, at 25 W power, in tert-butyl alcohol=1500 mg/l, after 30 min sonication time at 30°C and at pH=5.7.

In a study performed by Eren & Ince (2010) 49.50% C.I. Reactive Red 141 and 22.58% C.I. Direct Yellow 9 color removals were accomplished in TI ww containing 15.00 mg/l C.I. Reactive Red 141 and 30.00 mg/l C.I. Direct Yellow 9, in C_4H_9OH=1.00 g/l, at 1145 and 577 kHz frequencies, at 40 and 48.90 W powers, after 30 min sonication time at 60°C, respectively. In a study performed by Behnajady et al. (2008a) 70.00% TAAs removal was achieved in 10.00 mg/l Rhodamine B, at 35 kHz frequency, at 170 W power, at 0.163 W/ml power density after 180 min sonication time at 60°C with C_4H_9OH=1.00 g/l in TI ww.

Wu, C.-H (2009) and Wu & Yu (2009) 90.00% and 98.00% C.I. Reactive Red 2 color removals in TI ww containing 15.00 and 20.00 mg/l Reactive Red 2, at 40 kHz frequency, at 400 W power, in TiO_2=2.00 g/l, in $Na_2S_2O_8$=238 mg/l, in NaCl=5.00 g/l, after 120 min sonication time, at pH=7.0, at 30°C and at 50°C, respectively.

Singla et al. (2009) 95.00% Martius Yellow (Naphthol Yellow or Acid Orange 24) decolorization was found in TI ww containing 10.00 mg/l Martius Yellow, at 355 kHz frequency, at 30 W power, after 240 min sonication time, in 200 ml sonication volume, at pH=9.0 and at 25^oC.

Rehorek et al. (2004) 76.00% Acid Orange 5, 80.00% Acid Orange 52, 85.00% Direct Blue 71, 40.00% Reactive Black 5, 40.00% Reactive Orange 16 and 50.00% Reactive Orange 107 color removals were measured in TI ww containing, 10.00 mg/l each one of dyestuff concentrations, in H_2O_2=100 mg/l, at 850 kHz frequency, at 120 W power, after 150 min sonication time, at pH=9.5 and at 30^oC, respectively.

Okitsu et al. (2005) 75.00% C. I. Reactive Red 22 and 72.00% Methyl Orange color yields were obtained in TI ww containing 25.00 mg/l C. I. Reactive Red 22 and 25.00 mg/l Methyl Orange concentrations, in Fe^{+2}=20 mg/l, at 200 kHz frequency, at 200 W power, after 60 min sonication time, at pH=6.5 and at 20^oC, respectively.

In a study performed by Küncek & Sener (2010) 95.00% Methylene Blue decolorization was achieved in a TI ww containing 80.00 mg/l Methylene Blue, at 20 kHz frequency, at 750 W power, after 90 min sonication time at 60^oC and at pH=8.3 with 400 rpm agitation.

In a study performed by Entezari & Sharif Al-Hoseini (2007) 98.00% Methylene Blue decolorization was accomplished in a TI ww containing 50.00 mg/l Methylene Blue, at 20 kHz frequency, at 120 W power, after 30 min sonication time at 30^oC with 700 rpm agitation in a 125 ml sonicator reactor, at pH=3.5.

In a study performed by Byun & Kwak (2005) 90.00% Methylene Blue decolorization was accomplished in a TI ww containing 40.00 mg/l Methylene Blue (MB), at 20 kHz frequency, at 500 W power, after 30 min sonication time at 60^oC and at pH=3.85 with DO=5.00 mg/l.

In a study performed by Minero et al. (2008) and Minero et al. (2005) observed 90.00% Acid Blue 40 and 94.00% Methylene Blue color removals in TI ww containing 10.00 mg/l Acid Blue 40 and 15.00 mg/l Methylene Blue under Ar gas

(0.10 ml/min), at 354.50 kHz frequency, at 35 W power, after 20 min sonication time, a solution volume of 250 ml, at 25°C and at pH=9.0-11.0, respectively.

Vankar & Shanker (2008) found that the ultrasonic waves can reduce the concentration of Methylene Blue up to 10.00% at 15 kHz frequency, at 30 W power, after 30 min sonication time at 30°C and at pH=1.5.

The studies performed by Sivakumar & Pandit (2001) and Yuan et al. (2009) exhibited 76.00% and 35.00% TAAs removals in TI ww containing 10.00 mg/l Rhodamine B and 12.00 mg/l Methylene Blue, in 5.00 mg/l TiO_2, at 30 kHz frequency and at 100 W power, after 90 min sonication time at 60°C, respectively.

In a study performed by Tangestaninejad et al. (2008) 79.00% Bromothymol Blue, 85.00% Methylene Blue and 80.00% Rhodamine B color removals were achieved in a TI ww containing 40.00 mg/l Bromothymol Blue, 10.00 mg/l Methylene Blue and 30.00 mg/l Rhodamine B, respectively, at 24 kHz frequency, at 400 W power, under O_2=5.00 ml/min, after 30 min sonication time at 30°C and at pH=4.3.

Gayathri et al. (2010) between 89.00-97.00% color, 65.00-73.00% COD and 53.00-62.00% TOC removals were measured in TI ww containing, 30.00 mg/l Rhodamine B, 30.00 mg/l Methylene Blue, 30.00 mg/l Acid Orange II, 30.00 mg/l Acid scarlet red 3R, in persulphate=1.30 g/l, at 35 kHz frequency, at 140 W power, after 60 min sonication time, at pH=6.25 and at 25°C with 10.00 g/l cobalt chloride catalyst addition, respectively.

CHAPTER FOUR
MATERIALS AND METHODS

4.1 Experimental Set up

4.1.1. Sonicator Properties

4.1.1.1 BANDELIN Electronic RK510 H Sonicator

A BANDELIN Electronic RK510 H sonicator was used for sonication of the wastewater samples (Figure 4.1). The sonication frequency and the sonication power were 35 kHz and 640 W, respectively. Glass serum bottles in a glass reactor were filled to volumes of 100 and 500 ml with wastewater and were placed in a water bath. They were then closed with teflon coated stoppers throughout the measurement of the wastewater. The evaporation losses of PAHs and other volatile compounds were estimated to be 0.01% in the reactor and, therefore, assumed to be negligible. The serum bottles were filled with 0.10 ml methanol in order to prevent adsorption on the walls of the bottles and minimize evaporation. The temperature in the sonicator was monitored continuously and was adjusted to ambient temperature (25°C), 30°C and 60°C with an automatic heater. The stainless steel sonicator was equipped with a teflon holder to prevent temperature losses. The sonicator reactor was sealed with a water jacket to maintain a constant temperature and to minimize temperature loss. Cooling water was circulated through the jacket of the reactor throughout the experiment in order to remove the heat generated during sonication. This procedure maintains the temperature of the reaction medium almost constant. All experiments were in batch mode using an ultrasonic transducer (horn type), which has an active acoustical vibration area of 19.60 cm^2, and a maximum input power of 640 W. Ultrasonic waves for 35 kHz frequency were emitted from the bottom of the reactor through a piezoelectric disc (4.00–cm diameter) fixed on a pyrex plate (5.00–cm diameter). The shematic configuration of the sonicator used in this study is shown in Figure 4.2. Samples were taken after 60 min, 120 and 150 min of sonication and they were analyzed immediately.

Figure 4.1 BANDELIN Electronic RK510 H sonicator

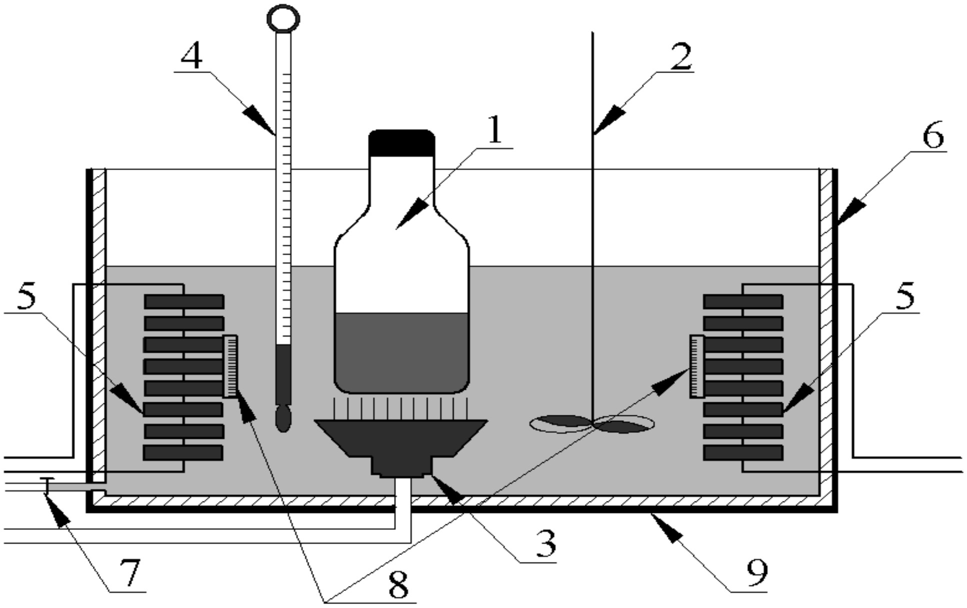


Figure 4.2 The structural diagram of the sonicator used in this study: (1) glass reactor, (2) stirrer, (3) energy conversion device, (4) thermometer, (5) heater, (6) stainless steel bath, (7) water exit valve, (8) thermostate, (9) teflon cover.

4.1.1.2 1K-MODEL Forward-Backward Moving Sonicator

A 1K-MODEL Forward-Backward Moving sonicator was used for sonication of the wastewater samples. The properties of sonicator are: A frequency of 25 kHz, A power of 3000 W, an external length of 110 cm, an external width of 53.00 cm, an external height of 80.00 cm, an internal length of 64.00 cm, an internal width of 15 cm, an internal height of 50.00 cm, an internal water height of 48.00 cm and a volume of 48.00 l, respectively (Figure 4.3).

Figure 4.3 1K-MODEL Forward-Backward Moving sonicator

4.1.1.3 1K-MODEL Sonicator

A 1K-MODEL sonicator was used for sonication of the wastewater samples. The properties of sonicator are: A frequency of 25 kHz, A power of 3000 W, an external length of 90.00 cm, an external width of 105 cm, an external height of 62.00 cm, an internal length of 60.00 cm, an internal width of 50.00 cm, an internal height of 40.00 cm, an internal water height of 40.00 cm and a volume of 96.00 l, respectively (Figure 4.4).

Figure 4.4 1K- MODEL sonicator

4.1.1.4 MINI 12 Sonicator

A MINI 12 sonicator was used for sonication of the wastewater samples. The properties of sonicator are a frequency of 25 kHz, a power of 350 W, a length of 30 cm, a width of 20.00 cm, a height of 24.00 cm and a volume of 14.00 l, respectively (Figure 4.5).

Figure 4.5 MINI 12 sonicator

4.1.1.5 VWR USC600 DF Sonicator

A VWR USC600 DF sonicator was used for sonication of the wastewater samples. The properties of sonicator are a frequency of 132 kHz, a power of 120 W, a length of 32.00 cm, a width of 14.00 cm, a height of 25.00 cm, a water height of 15.00 cm, a volume of 18.00 l, respectively (Figure 4.6).

Figure 4.6 VWR USC600 DF sonicator

4.2 Operational Conditions in PCI ww, OMI ww and TI ww

4.2.1 Effect of Sonication Frequency, Power, Time, Volume, Temperature, Intensity, Density and Specific Energy on the PAH Removals in PCI ww and COD_{dis} Removals in PCI ww, OMI ww and TI ww

4.2.1.1 Effect of Sonication Frequency on the PAH Removals in PCI ww and COD_{dis} Removals in PCI ww, OMI ww and TI ww

25–35 and 132 kHz sonication frequencies was researched at ambient conditions (25^oC), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication frequency for maximum PAH and COD_{dis} removals in PCI ww, OMI ww and TI ww.

4.2.1.2 Effect of Sonication Power on the PAH Removals in PCI ww and COD_{dis} Removals in PCI ww, OMI ww and TI ww

120–350–640 and 3000 W sonication powers was researched at ambient conditions (25°C), constant sonication frequency (35 kHz) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication power for maximum PAH and COD_{dis} removals in PCI ww, OMI ww and TI ww.

4.2.1.3 Effect of Sonication Time on the PAH Removals in PCI ww and COD_{dis} Removals in PCI ww, OMI ww and TI ww

0–5–10–15–20–25–30–35–40–45–50–55–60–120 and 150 min sonication times was researched at ambient conditions (25°C), constant sonication frequency (35 kHz) and constant sonication power (640 W) to determine the optimum sonication time for maximum PAH and COD_{dis} removals in PCI ww, OMI ww and TI ww.

4.2.1.4 Effect of Sonication Volume on the PAH Removals in PCI ww and COD_{dis} Removals in PCI ww, OMI ww and TI ww

25–50–100–150–250–500 and 1000 ml sonication volumes was researched at ambient conditions (25°C), constant sonication frequency (35 kHz), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication volume for maximum PAH and COD_{dis} removals in PCI ww, OMI ww and TI ww.

4.2.1.5 Effect of Sonication Temperature on the PAH Removals in PCI ww and COD_{dis} Removals in PCI ww, OMI ww and TI ww

25°C, 30°C and 60°C sonication temperatures was researched at constant sonication frequency (35 kHz), sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication temperature for maximum PAH and COD_{dis} removals in all three wastewaters.

4.2.1.6 Effect of Sonication Intensity on the PAH Removals in PCI ww and COD_{dis} Removals in PCI ww, OMI ww and TI ww

12.73–16.63–22.64–32.60–50.93 and 90.54 W/cm^2 sonication intensities was researched at ambient conditions (25^{o}C), constant sonication frequency (35 kHz), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication intensity for maximum PAH and COD_{dis} removals in PCI ww, OMI ww and TI ww. Sonication intensity was determined with the Eq. (4.1).

$$Sonication\ \mathrm{int}ensity\,(W/cm^2) = \frac{Ultrasonic\ power\ (W)}{Glass\ reactor\ area\ (cm^2)} \tag{4.1}$$

where;

Sonication intensity: The effective intensity of sonication (W/cm^2),

Ultrasonic power: The effective power during sonication process (W),

Glass reactor area: The area of glass reactor during sonication process (cm^2).

4.2.1.7 Effect of Sonication Density on the PAH Removals in PCI ww and COD_{dis} Removals in PCI ww, OMI ww and TI ww

0.24–0.70–1.28 and 6.00 W/ml sonication densities was researched at ambient conditions (25^{o}C), constant sonication frequency (35 kHz), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication density for maximum PAH and COD_{dis} removals in PCI ww, OMI ww and TI ww. Sonication density could be illustrated with Eq. (4.2).

$$Sonication\ density\,(W/ml) = \frac{Sonication\ power\ (W)}{Glass\ reactor\ volume\ (ml)} \tag{4.2}$$

where;

Sonication density: The effective density of sonication power (W/ml), Sonication power: The effective power during sonication process (W),

Glass reactor volume: The volume of glass reactor during sonication process (ml).

4.2.1.8 Effect of Specific Energy (E_s) on PAH Removals in PCI ww and COD_{dis} Removals in PCI ww, OMI ww and TI ww

8.23–8.75–9.21–9.96–10.69 and 11.50 kWh/kg COD in influent for specific energies was researched at ambient conditions (25°C), constant sonication frequency (35 kHz), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum specific energy for maximum PAH and COD_{dis} removals in PCI ww, OMI ww and TI ww.

Since the reaction time and the applied sonic power are the major parameters influencing the sonication process, it was defined an energy parameter which is called the specific energy (E_s) and it is obtained by dividing the energy given into the heterogeneous system by the mass of total COD initially present. The E_s input into the system should be sufficient to guarantee a good COD_{dis} removal improvement. Therefore, the energetic calculation was based on the total energy requirement for COD_{dis} removal yield achieved by sonication. Specific energy (E_s) was determined by the Eq. (4.3).

$$E_s\ (kWh/kg\ COD_0) = \frac{Sonicator\ Power(W) * Time(h) * (1\ kj/1000\,j)}{V(l) * COD_0\,(g/l) * (1\ kg/1000\,g)} \tag{4.3}$$

where;

E_s: The specific energy for the maximum COD_{dis} removal after sonication process (kWh/kg COD_0),

Sonicator power: The input power of sonicator during sonication experiments (W), Time: The sonication time during sonication process (h),

(1 kj/1000 j): The equation of transformation from 1 kilojoule to 1 joule,

V: The sample volume during sonication process (l),

COD_0: Initial COD_{dis} concentration before sonication process (g/l),

(1 kg/1000 g): The equation of transformation from 1 kilogram to 1 gram.

4.2.2 Administration of Air

The raw wastewater samples were aerated for 1 hour with an air pump having a velocity of around 200 ml/min before the sonication experiments. The air has a scavenger effect to the organics present in raw wastewater samples during sonication process.

4.2.3 Administration of Oxygen gas, $O_2(g)$

The raw wastewater samples were oxygenated for increasing dissolved oxygen (DO) concentrations (2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l) with a pure $O_2(g)$ tubing with a velocity of varying between 150 and 200 ml/min and a gas pressure of 230 atm before the sonication experiments. DO have a scavenger effect to the organics present in raw wastewater samples during sonication process.

4.2.4 Administration of Nitrogen Gas, $N_2(g)$

The raw wastewater samples were sparged under 15 and 30 min with pure $N_2(g)$ (3.00 and 6.00 mg/l N_2) prior the sonication experiments with a velocity varying between 150 and 200 ml/min and a gas pressure of 230 atm. The pure $N_2(g)$ has a scavenger effect to the organics present in raw wastewater samples during sonication process.

4.2.5 Adjusting of pH

The pH values (4.0 – 7.0 and 10.0) were adjusted in the raw wastewater before sonication process. The pH has a scavenger effect to the organics present in raw wastewater samples during sonication process. The pH was adjusted to neutral, acidic and alkaline conditions by 10.00% H_2SO_4 (Merck) and 10.00% NaOH (Merck) solutions through sonication to the glass bottle of the sonicator with a magnetic stirrer to keep the solution homogenous. The pH was monitored by a WTW pH-meter.

4.2.6 Administration of Hydrogen Peroxide (H_2O_2)

The concentration of H_2O_2 generated in the deionized water (pH=0.10) with the presence of O_2(g) by ultrasonic irradiation was determined by the Titanic Sulfate Method, wherein the light absorbance of Titanic–H_2O_2 was measured using an Aquamate thermo electron corporation UV visible spectrophotometer (2007) at a wavelength of 410 nm (Standard Methods, 2005). The sample (ca. 4.00 ml) was placed in a quartz holder and directly analyzed to meet the measuring limit requirement of 0.01–80 mg/l, corrected by the standard solution of H_2O_2. H_2O_2 was quantified with a colorimetric method following Standard Methods 3550 (Standard Methods, 2005). In order to optimize the sonication process of organics in wastewaters 100 mg/l, 500 and 2000 mg/l H_2O_2, as oxidant, were added to the raw wastewater samples before the sonication experiments. 100 mg/l (0.90 ml/l), 500 mg/l (4.50 ml/l) and 2000 mg/l (18.00 ml/l) H_2O_2 solution mixtures were prepared from a stock solution of 111 g/l H_2O_2.

4.2.7 Administration of Titanium Dioxide (TiO_2)

0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, as catalyst, were added to the raw wastewater before the sonication experiments. 0.10 mg/l (0.04 ml/l), 0.50 mg/l (0.20 ml/l), 10.00 mg/l (4.00 ml/l) and 20.00 mg/l (8.00 ml/l) TiO_2 solution mixtures were prepared from a 10.00 g/l of titanium (IV) oxide (TiO_2) stock solution.

4.2.8 Administration of Sodium Chloride (NaCl)

1.00 g/l, 2.50 and 15.00 g/l NaCl, as catalyst, were added to the raw wastewater prior to the sonication experiments. 1.00 g/l (10.00 ml/l), 2.50 g/l (25.00 ml/l) and 15.00 g/l (150 ml/l) NaCl solutions were prepared from a 100 g/l stock NaCl solution.

4.2.9 Administration of Ferrous Iron Ions (Fe^{+2})

2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2} ions (from $FeSO_4.7H_2O$), as catalyst, were added to the raw wastewater before the sonication experiments. 2.00 mg/l (2.00 ml/l), 8.00 mg/l (8.00 ml/l) and 20.00 mg/l (20.00 ml/l) Fe^{+2} solutions were prepared from a 1.00 g/l $FeSO_4.7H_2O$ stock solution.

4.2.10 Administration of Ferric Iron Ions (Fe^{+3})

10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3} ions (from $FeCl_3.6H_2O$), as catalyst, were added to the raw wastewater before the sonication experiments. 10.00 mg/l (10.00 ml/l), 20.00 mg/l (20.00 ml/l) and 50.00 mg/l (50.00 ml/l) Fe^{+3} solutions were prepared from a 1.00 g/l $FeCl_3.6H_2O$ stock solution.

4.2.11 Administration of Bicarbonate Ions (HCO_3^{-1})

0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1} ions (from $NaHCO_3$), as scavenger, were added to the raw wastewater before the sonication experiments. 0.50 g/l (6.00 ml/l), 1.00 g/l (12.00 ml/l) and 5.00 g/l (60.00 ml/l) HCO_3^{-1} solutions were prepared from a 10.00 g/l $NaHCO_3$ stock solution.

4.2.12 Administration of Butanol (C_4H_9OH)

0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, as scavenger, were added to the raw wastewater before to the sonication experiments. 0.10 g/l (1.30 ml/l), 0.50 g/l (6.50 ml/l) and 2.00 g/l (26.00 ml/l) C_4H_9OH solutions were prepared from a 78.44 g/l (96.00 ml/l) C_4H_9OH stock solution.

4.3 Analytical Procedure

4.3.1 PAH Measurements

4.3.1.1 Sample Extraction and Concentrate of PAHs

Water samples to filter through a glass fiber filter (47 mm – diameter) to collect particle-phase in series with a resin column (≈ 10 g XAD-2) to collect dissolved-phase poylbrominated diphenyl ethers (PCBEs). Resin and H_2O filters to ultrasonically extract for 60 min with a mixture of 1/1 acetone/hexane. Prior to extraction, all samples to spike with PAH surrogate standards to monitor analytical recovery efficiencies. The volume of extracts to reduce and to transfer into hexane using a rotary evaporator and a high-purity $N_2(g)$ stream. After volume reduction to 2 ml by a gentle flow of $N_2(g)$, the samples to clean up on an alumina-silicic acid column containing 3.00 g of silicic acid (3.00% H_2O) and 2.00 g of alumina (6.00% H_2O). The column to pre-wash with 20.00 ml of dichloromethane (DCM) followed by 20.00 ml of petroleum ether (PE). The sample in 2.00 ml of hexane to add to the top of the column and PAHs to elute with 20.00 ml of DCM. After solvent exchange into hexane, the final sample volume to adjust to 1.00 ml by $N_2(g)$ blow-down.

4.3.1.2 Clean Up and Fractionation

To remove interferences before GC/MS analysis, the samples were cleaned up and fractionated on an alumina-silicic acid column. Before use, Na_2SO_4 and alumina were placed in ceramic plates covered loosely with aluminum foil, and then they were baked in a muffle furnace at 450°C for 4 h. Silicic acid was placed in a flask covered loosely with aluminium foil, dried in an oven at 105°C overnight to remove moisture. Then, they were allowed to cool to room temperature in a desiccator.

In an amber vial, three grams of silicic acid was deactivated by adding 100 µl of deionized H_2O (3.00% H_2O), and then the mixture was shaken until homogenized. Similarly, 2.00 g of alumina was deactivated by adding of 120 µl of deionized H_2O

(6.00% H_2O) and the mixture was homogenized by shaking. These mixtures were left at room temperature at least 1 h before use, and used within 12 hours.

Alumina-silicic acid column was prepared by adding a piece of glass wool, 3.00 g of silicic acid (3.00% H_2O), 2.00 g of alumina (6.00% H_2O), and ~1.00 cm column height of anhydrous Na_2SO_4 in series. The column was pre-washed with 20.00 ml of DCM followed by 20.00 ml of PE. Then, the sample in 2.00 ml of hexane was added to the top of the column with a 2.00 ml rinse of PE, and eluent was collected in a vial at a rate of two drops per second. After letting the sample pass through the column, 20.00 ml of PE was added and eluent collected in the same vial (Fraction 1). Fraction 1 contained PCBs. Then the vial used for eluent collection was changed, 20.00 ml of DCM was added into the column, and eluent was collected at the same rate (Fraction 2). Fraction 2 contained PAHs. For both fractions, the sample volume was reduced, and the solvent was exchanged into hexane using a high purity stream of $N_2(g)$ (~150-200 ml/min). The sample was blown-down to ~5.00 ml, and 10.00 ml of hexane was added to the vial. After, volume reduction to ~5.00 ml, again 10.00 ml of hexane was added into the sample volume. Then, the final sample volume was adjusted to exactly 1.00 ml by $N_2(g)$ blow-down. All samples were stored in a freezer until analysis.

4.3.1.3 Analysis of PAH Samples

All extract to analyze for seventeen PAHs with a gas chromotography (Agilent 6890) combined with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-MS, 30.00 m, 0.25 mm, 0.25 μm) was used. The initial oven temperature to hold at 50^{o}C for 1 min, to rise to 200^{o}C at 25^{o}C 1/min and from 200^{o}C to 300^{o}C at 80^{o}C 1/min and was held for 5.50 min. The injector ion source and quadrupole temperatures were 295^{o}C, 300^{o}C and 180^{o}C, respectively. High purity helium (He) was used as the carrier gas at constant flow mode (1.50 ml/min, 45.00 cm/s linear velocity). The MSD to run in selected ion-monitoring mode. Compounds were identified on the basis of their retention times, target and qualifier ions. Qualification was based on the Internal Standard Calibration Procedure.

4.3.1.4 Procedural Recoveries

Prior to extraction, all sample and blank matrices were spiked with internal standard mixtures of PAHs (naphthalene–d_8, acenaphthene–d_{10}, phenanthrene–d_{10}, chrysene–d_{12} and perlylene–d_{12}) to monitor the analytical recovery efficiency. Each sample was checked for the recovery efficiencies if they were in the range of 75.00-89.00% (Table 4.1). The recoveries of the internal standards were used to correct the amounts of the specific PAHs found in the samples, correspondingly.

Table 4.1 The recoveries of the internal standards of PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12})

PAHs	**Retention Time (min)**	**Influent Concentration Units (ng/ml)**	**Recovery (%)**
Naphthalene–d_8	5.247	8000	80.42
Acenaphthene–d_{10}	6.957	8000	88.79
Phenanthrene–d_{10}	8.659	8000	78.75
Chrysene–d_{12}	14.088	8000	76.91
Perlylene–d_{12}	17.679	8000	75.14

4.3.1.5 Calibration Standards

The PAH calibration standard solution contained 16 PAHs, carbazole, and five deuterated PAHs (naphthalene–d_8, acenaphthene–d_{10}, phenanthrene–d_{10}, chrysene–d_{12} and perlylene–d_{12}) that were used to determine the analytical recoveries. Six levels of calibration standards (0.04, 0.40, 1.00, 4.00, 6.00, 10.00 μg/ml for PAHs, and deuterated PAHs at a fixed concentration of 8.00 μg/ml) were used to calibrate the Agilent GC-MS system.

4.3.1.6 Limit of quantification (LOQ) and limit of detection (LOD) of PAHs

The signal/noisy (S/N) values were taken into consideration for every PAHs compound in their lowest concentrations. The measured S/N ratios varied between 64 and 559. Limit of quantification (LOQ) is defined as the standard PAH concentration which is equal to 10 while the limit of detection (LOD) was detected with the standard PAH concentration which is equal to 10. The LOD and LOQ data varied at between 0.909 and 1.908 and at between 1.175 and 5.201, respectively. Calculation of LOQ and LOD of PAHs were performed as follows (Figure 4.7):

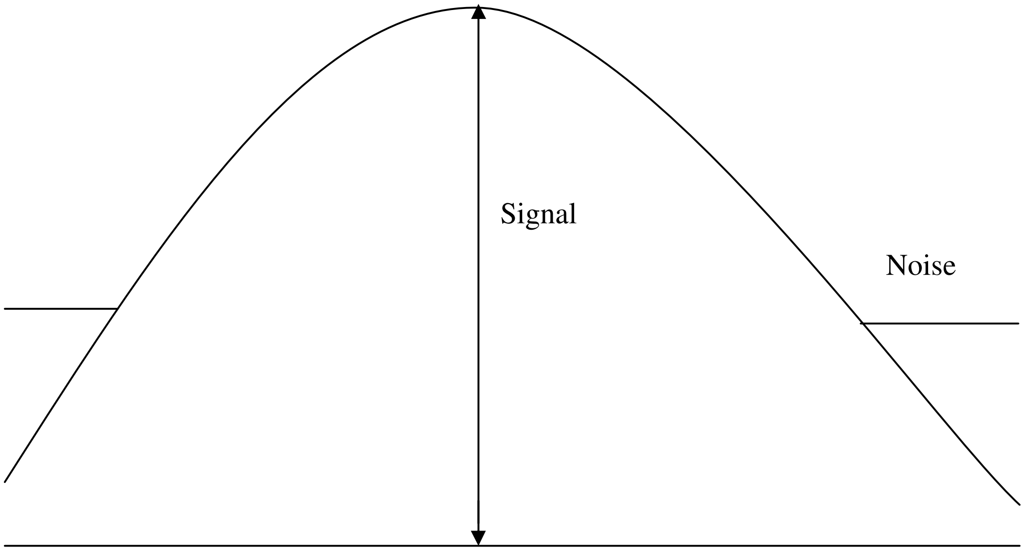


Figure 4.7 Configuration of signal peak value and noise peak value

The highest level of noise peak was taken as ppb (pers per billion) and signal value of this noise peak was used for calculate the LOQ of the PAHs.

Example:

40.00 ppb the highest level of noise peak is equal to 138 signal value
X 10.00 signal value

X= 40.00 ppb * 10.00 signal / 138 signal = 2.89 ppb (Nicel) = LOQ

LOD value of PAHs is equal 1/3 times of LOQ value of PAHs.

LOD = X/3 = 2.89 / 3 = 0.96 ppb (Nitel)

GC-MS chromatograms of internal standards of PAHs were illustrated between Figures 4.8 and 4.13.

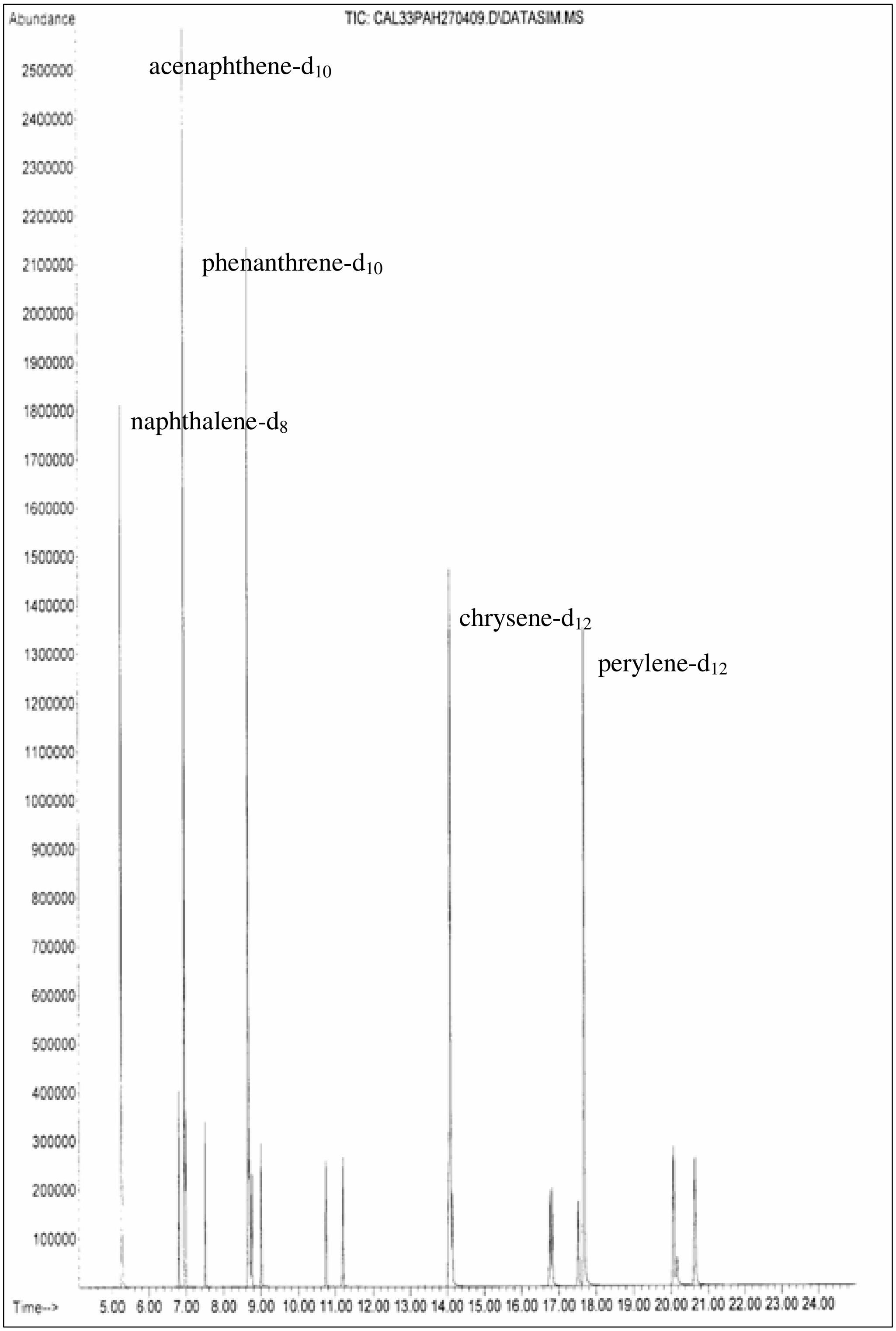


Figure 4.8 GC-MS chromatograms of internal standards of PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}).

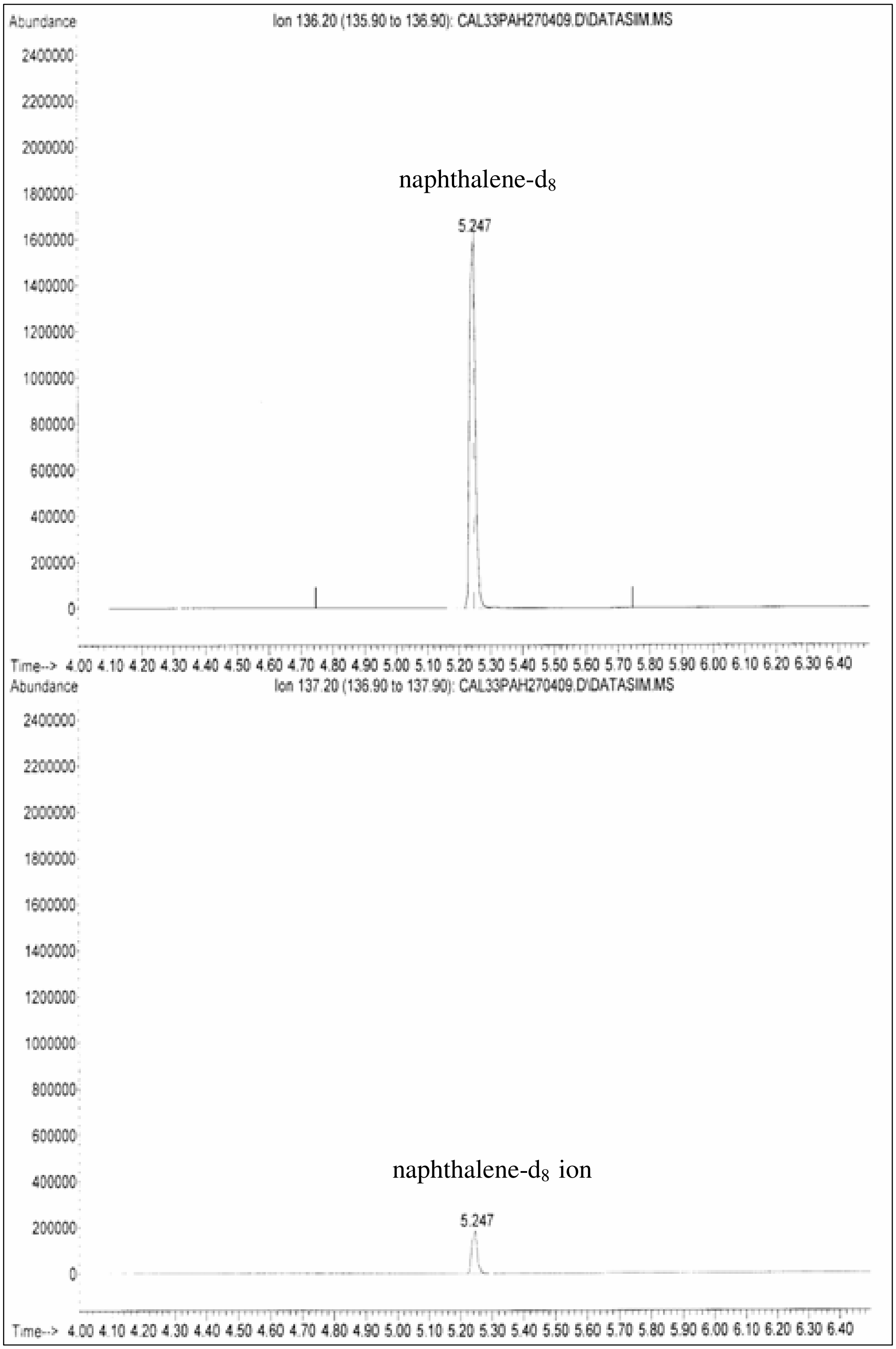


Figure 4.9 The GC-MS chromatogram of internal standard of PAH (naphthalene-d_8) and naphthalene-d_8 ion

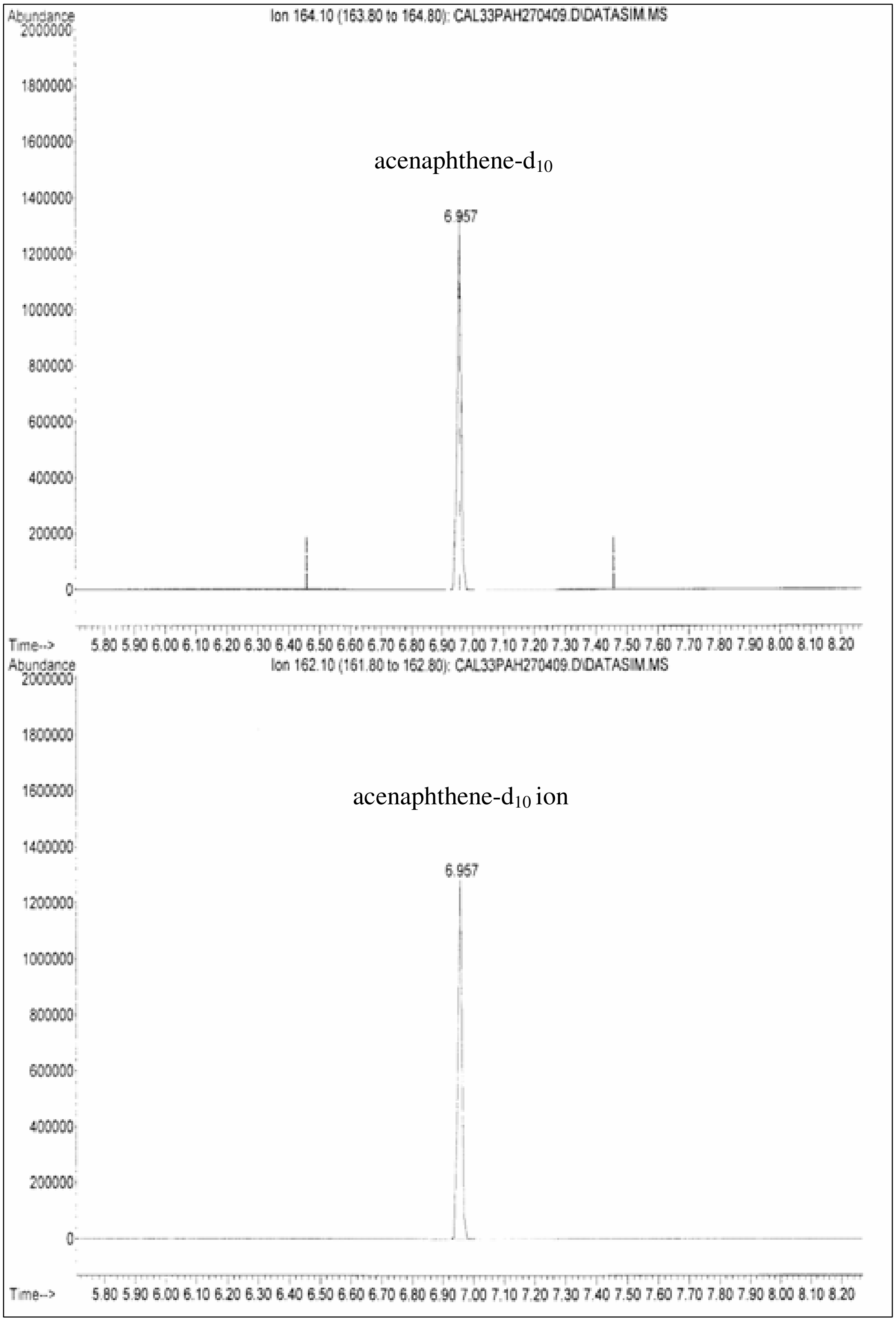


Figure 4.10 The GC-MS chromatogram of internal standard of PAH (acenaphthene-d_{10}) and acenaphthene-d_{10} ion

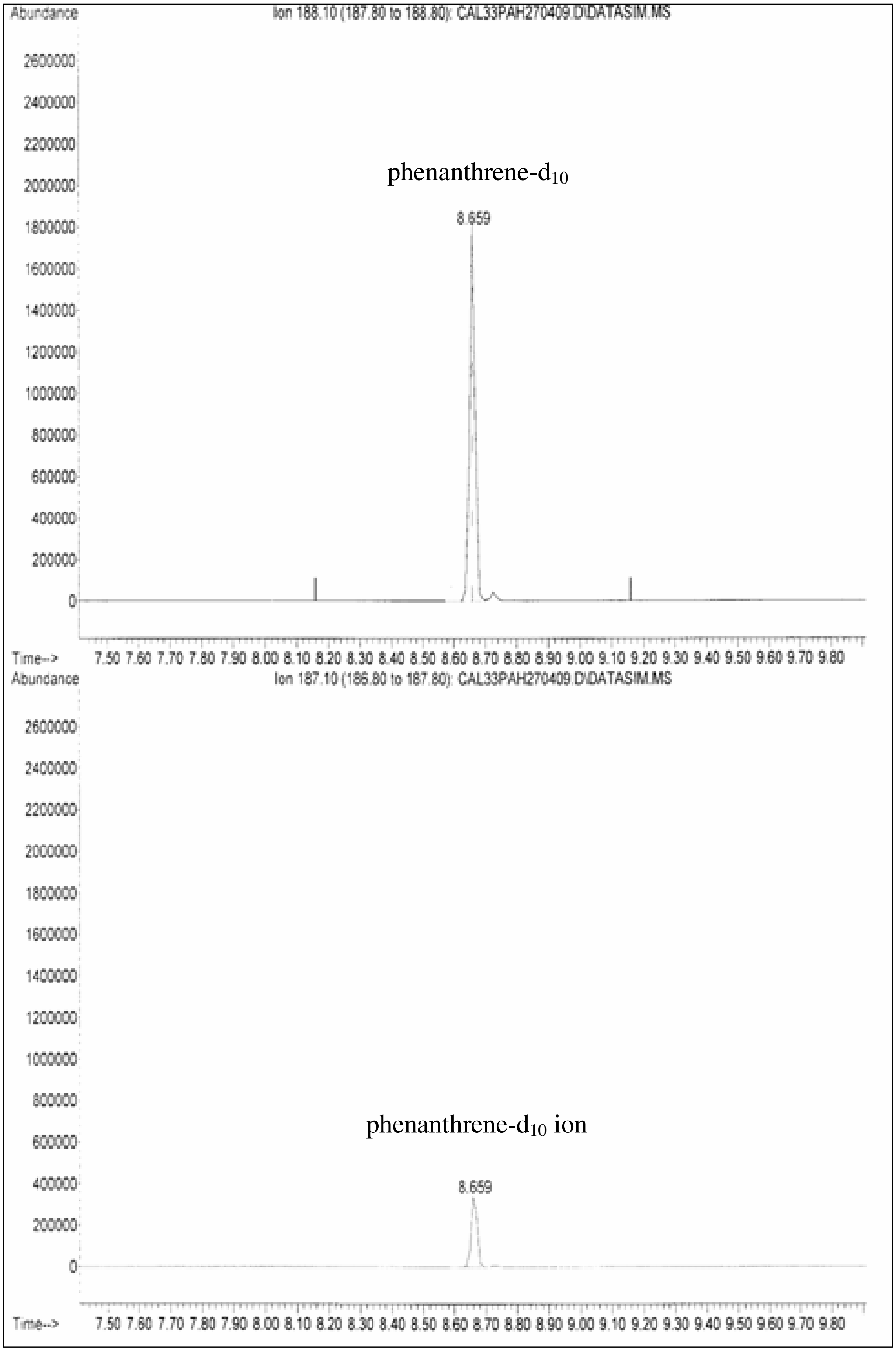


Figure 4.11 The GC-MS chromatogram of internal standard of PAH (phenanthrene-d_{10}) and phenanthrene-d_{10} ion

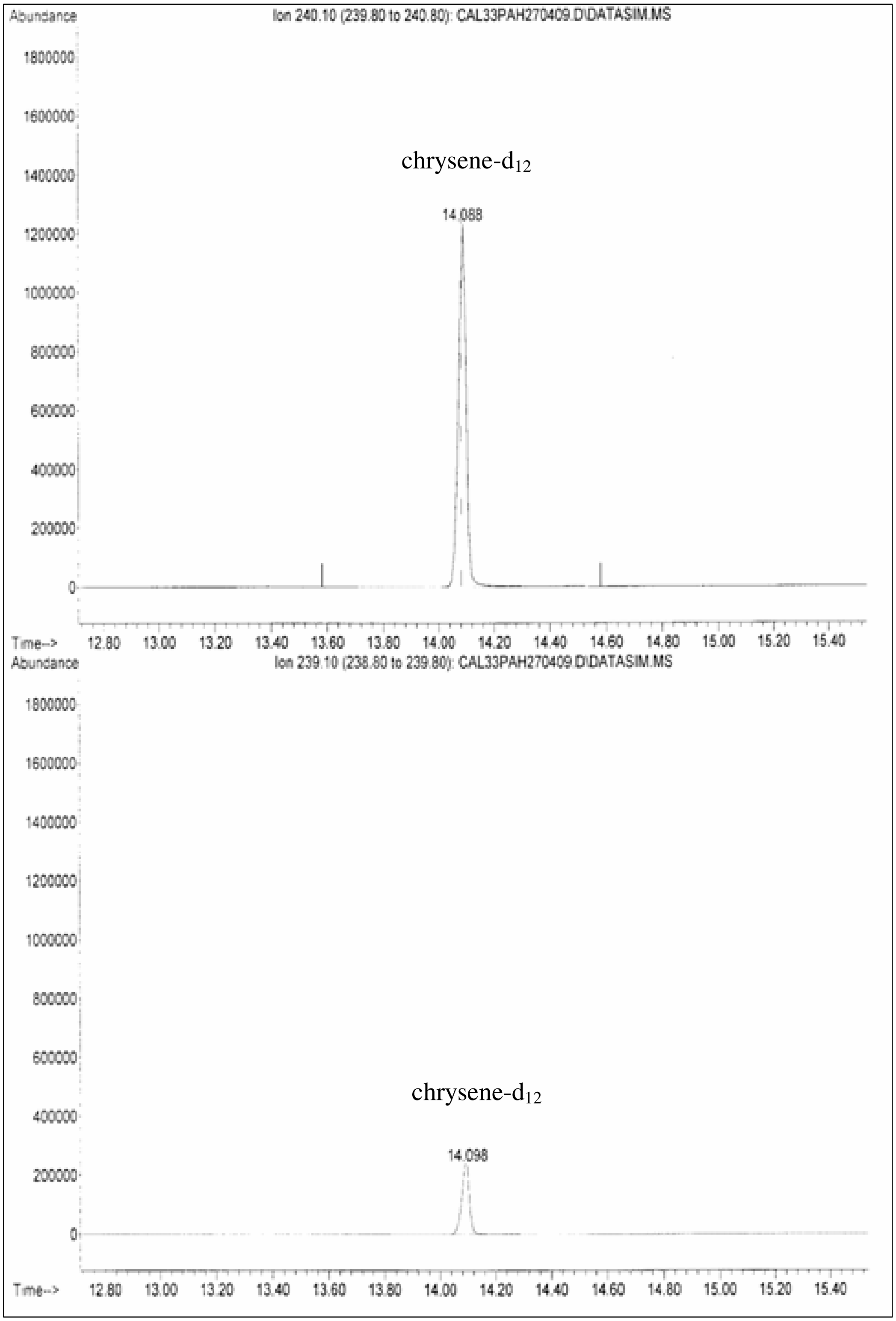


Figure 4.12 The GC-MS chromatogram of internal standard of PAH (chrysene-d_{12}) and chrysene-d_{12} ion

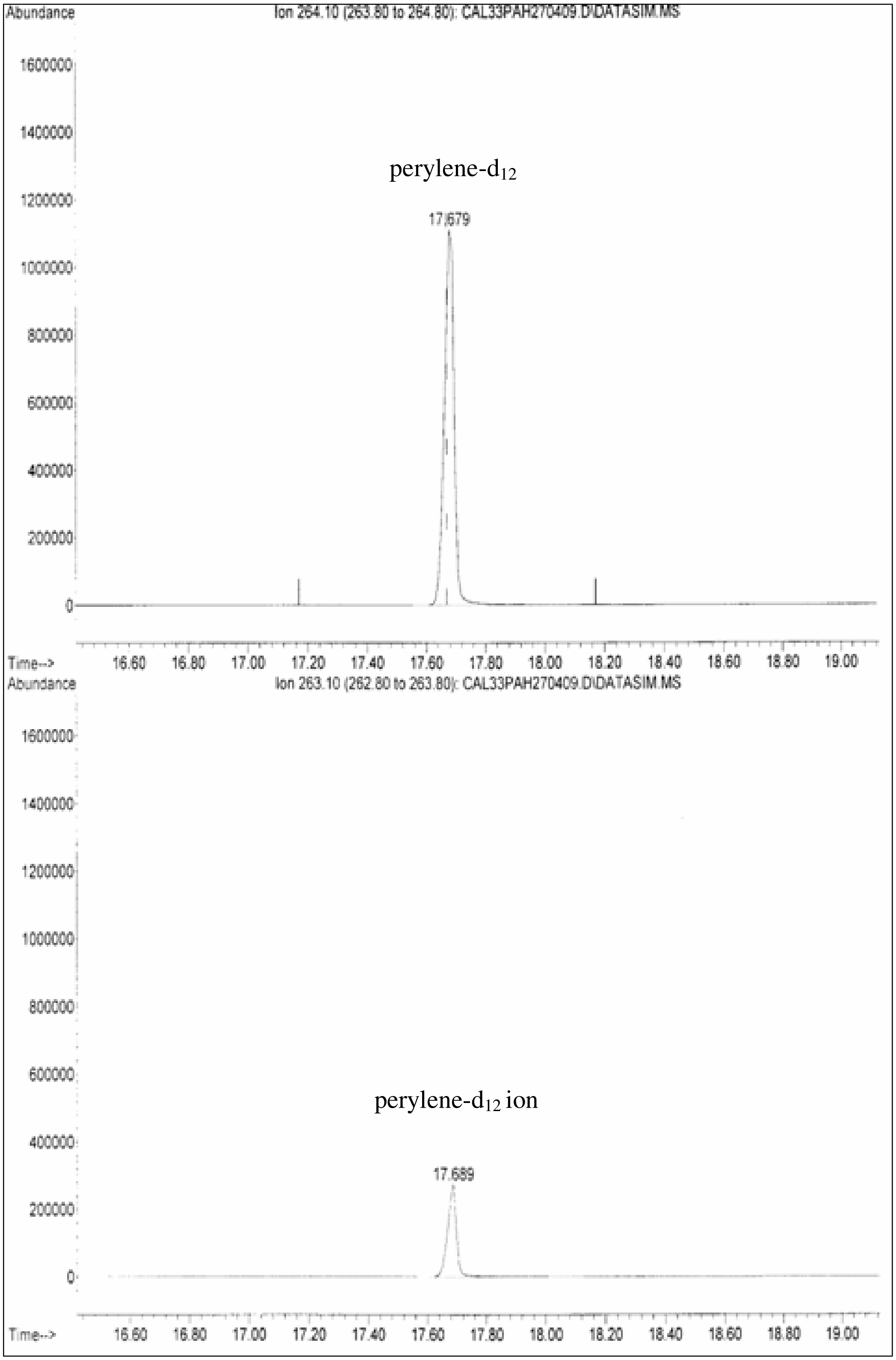


Figure 4.13 The GC-MS chromatogram of internal standard of PAH (perylene-d_{12}) and perylene-d_{12} ion

4.3.2 Total Solids (TS) and Total Suspended Solids (TSS) Measurements

TS and TSS were measured following the Standard Methods 2540 B and 2540 C (Standard Methods, 2005) with NUVE EN 500 Etuv (2006).

4.3.3 Volatile Solids (VS) and Total Volatile Suspended Solids (TVSS) Measurements

VS and TVSS were measured following the Standard Methods 2540 D and 2540 E (Standard Methods, 2005) with Lenton furnaces (1997).

4.3.4 pH, T(^{o}C) and Oxidation-Reduction Potential (ORP) Measurements

pH, T(^{o}C) and ORP (mV) were monitored following the Standard Methods 2550 and 2580 (Standard Methods, 2005) with a pH-Meter pH 330i/SET WTW (2001) and DO – meter DO/SET WTW (2001).

4.3.5 Total Nitrogen (Total-N) Measurements

Total-N was determined with 1.14537.0001 nitrogen (total) (0.50-15 mg/l N) cell test spectroquant kit (Merck) using a spectroquant NOVA 60 (Merck) spectrophotometer (2003).

4.3.6 Ammonium-Nitrogen (NH_4-N) Measurements

NH_4-N was applied with 1.14752.0001 ammonium nitrogen (0.05-3.00 mg/l NH_4-N, 0.06-3.86 mg/l NH_4) reagent test spectroquant kit (Merck) using a spectroquant NOVA 60 (Merck) spectrophotometer (2003).

4.3.7 Nitrite-Nitrogen (NO_2-N) Measurements

NO_2-N was made with 1.14776.0001 nitrite nitrogen (0.02-1.00 mg/l NO_2-N, 0.07-3.28 mg/l NO_2) cell test spectroquant kit (Merck) using a spectroquant NOVA 60 (Merck) spectrophotometer (2003).

4.3.8 Nitrate-Nitrogen (NO_3-N) Measurements

NO_3-N was done with 1.14563.0001 nitrate nitrogen (0.50-25.0 mg/l NO_3-N, 2.20-110.70 mg/l NO_3) cell test spectroquant kit (Merck) using a spectroquant NOVA 60 (Merck) spectrophotometer (2003).

4.3.9 Total Phosphorus (Total-P) Measurements

Total-P was measured with 1.14729.0001 phosphate [(determination of phosphorus (total)] (0.50-25.00 mg/l P) cell test spectroquant kit (Merck) using a spectroquant NOVA 60 (Merck) spectrophotometer (2003).

4.3.10 Phosphate-Phosphorus (PO_4-P) Measurements

PO_4-P was measured with 1.14729.0001 phosphate (determination of ortho-phosphate) (0.50-25.00 mg/l PO_4-P, 1.50-76.70 mg/l PO_4) cell test spectroquant kit (Merck) using a spectroquant NOVA 60 (Merck) spectrophotometer (2003).

4.3.11 Sulfate (SO_4) Measurements

SO_4 was measured with 1.14548.0001 sulfate (5-250 mg/l SO_4) cell test spectroquant kit (Merck) using a spectroquant NOVA 60 (Merck) spectrophotometer (2003).

4.3.12 Total Phenol (T-Ph) Measurements

Total-Ph was measured with 1.14551.0001 phenol (0.10-2.50 mg/l phenol) cell test spectroquant kit (Merck) using a spectroquant NOVA 60 (Merck) spectrophotometer (2003).

4.3.13 Biological Oxygen Demand (BOD) and Biological Oxygen Demand-5 days (BOD_5) measurements

BOD_5 was measured following the Standard Methods 5210 and 5210 B (Standard Methods, 2005).

4.3.14 Total Organic Carbon (TOC) Measurements

TOC was measured following the Standard Methods 5310 (Standard Methods, 2005) with a Rosemount Dohrmann DC-190 high-temperature total organic carbon (TOC) analyzer (1994).

4.3.15 Chemical Oxygen Demand (COD) Measurements

COD was determined with Close Reflux Method following the Standard Methods 5220 D (Standard Methods, 2005) using an Aquamate thermo electron corporation UV visible spectrophotometer (2007). First the samples were centrifuged for 10 min at 7000 rpm. Secondly, 2.50 ml volume samples were treated with 1.50 ml 10216 mg/l $K_2Cr_2O_7$ with 33.30 g/l $HgSO_4$ and 3.50 ml 18.00 M H_2SO_4 which contains 0.55% (w/w) Ag_2SO_4. Thirdly the closed sample tubes were stored in a 148°C heater (thermoreactor, CR 4200 WTW, 2008) for 2 h. Finally, after cooling, the samples were measured at 600 nm with an Aquamate thermo electron corporation UV visible spectrophotometer (2007). The Close Reflux Method COD was used to measure the COD in PCI ww, OMI ww and TI ww before and after sonication experiments

4.3.15.1 Total COD (COD_t)

Wastewater samples were used to measure the total COD (COD_t) in PCI ww, OMI ww and TI ww before and after sonication process.

4.3.15.2 Dissolved COD (COD_{dis})

0.45 µm membrane-filtered (Schleicher & Schuell ME 25, Germany) wastewater samples were used to measure the dissolved COD (COD_{dis}) in PCI ww, OMI ww and TI ww prior and after sonication experiments.

4.3.15.3 Soluble Inert COD

Soluble inert COD was measured in influent and effluent samples with Glucose Comparison Method (Germirli et al., 1991). Both wastewater and synthetic glucose solution have the same influent soluble COD values. The inert COD value of glucose is zero. The minimum soluble COD value of glucose was indicated to the inert COD. The soluble inert COD value of wastewater was determined to the difference between the minimum soluble COD value of wastewater and the inert COD value of glucose in Eq. (4.4):

Soluble inert COD = [the minimum soluble COD value of wastewater] – [the inert COD value of glucose] (4.4)

Soluble inert COD was used for PCI ww before sonication experiments.

4.3.16 Color Measurements

In the studies with real colorful TI ww which is including Methylene Blue ($C_{16}H_{18}N_3SCl$). The measurement of color was carried out following the approaches described by Olthof et al. (1976) and Eckenfelder (1989). According these methods, the color content was determined by measuring the absorbance at three wavelengths (445 nm, 540 nm and 660 nm), and taking the sum of the absorbances at these wavelengths. To convert the absorbance into (m^{-1}) the equation given below Eq. (4.5) was used.

$$\alpha = \left(\frac{A}{d}\right) f \qquad (4.5)$$

where;

a: Color in (m^{-1}) unit,

A: Measured absorbance value from the spectrophotometer,

d: Sample length (cell width, 10 mm),

f: Factor (1000).

Raw wastewater was diluted with deionized H_2O between 100 and 1000 mg/l at ten different concentrations for the calibration graphic and calibration equation of color measurement. These ten different wastewater concentrations were measured at three different wavelents (445 nm, 540 nm and 660 nm) with an Aquamate thermo electron corporation UV visible spectrophotometer (2007). Results of three different wavelents were illustrated in Tables 4.2, 4.3 and 4.4. Three different calibration graphics (Figures 4.14, 4.15 and 4.16) and calibration in Eqs. (4.6), (4.7) and (4.8) were obtained for color measurement at three different wavelents (445 nm, 540 nm and 660 nm).

Table 4.2 Standard concentrations (mg/l) versus absorbance (nm) values of color A1:445 nm (λ = 445 nm) using an Aquamate thermo electron corporation UV visible spectrophotometer (2007).

Concentrations (mg/l)	**Absorbance (nm)**
100	0.098
200	0.199
300	0.296
400	0.412
500	0.534
600	0.591
700	0.705
800	0.816
900	0.910
1000	0.998

$$y = 1.0068 * X + 2.133 \qquad R^2 = 0.9983 \tag{4.6}$$

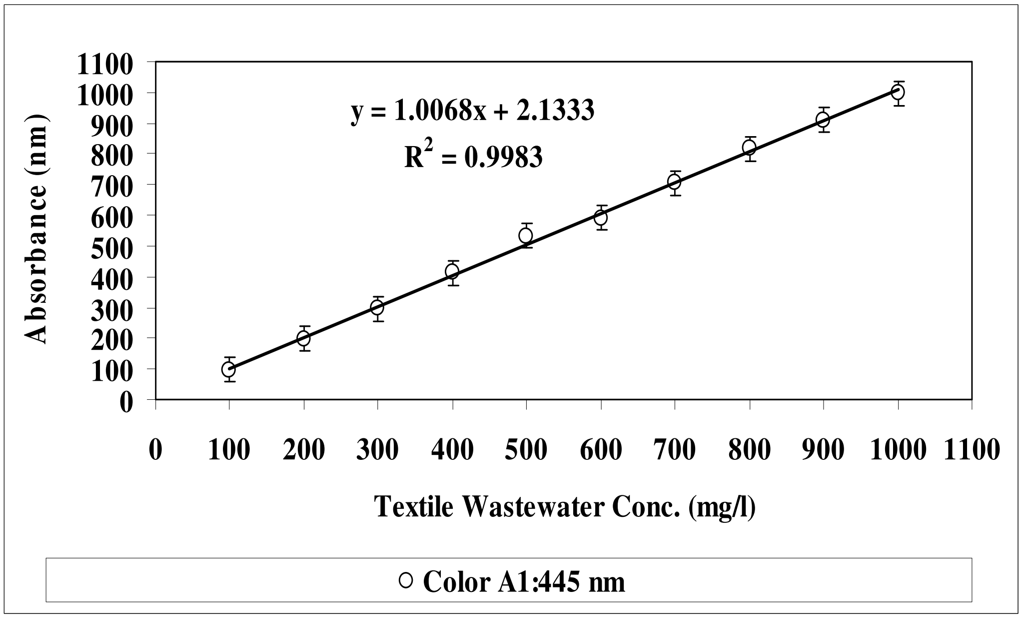


Figure 4.14 Color A1:445 nm calibration graphic for sonication experiments.

Table 4.3 Standard concentrations (mg/l) versus absorbance (nm) values of color A2:540 nm ($\lambda = 540$ nm) using an Aquamate thermo electron corporation UV visible spectrophotometer (2007).

Concentrations (mg/l)	**Absorbance (nm)**
100	0.102
200	0.214
300	0.313
400	0.428
500	0.507
600	0.653
700	0.711
800	0.826
900	0.900
1000	0.994

$$y = 0.9933 * X + 18.467 \qquad R^2 = 0.9968 \tag{4.7}$$

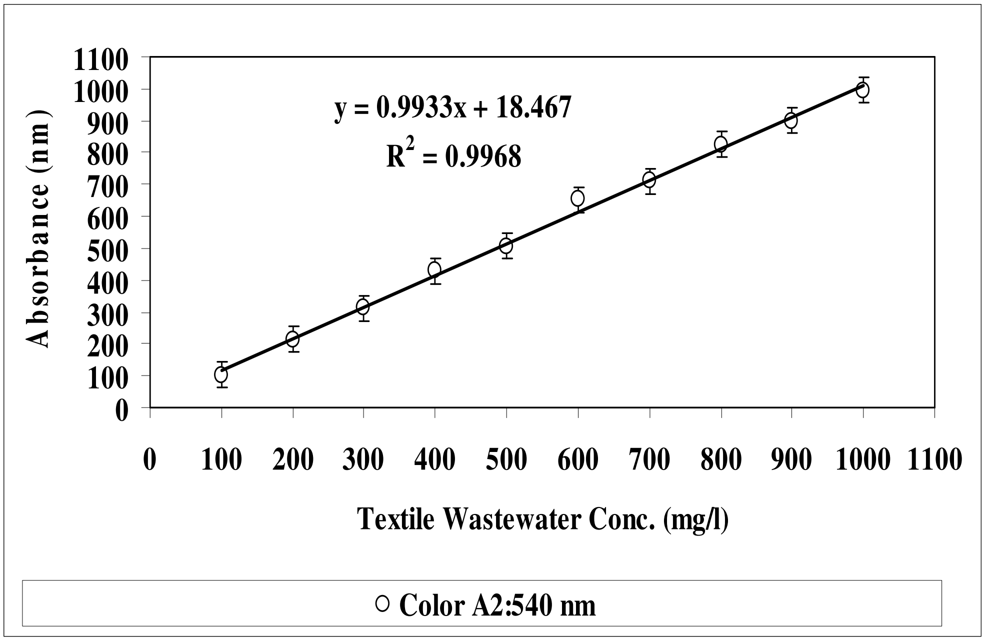


Figure 4.15 Color A2:540 nm calibration graphic for sonication experiments.

Table 4.4 Standard concentrations (mg/l) versus absorbance (nm) values of color A3:660 nm (λ = 660 nm) using an Aquamate thermo electron corporation UV visible spectrophotometer (2007).

Concentrations (mg/l)	**Absorbance (nm)**
100	0.091
200	0.197
300	0.302
400	0.401
500	0.523
600	0.630
700	0.724
800	0.812
900	0.927
1000	0.990

$$y = 1.0198 * X - 1.2 \qquad R^2 = 0.9979 \tag{4.8}$$

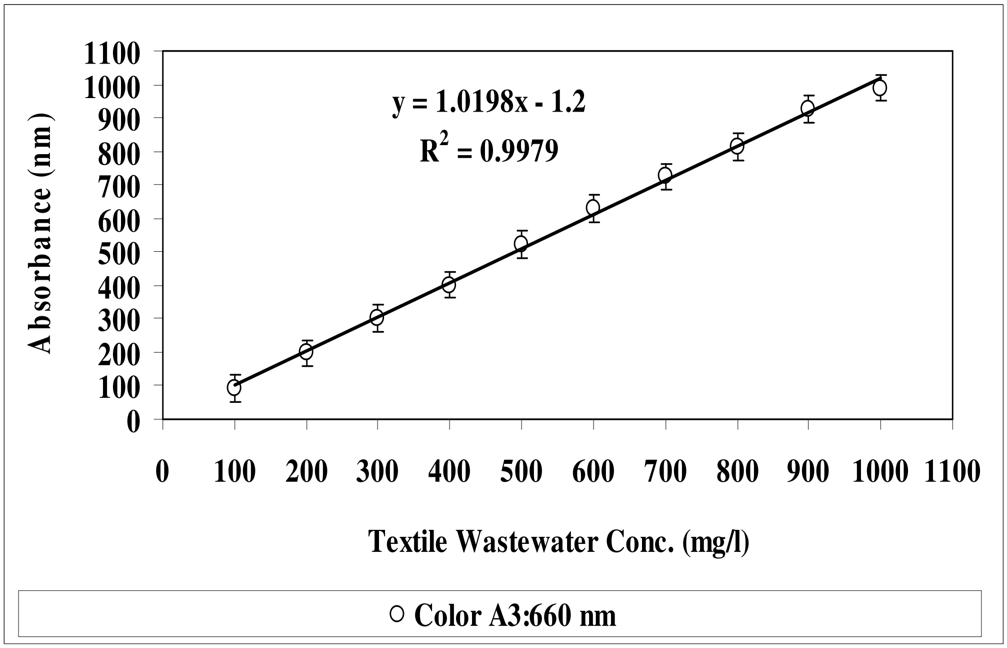


Figure 4.16 Color A3:660 nm calibration graphic for sonication experiments.

4.3.17 Total Fatty Acid (TFA) Measurements

Bicarbonate (HCO_3) alkalinity and total fatty acid (TFA) concentrations were measured simultaneously using titrimetric method proposed by Anderson & Yang (1992). The test was carried out as follows: firstly the pH of the sample was measured, secondly the sample was titrated with standard H_2SO_4 (0.10 N) through two stages (first to pH=5.10, then from 5.10 to 3.50), and finally the TFA and HCO_3 alkalinity concentrations were calculated with a computer program by solved the Eqs. (4.9) and (4.10):

$$A_1 = \frac{\lfloor HCO_3^- \rfloor * ([H]_2 - [H]_1)}{[H]_1 + K_C} + \frac{[TFA] * ([H]_2 - [H]_1)}{[H]_2 + K_{TFA}} \quad (4.9)$$

$$A_2 = \frac{\lfloor HCO_3^- \rfloor * ([H]_3 - [H]_1)}{[H]_3 + K_C} + \frac{[TFA] * ([H]_3 - [H]_1)}{[H]_3 + K_{TFA}} \quad (4.10)$$

where;

A_1 and A_2: The molar equivalent of the standard acid consumed to the first and second end points,

$[HCO_3^-]$: The bicarbonate concentration (mg HCO_3/l),

$[TFA]$: The total fatty acid ion concentration (mg/l),

$[H]_{1,2,3}$: The hydrogen ion concentrations of the original sample and at the first and the second end points,

K_C: The conditional dissociation constant of carbonic acid,

K_{TFA}: The combined dissociation constant of the volatile fatty acids (C_2–C_6), this pair of constants was assumed, being 6.6×10^{-7} for bicarbonate and 2.40×10^{-5} for volatile acids.

HCO_3 concentrations also were calculated for the wastewater from the Eqs. (4.9) and (4.10). The HCO_3 concentration was not showed in the results since did not discuss through sonication with the exception of section "effect of HCO_3 on sonication".

4.3.18 Determination of Aromatic Amines

The total aromatic amines (TAAs) were determined colorimetrically at 440 nm after reacting with 4-dimethylaminobenzaldehyde-HCl according to the method described by Oren et al. (1991). 1.00 g/l benzidine chemical was prepared to a standard solution for using TAAs standard measurements. TAAs calibration graphic was obtained with benzidine concentrations varying between 100 and 1000 mg benzidine/l from the stock 1.00 g/l benzidine concentration at 440 nm using an Aquamate thermo electron corporation UV visible spectrophotometer (2007) (Table 4.5). A calibration equation (Eq. 4.13) was found from calibration graphic given in Figure 4.17.

Firstly, 0.20 ml wastewater sample was added in 14.00 ml glass test tube. Secondly, 0.80 ml deionized H_2O was appended in 14.00 ml glass test tube. Thirdly, 0.05 ml HCl (30.00% purity) solution was affixed in 14.00 ml glass test tube. After, 3 ml absolute ethanol solution was added in 14.00 ml glass test tube. Then, 0.50 ml of 5.00% of p-dimethileaminobenzaldehit/ethanol solution was appended in 14.00 ml glass test tube. After that, 0.50 ml 15.70% of citric acid ($C_6H_8O_7$) / 6.00% of NaOH solution was affixed in 14.00 ml glass test tubes. Afterwards, the glass test tube was closed with a black plastic stopper and was waited for 10 min. Then, 10 min, 2.50 ml deionized H_2O was added in this 14.00 ml glass test tube. Finally, TAAs concentration was measured at 440 nm in an Aquamate thermo electron corporation UV visible spectrophotometer (2007).

Table 4.5 Standard concentrations versus absorbance values at λ=440 nm using an Aquamate thermo electron corporation UV visible spectrophotometer (2007).

Concentrations (mg benzidine / l)	Absorbance (nm)
100	0.115
200	0.214
300	0.310
400	0.411
500	0.512
600	0.628
700	0.721
800	0.802
900	0.925
1000	0.998

$$y = 0.9958 * X + 15.933 \qquad R^2 = 0.9990 \tag{4.11}$$

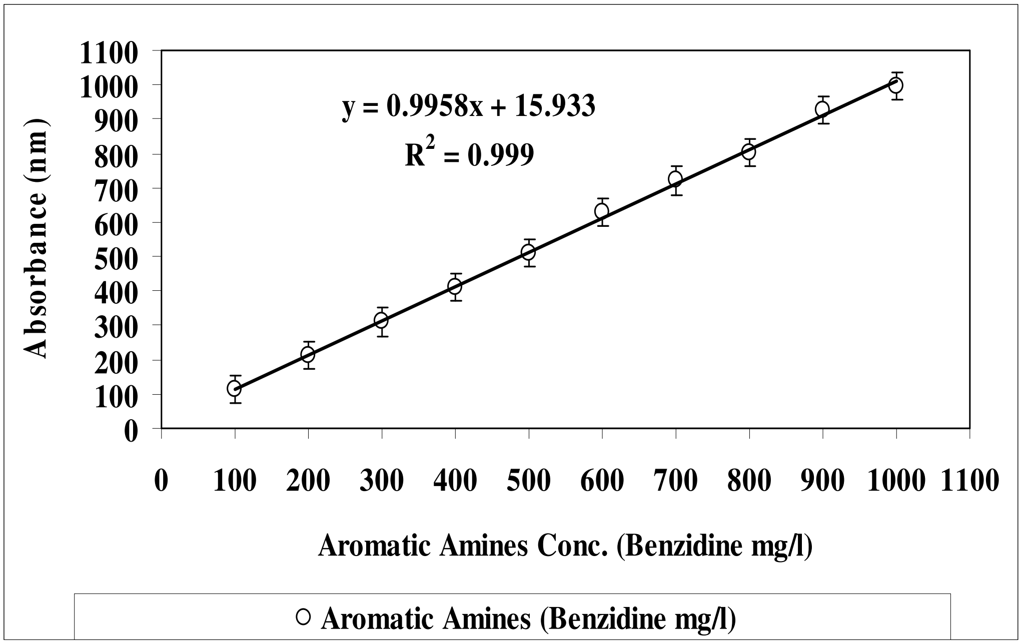


Figure 4.17 Aromatic amines calibration graphic for sonication experiments.

4.3.19 Oil Measurements

Oil measurement was performed following the Standard Methods 5520 B (Standard Methods, 2005). A representative grab sample was collected in a wide-mouth glass bottle that was washed with soap, was rinsed with water and finally was rinsed with solvent to remove any residues that might interfere with the analysis. As an alternative the sample was solvented when rinsing, the bottle was cepped with aluminum foil and it was baked at 200 to 250°C for at least 1 h. Teflon lined caps was used for sample bottles; clean liners as above, but was limited to temperature between 110 and 200°C. A separate sample was collected for an oil and grease determination. Replicates were collected either in rapid succession, in parallel, or in one large container with mechanical stirring (in the latter case, siphon individual partions). Typically, wastewater samples were accumulated approximately 1.00 l. If sample concentration was expected to be greater than 1000 mg extractable material/l, collect proportionately smaller volumes. If sample has not been acidified previously, acidify with either 1/1 HCl or 1/1 H_2SO_4 to pH=2.0 or lower (generally, 5.00 ml is sufficient for 1.00 l sample). Liquid funnel was transferred from sample to a separatory funnel. Carefully rinse sample bottle with 30.00 ml extracting solvent and add solvent was washed to separatory funnel. And, was shaked vigorously for 2 min. Let layers was separated. Aqueous layer and small amount of organic layer was drained into original sample container. Solvent layer was drained through a funnel containing a filter paper and 10.00 g Na_2SO_4, both of which have been solvent-rinsed, into a clean, tared distilling flask containing boiling chips. If a clear solvent layer cannot be obtained and an emulsion of more than about 5.00 ml exists, emulsion and solvent layers into a glass centrifuge tube and was centrifuged for 5 min at approximately 2400 rpm. Centrifuge material was transfered to an appropriate separatory funnel and solvent layer was drained through a funnel with a filter paper and 10.00 g Na_2SO_4, both of which have been prerinsed, into a clean, tared distiiling flask. Aqueous layers and remaining emulsion or solids were recombined in separatory funnel. For samples with < 5.00 ml of emulsion and only clear solvent was drained through a funnel witnh pre-moistened filter paper and Na_2SO_4. Aqueous layers and any remaining emulsion or solids was recombined in separatory funnel. Twice more was extracted with 30.00 ml solvent each time, but, first rinse sample container with each solvent portion. Centrifuge step was repeated, if emulsion persisted in subsequent extraction steps. Extracts was combined in tared distilling flask and was included in flask a final rinsing of filter and Na_2SO_4 with an additional 10.00 to 20.00 ml solvent. Solvent was distilled from flask in a water bath at 85°C. Solvent recovery was maximized; distillation flask was fitted with a distillation cooler receiver. When visible solvent condensation stoped, bent distillation apparatus was replaced with vacuum/air adapter, and vacumm source was connected. Air was immediately was drawn through flask with an applied vacumm for the final 1 min. Flask was removed from bath and wipe outside surface and moisture was removed. Flask was cooled in desiccator until a constant weight is obtained. Initial sample volume was determined to either fill sample bottle was marked with H_2O and then poor water into a 1.00 l graduated cylinder, or weight empty container and cap. The sample volume was calculated by difference from the initial weight (sample density was assumed of 1.00). The calculation of oil and grease in sample as following in Eq. (4.12):

$$mg\ oil\ and\ grease / l = \frac{W_r}{V_s} \tag{4.12}$$

where;

W_r: Total weight of flask and residue, minus tare weight of flask (mg), and

V_s: Initial sample volume, (l).

4.3.20 Polyphenol Measurements

Polyphenol measurement was performed following the Standard Methods 5520 B (Standard Methods, 2005). Firstly, 5.00 ml of OMI ww sample was added in 40.00 ml dark brown color Amber I–cem vial (Catalog number: 98716). Secondly, 5.00 ml of mixture of siklohexane (50.00%) and etilacetate (50.00%) was added on 5.00 ml of OMI ww sample in 40.00 ml dark brown color Amber I–cem vial. After, this solutions were mixtured at 15 min. Upper part of mixtured solution was taken with a pasteur pipette in a new 40.00 ml dark brown color Amber I–cem vial. 0.50 g Na_2SO_4 chemical was added for waterless condition in a new 40.00 ml dark brown color Amber I–cem vial. After that, this 40.00 ml dark brown color Amber I–cem vial again was mixtured at 15 min. The upper part of 40.00 ml dark brown color Amber I–cem vial was taken with a pasteur pipette in a 1.50 ml of colorless glass vial (Agilent). 1.00 ml sample was added in a 1.50 ml of colorless glass vial for GC-MS analysis. Polyphenol was analysed with a gas chromotography (Agilent 6890) combined with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-MS, 30.00 m, 0.25 mm, 0.25 μm) was used. The initial oven temperature to hold at 50^{o}C for 1 min, to rise to 200^{o}C at 25^{o}C /min and from 200^{o}C to 300^{o}C at 80^{o}C /min and was held for 5.5 min. The injector ion source and quadrupole temperatures were 295^{o}C, 300^{o}C and 180^{o}C, respectively. High purity helium (He) was used as the carrier gas at constant flow mode (1.50 ml/min, 45.00 cm/s linear velocity). The MSD to run in selected ion-monitoring mode. Compounds were identified on the basis of their retention times, target and qualifier ions. Qualification was based on the Internal Standard Calibration Procedure.

4.3.21 The Measurement Procedure of Sonication By-Products for PCI ww and OMI ww

4.3.21.1 The Measurement Procedure of Sonication By-Product for PCI ww

4.3.21.1.1 Sample Extraction and concentrate of PAHs By-Products. Water samples to filter through a glass fiber filter (47 mm-diameter) to collect particle-phase in series with a resin column (≈ 10.00 g XAD-2) to collect dissolved-phase poylbrominated diphenyl ethers (PCBEs). Resin and H_2O filters to ultrasonically extract for 60 min with a mixture of 1/1 acetone/hexane. Prior to extraction, all samples to spike with PAH by-products surrogate standards to monitor analytical recovery efficiencies. The volume of extracts to reduce and to transfer into hexane using a rotary evaporator and a high-purity N_2(g) stream. After volume reduction to 2.00 ml by a gentle flow of N_2(g), the samples to clean up on an alumina-silicic acid column containing 3.00 g of silicic acid (3.00% H_2O) and 2.00 g of alumina (6.00% H_2O). The column to pre-wash with 20.00 ml of dichloromethane (DCM) followed by 20.00 ml of petroleum ether (PE). The sample in 2.00 ml of hexane to add to the top of the column and PAH by-products to elute with 20.00 ml of DCM. After solvent exchange into hexane, the final sample volume to adjust to 1.00 ml by N_2(g) blow-down.

4.3.21.1.2 Clean Up and Fractionation. To remove interferences before GC/MS analysis, the samples were cleaned up and fractionated on an alumina-silicic acid column. Before use, Na_2SO_4 and alumina were placed in ceramic plates covered loosely with aluminium foil, and then they were baked in a muffle furnace at 450°C for 4 h. Silicic acid was placed in a flask covered loosely with aluminium foil, dried in an oven at 105°C overnight to remove moisture. Then, they were allowed to cool to room temperature in a desiccator.

In an Amber I–cem vial, three grams of Silicic acid was deactivated by adding 100 µl of deionized H_2O (3.00% H_2O), and then the mixture was shaken until homogenized. Similarly, 2.00 g of alumina was deactivated by adding of 120 µl of deionized H_2O (6.00% H_2O) and the mixture was homogenized by shaking. These mixtures were left at room temperature at least 1 h before use, and used within 12 h.

Alumina-silicic acid column was prepared by adding a piece of glass wool, 3.00 g of silicic acid (3.00% H_2O), 2.00 g of alumina (6.00% H_2O), and ≈ 1.00 cm column height of anhydrous Na_2SO_4 in series. The column was pre-washed with 20.00 ml of DCM followed by 20.00 ml of PE. Then, the sample in 2.00 ml of hexane was added to the top of the column with a 2.00 ml rinse of PE, and eluent was collected in a vial at a rate of two drops per second. After letting the sample pass through the column, 20.00 ml of PE was added and eluent collected in the same vial (Fraction 1). Fraction 1 contained PCBs. Then the Amber I–cem vial used for eluent collection was changed, 20.00 ml of DCM was added into the column, and eluent was collected at the same rate (Fraction 2). Fraction 2 contained PAHs by-products. For both fractions, the sample volume was reduced, and the solvent was exchanged into hexane using a high purity stream of N_2(g) (≈ 150-200 ml/min). The sample was blown-down to ≈ 5.00 ml, and 10.00 ml of Hexane was added to the Amber I–cem vial. After volume reduction to ≈ 5.00 ml, again 10.00 ml of hexane was added into the sample volume. Then, the final sample volume was adjusted to exactly 1.00 ml by $N_2(g)$ blow-down. All samples were stored in a freezer until analysis.

4.3.21.1.3 The Measurement of Phenanthrenediol (by-product of PAHs). The phenanthrenediol analysis was performed using a high-pressure liquid chromatography (HPLC) (Agilent–1100) with a method developed by Lindsey & Tarr (2000b). The chromatographic conditions for phenanthrenediol determination were as follows: C–18 reverse phase HPLC column (Ace 5C18; 25.00–cm x 4.60–mm, 5.00 μm, mobile phase: 50/50 (v/v) methanol/organic-free reagent water).

4.3.21.1.4 The Measurements of Methane, $CH_4(g)$, Hydrogen, $H_2(g)$ and Carbondioxide, $CO_2(g)$ gases in PCI ww. The $CH_4(g)$, $H_2(g)$ and $CO_2(g)$ analysis was performed following Standard Methods (2005). As aforementioned aqueous phase sonolysis is likely to result in the formation of H_2O_2 which may be formed through the recombination of $OH^\bullet$ at the gas–liquid interface and/or in the solution bulk. Moreover, if the solution is saturated with O_2, (H_2O) and more $OH^\bullet$ are formed in the bubble, the recombination of the former at the interface and/or in the solution bulk results in the formation of additional H_2O_2 (Wu & Ondrucschka, 2005). It was found that PAHs mainly decomposed at the gas–liquid interface through both $OH^\bullet$ oxidation and pyrolytic reactions (for instance, $CH_4(g)$ and $CO_2(g)$ were identified as the primary pyrolysis by-products) rather than in the solution bulk (David, 2009). This was attributed to the fact that the PAHs, in this study, although, less water soluble and non-volatile molecules, tended to accumulate at the gas–liquid interface. Furthermore, it was also found that the concentration of H_2O_2 formed during PAH sonication experiments was substantially lower than that formed during H_2O sonication in the absence of PAHs. In this study, $CH_4(g)$, $H_2(g)$ and $CO_2(g)$ were identified in the headspace of the sonicator reactor. The gas chromatography (GC) spectra of these gases are illustrated in Figure 4.18.

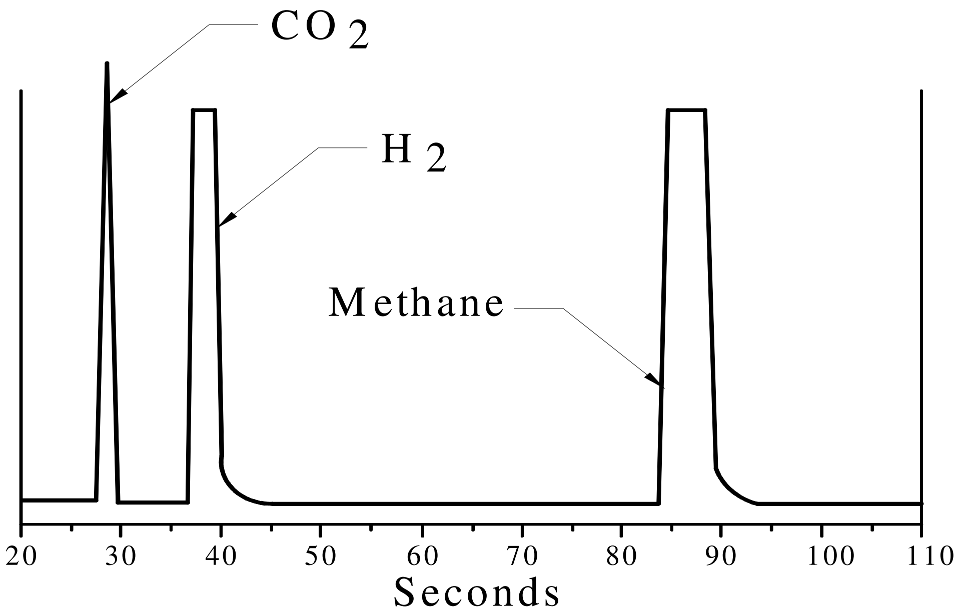


Figure 4.18 $CH_4(g)$, $H_2(g)$ and $CO_2(g)$ spectra measured in the headspace of the sonicator by GC

In this study, the presence of these gases indicated not only the destruction of the PAHs but also confirmed the mechanism "pyrolysis" with degassing of the medium throughout sonication. The results given above are consistent with our results.

4.3.21.1.5 Analysis of PAH By-Products Samples with GC-MS. All extract to analyze for PAHs by-products with a gas chromotography (Agilent 6890, GC) combined with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-MS, 30.00 m, 0.25 mm, 0.25 µm) was used. The initial oven temperature to hold at 50°C for 1 min, to rise to 200°C at 25°C /min and from 200°C to 300°C at 80°C /min and was held for 5.50 min. The injector ion source and quadrupole temperatures were 295°C, 300°C and 180°C, respectively. High purity helium (He) was used as the carrier gas at constant flow mode (1.50 ml/min, 45.00 cm/s linear velocity). The MSD to run in selected ion-monitoring mode. Compounds were identified on the basis of their retention times, target and qualifier ions. Qualification was based on the Internal Standard Calibration Procedure.

4.3.21.1.6 Analysis of PAHs By-Products Samples with GC-FID. Measurements were performed following the Standard Methods 5520 B (Standard Methods, 2005). Firstly, 400 ml wastewater was extracted in 50.00 ml DCM with liquid–liquid extraction. Seconly, phase separation of sample was waited after mixed at 2 or 3 min. This procedure was applied triplicate condition for sample. Thirdly, DCM was evaporated with N_2(g) sparging. After, acetonitrile was added in sample. Then, sample was taken in acetonitrile solution. Excess solvent was removed in media with N_2(g) sparging. Therefore, DCM was leaved at this sample. After then, sample was passed through in Na_2SO_4 column for waterless condition before gas chromatography-flame ionization detector (GC-FID) analysis. Sample was analyzed with a GC-FID system was performed an Agilent 6890 N Network GC equipped with a FID, Agilent 7683 series autosampler, Agilent Chemstation and HP–5 column with 0.25 µm film thickness (30.00 m x 0.320 mm I.D.). Injection and detector temperature is 250^{o}C and 300^o□C, respectively. 2.00 µl was injected in splitless mode. The carrier gas (N_2) flow-rate was kept constant during the run at 2 ml/min. N_2 (30.00 ml/min), H_2 (44.00 ml/min) and synthetic air (400 ml/min) were used as auxiliary gases for the FID. By-product names of PCI ww were given in Table 4.6, Table 4.7 and Table 4.8. Measurement methods of by-products of PCI ww in DO=10.00 mg/l concentration after 120 min sonication at pH=7.0 and at 25^{o}C with GC-MS, GC-FID and HPLC (Table 4.6). Measurement methods of by-products of PCI ww in H_2O_2=2000 mg/l concentration after 120 min sonication at pH=7.0 and at 25^{o}C was determined with GC-MS, GC-FID and HPLC (Table 4.7). Measurement methods of PCI ww by-products in TiO_2=20.00 mg/l concentration after 120 min sonication at pH=7.0 and at 25^{o}C was applied with GC-MS, GC-FID and HPLC (Table 4.8).

4.3.21.1.7 Analysis of PAHs By-Products Samples with HPLC. Measurements were performed following the Standard Methods 5520 B (Standard Methods, 2005). Firstly, 400 ml wastewater was extracted in 50.00 ml DCM with liquid-liquid extraction. Seconly, phase separation of sample was waited after mixed at 2 or 3 min. This procedure was applied triplicate condition for sample. Thirdly, DCM was evaporated with N_2(g) sparging. After, acetonitrile was added in sample. Then, sample was taken in acetonitrile solution. Excess solvent was removed in media with N_2(g) sparging. Therefore, DCM was leaved at this sample. After then, sample was passed through in Na_2SO_4 column for waterless condition before HPLC analysis. Sample was analyzed with Shimadzu CLASS–VP V6.14 HPLC, Phenomenex Hyperclone 125 mm x 4.60 mm 5.00 µm PAHs HPLC columns at liquid phase (water and acetonitrile). Liquid phase diagram of HPLC for by-product measurements of PCI ww after sonication process was shown as following Table 4.9.

Table 4.6 Measurement methods of by-products of PCI ww in DO=10.00 mg/l after 120 min sonication time at pH=7.0 and at 25^{o}C with GC-MS, GC-FID and HPLC

Parameters		**GC-MS**	**GC-FID**	**HPLC**
DO=10.00 mg/l, after 120 min sonication time at pH=7.0 and at 25^{o}C in PCI ww		Measurement method: Standard Methods 5520 B. Instruments: GC (Agilent 6890) combined with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-MS, 30.00 m, 0.25 mm, 0.25 µm) was used. Carrier gas: High purity He (1.50 ml/min, 45.00 cm/s linear velocity). The MSD to run in selected ion-monitoring mode.	Measurement method: Standard Methods 5520 B. Instruments: An Agilent 6890 N Network GC equipped with a flame ionization detector, Agilent 7683 and HP–5 column with 0.25 µm film thickness (30.00 m x 0.320 mm I.D.). Carrier gas (N_2) (2.00 ml/min). N_2 (30.00 ml/min), H_2 (44.00 ml/min) and synthetic air (400 ml/min).	Measurement method: Standard Methods 5520 B. Instruments: Shimadzu CLASS–VP V6.14 HPLC, Phenomenex Hyperclone 125 mm x 4.60 mm 5.00 µm PAHs HPLC column at liquid phase (water and acetonitrile).
Sonication Time (min)	**By-Product Names**	**Retention Time (min)**	**Retention Time (min)**	**Retention Time (min)**
120	1–methylnaphthalene	4.127	4.236	4.820
120	9–hydroxyfluorene	5.367	5.442	5.758
120	9,10–phenanthrenequione	6.558	6.617	5.725
120	benzoic acid	1.750	1.567	1.675
120	1,2,3–thiadiazole–4–carboxylic acid	1.117	1.083	1.098

Table 4.7 Measurement methods of by-products of PCI ww in H_2O_2=2000 mg/l after 120 min sonication time at pH=7.0 and at 25°C with GC-MS, GC-FID and HPLC.

Parameters		**GC-MS**	**GC-FID**	**HPLC**
H_2O_2=2000 mg/l, after 120 min sonication time at pH=7.0 and at 25°C in PCI ww		Measurement method: Standard Methods 5520 B. Instruments: GC (Agilent 6890) combined with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-MS, 30.00 m, 0.25 mm, 0.25 µm) was used. Carrier gas: High purity He (1.50 ml/min, 45.00 cm/s linear velocity). The MSD to run in selected ion-monitoring mode.	Measurement method: Standard Methods 5520 B. Instruments: An Agilent 6890 N Network GC equipped with a flame ionization detector, Agilent 7683 and HP–5 column with 0.25 µm film thickness (30.00 m x 0.320 mm I.D.). Carrier gas (N_2) (2.00 ml/min). N_2 (30.00 ml/min), H_2 (44.00 ml/min) and synthetic air (400 ml/min).	Measurement method: Standard Methods 5520 B. Instruments: Shimadzu CLASS–VP V6.14 HPLC, Phenomenex Hyperclone 125 mm x 4.60 mm 5.00 µm PAHs HPLC column at liquid phase (water and acetonitrile).
Sonication Time (min)	**By-Product Names**	**Retention Time (min)**	**Retention Time (min)**	**Retention Time (min)**
120	1–methylnaphthalene	4.987	5.112	5.703
120	9–hydroxyfluorene	5.383	5.430	5.392
120	9,10–phenanthrenequione	6.467	6.410	6.425
120	benzoic acid	1.567	1.578	1.617
120	1,2,3–thiadiazole–4–carboxylic acid	1.158	1.101	1.175

Table 4.8 Measurement methods of by-products of PCI ww in TiO_2=20.00 mg/l after 120 min sonication time at pH=7.0 and at 25°C with GC-MS, GC-FID and HPLC

Parameters		**GC-MS**	**GC-FID**	**HPLC**
TiO_2=20 mg/l, after 120 min sonication time at pH=7.0 and at 25°C in PCI ww		Measurement method: Standard Methods 5520 B. Instruments: GC (Agilent 6890) combined with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-MS, 30 m, 0.25 mm, 0.25 µm) was used. Carrier gas: High purity He (1.50 ml/min, 45 cm/s linear velocity). The MSD to run in selected ion-monitoring mode.	Measurement method: Standard Methods 5520 B. Instruments: An Agilent 6890 N Network GC equipped with a flame ionization detector, Agilent 7683 and HP–5 column with 0.25 µm film thickness (30 m x 0.320 mm I.D.). Carrier gas (N_2) (2 ml/min). N_2 (30 ml/min), H_2 (44 ml/min) and synthetic air (400 ml/min).	Measurement method: Standard Methods 5520 B. Instruments: Shimadzu CLASS–VP V6.14 HPLC, Phenomenex Hyperclone 125 mm x 4,60 mm 5 µm PAHs HPLC column at liquid phase (water and acetonitrile).
Sonication Time (min)	**By-Product Names**	**Retention Time (min)**	**Retention Time (min)**	**Retention Time (min)**
120	1–methylnaphthalene	3.716	4.560	4.987
120	9–hydroxyfluorene	5.210	5.317	5.367
120	9,10–phenanthrenequione	6.665	6.540	6.358
120	benzoic acid	1.920	1.810	1.825
120	1,2,3–thiadiazole–4–carboxylic acid	1.160	1.324	1.108

4.3.21.2 The Measurement Procedure of Sonication By-Products for OMI ww

Measurements were performed following the Standard Methods 5520 B (Standard Methods, 2005). Firstly, 400 ml wastewater was extracted in 50.00 ml DCM with liquid-liquid extraction. Seconly, phase separation of sample was waited after mixed at 2 or 3 min. This procedure was applied triplicate condition for sample. Thirdly, DCM was evaporated with N_2(g) sparging. After, acetonitrile was added in sample. Then, sample was taken in acetonitrile solution. Excess solvent was removed in media with N_2(g) sparging. Therefore, DCM was leaved at this sample. After that, sample was passed through in Na_2SO_4 column for waterless condition before HPLC analysis. After then, sample was extracted with 1/4 hexane/acetonitrile solvent. Finally, sample was analyzed with Shimadzu CLASS-VP V6.14 HPLC, Phenomenex Hyperclone 125 mm x 4.60 mm 5.00 μm HPLC columns at liquid phase (water and acetonitrile). Liquid phase diagram of HPLC for by-product measurements of OMI ww after sonication process was shown as following Table 4.9. Measurement methods of by-products of OMI ww with HPLC was given in Table 4.10.

Table 4.9 HPLC solvent conditions for by-products measurements of PCI ww and OMI ww after sonication process

Time (min)	**Liquid phase**	**Solvent conditions**
4	acetonitrile	40.00% acetonitrile
30	acetonitrile	100.00% acetonitrile
30.01	acetonitrile	95.00% acetonitrile
40	acetonitrile	60.00% acetonitrile
43	acetonitrile	40.00% acetonitrile
43	STOP	

Table 4.10 Measurement methods of by-products of OMI ww in raw ww after 60 and 120 min sonication time with HPLC

Parameters		**HPLC**
OMI ww after 60 min sonication time		Measurement method: Standard Methods 5520 B. Instruments: Shimadzu CLASS–VP V6.14 HPLC, Phenomenex Hyperclone 125 mm x 4.60 mm 5 µm HPLC column at liquid phase (water and acetonitrile).
Sonication Time (min)	**By-Product Names**	**Retention Time (min)**
60	2–phenyl–phenol	7.125
60	3–phenyl–phenol	8.033
Parameters		**HPLC**
OMI ww after 120 min sonication time		Measurement method: Standard Methods 5520 B. Instruments: Shimadzu CLASS–VP V6.14 HPLC, Phenomenex Hyperclone 125 mm x 4.60 mm 5 µm HPLC column at liquid phase (water and acetonitrile).
Sonication Time (min)	**By-Product Names**	**Retention Time (min)**
120	2–phenyl–phenol	7.425
120	3–phenyl–phenol	8.525

Table 4.11 summarizes the analytical parameters measured before and after sonication process in PCI ww, OMI ww and TI ww.

Table 4.11 Analytical parameters before and after sonication process for PCI ww, OMI ww and TI ww.

Parameters	**PCI ww**	**OMI ww**	**TI ww**
Total COD (mg/l)	+	+	+
Dissolved COD (mg/l)	+	+	+
Inert COD (mg/l)	+		
Slowly degradable COD (mg/l)	+		
Readly degradable COD (mg/l)	+		
Filtered COD (mg/l)	+		
Suspended COD (mg/l)	+		
Colloidal COD (mg/l)	+		
TOC (mg/l)	+	+	+
T (^oC)	+	+	+
BOD_5 (mg/l)	+	+	+
BOD_5/COD (mg/l)	+	+	+
TS (mg/l)	+	+	+
TSS (mg/l)	+	+	+
VS (mg/l)	+	+	+
TVS (mg/l)	+	+	+
Total-N (mg/l)	+	+	+
NO_3-N (mg/l)	+	+	+
NO_2-N (mg/l)	+	+	+
NH_4-N (mg/l)	+	+	+
Total-P (mg/l)	+	+	+
PO_4-P (mg/l)	+	+	+
SO_4 (mg/l)	+	+	+
pH	+	+	+
DO (mg/l)	+	+	+
Toxicity	+	+	+
ORP (mV)	+	+	+
Color (m^{-1})		+	+
Total aromatic amines (mg benzidine /l)		+	+
Total phenol (mg/l)		+	
Oil (mg/l)		+	
Total fatty acids (TFAs) (mg/l)		+	
PAHs naphthalene (NAP), acenaphthylene (ACL), acenaphthene (ACT), fluorene (FLN), phenantrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benz[b]fluoranthene (BbF), benz[k]fluoranthene (BkF), benz[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP)	+		

4.4 Properties of Chemicals used in the Analysis for PCI ww, OMI ww and TI ww

4.4.1 Standard Chemicals used for Sonication By-Products of PAHs

4.4.1.1 PAHs Calibration Standards

The PAHs calibration standard solution contained 16 PAHs, carbazole and five deuterated PAHs (naphthalene–d_8, acenaphthene–d_{10}, phenanthrene–d_{10}, chrysene–d_{12} and perylene–d_{12}) was taken from Merck ($\geq$ 99.90% purity, GC grade) for PAHs measurements at GC-MS instrument.

4.4.1.2 Sodium Sulfate Anhydrous (Na_2SO_4)

Sodium sulfate anhydrous (Na_2SO_4), [CAS number: 7757-82-6, HS code: 2833 11 00, EC number: 231-820-9, M_A: 142.04 g/mol, d: 2.70 g/cm^3 (at 20°C)], with a purity of 99.99% (Merck) was used for preparation the PAHs extraction from the samples before GC-MS analysis. 1.00–2.00 g Na_2SO_4 was added after 3.00 g silicic acid + 2.00 g alumina in a glass column before filtration process of the samples.

4.4.1.3 n–Hexane (C_6H_{14})

Hexane (C_6H_{14}), [CAS number: 110-54-3, HS code: 2901 10 00, EC number: 203-777-6, M_A: 86.18 g/mol, d: 0.66 g/cm^3 (at 20°C)], with a purity of 99.90% (for GC SupraSolv®, Product number: 1.04371.2500, Merck) was used for preparation the PAHs extraction of the samples before GC-MS analysis.

4.4.1.4 Acetone (C_3H_6O)

Acetone (C_3H_6O), [CAS number: 67-64-1, HS code: 2914 11 00, EC number: 200-662-2, M_A: 58.07 g/mol, d: 0.79 g/cm^3 (at 20°C)], with a purity of 99.80% (for GC SupraSolv®, Product number: 1.00012.2500, Merck) was used for preparation the PAHs extraction before GC-MS analysis.

4.4.1.5 Silicic Acid (H_2O_3Si)

Silicic acid (H_2O_3Si), [SILA–200–500 G; CAS number: 7699-41-4, Batch number: 018K0048, EC number: 231-716-3, MDL number: MFCD00054122, PubChem Substance ID: 24899865, M_A: 78.10 g/mol], (suitable for column chromatography, 60–200 mesh, Sigma-Aldrich) was used for preparation of the PAHs extraction before GC-MS Analysis. Silicic acid (H_2O_3Si) was dried at 103^oC etuv between 12 and 24 h before the PAHs analysis. After 3.00 g H_2O_3Si was put 40 ml dark brown color Amber I–cem vial (Catalog number: 98716) and was added 100 µl deionized H_2O. After Amber I–cem vial was shaked and was put in glass column for filtration process of the PAHs samples.

4.4.1.6 Aluminium Oxide 90 Active Neutral (Al_2O_3 or Alumina)

Aluminium oxide 90 active neutral (Al_2O_3 or alumina), [TA1575477 909, CAS number: 1344-28-1, HS code: 2818 20 00, EC number: 215-691-6, M_A: 101.96 g/mol, d: 3.94 g/cm^3 (at 20°C)], [(activity stage I) for column chromatography 0.063–0.200 mm (70–230 mesh ASTM), Product number: 1.01077.1000, Merck] was used for preparation of the PAHs extraction before GC-MS analysis. Al_2O_3 was covered aluminium folio and was dried at 450^oC etuv between 2 and 3 h before the PAH analysis. After 2.00 g Al_2O_3 was put 40 ml dark brown color Amber I–cem vial and was added 120 µl deionized H_2O. After Amber I–cem vial was shaked and was put in glass column for filtration process of the PAHs samples.

4.4.1.7 Dichloromethane (CH_2Cl_2)

Dichloromethane (CH_2Cl_2), [CAS number: 75-09-2, HS code: 2903 12 00, EC number: 200-838-9, M_A: 84.93 g/mol, d: 1.33 g/cm^3 (at 20°C)], with a purity of $\geq$ 99.80%, (for GC SupraSolv®, Product number: 1.06054.2500, Merck) was used for preparation of the PAHs extraction before GC-MS analysis.

4.4.1.8 Petroleum Ether (Petroleum Benzine)

Petroleum ether (petroleum benzine boiling range 40–60°C), [CAS number: 64742-49-0, HS code: 2710 11 25, EC number: 265-151-9, d: 0.645 – 0.665 g/cm^3 (at 15°C)], with a purity of $\geq$ 99.99%, (for GC SupraSolv®, Product number: 1.01772.2500, Merck) was applied for preparation of the PAHs extraction before GC–MS analysis.

4.4.1.9 Sodium Sulfate Anhydrous (Na_2SO_4)

Sodium sulfate anhydrous (Na_2SO_4), [CAS number: 7757-82-6, HS code: 2833 11 00, EC number: 231-820-9, M_A: 142.04 g/mol, d: 2.70 g/cm^3 (at 20°C)], with a purity of 99.99%, (Product number: 1.06649.1000, Merck) was used for preparation of the PAHs extraction before GC-MS analysis. 1.00–2.00 g Na_2SO_4 was added after 3.00 g silicic acid + 2.00 g alumina in glass column before PAHs sample filtration process.

4.4.1.10 Benzoic Acid (Carboxybenzene) ($C_7H_6O_2$)

Benzoic acid (carboxybenzene) ($C_7H_6O_2$), which is a by-product of the PAH sonication (1 analyte(s) at 100 μg/l in methanol) with a purity of $\geq$ 99.50%, [Cat number: SV-130-1, Lot number: CB-1920A, CAS number: 65-85-0, HS code: 291631, M_A: 122.13 g/mol, d: 1.321 g/cm^3], (1 ml, for laboratory use only, Ultra Scientific Analytical Solutions, Product number: 242381–25G, Sigma-Aldrich) was used as standard.

4.4.1.11 1,2,3–Thiadiazole–4–carboxylic Acid ($C_3H_2N_2O_2S$)

1,2,3–Thiadiazole–4–carboxylic acid ($C_3H_2N_2O_2S$), which is a by-product of the PAHs sonication with a purity of 97.00% [Producer Cat number: B20842/L20212, Lot number: 10128960, CAS number: 4100-13-4, Batch number: 10128960, Art number: 126765, M_A: 130.13 g/mol], (5.00 g, Chem S GmbH, Sigma-Aldrich) was used as standard.

4.4.1.12 1–Methylnaphthalene ($C_{11}H_{10}$)

1–Methylnaphthalene ($C_{11}H_{10}$), which is a by-product of the PAHs sonication with a purity of 99.50% [L 20895000L, Lot number: 90402AL, CAS number: 90-12-0, M_A: 142.20 g/mol], (10.00 ml, HPLC/DAD reprosil 100 C18 5.00 µm 250x3, for laboratory use only, Dr. Ehrenstorfer GmbH, Sigma-Aldrich) was used as standard.

4.4.1.13 9–Hydroxyfluorene ($C_{13}H_{10}O$)

9–Hydroxyfluorene ($C_{13}H_{10}O$), which is a by-product of the PAHs sonication with a purity of 96.00%, [Cat number: H3,120-4, CAS number: 1689-64-1, Lot number: S72094-508, EC number: 216-879-0, M_A: 182.22 g/mol], (5.00 g, Sigma-Aldrich) was used as standard.

4.4.1.14 9–10–Phenanthrenequinone ($C_{14}H_8O_2$)

9–10–Phenanthrenequinone ($C_{14}H_8O_2$), which is a by-product of the PAHs sonication with a purity of $\geq$ 99.00%, [CAS number: 84-11-7, HS code: 2914 69 90, EC number: 201-515-5, M_A: 208.21 g/mol], (5.00 g, for synthesis, Merck) was used as standard.

4.4.1.15 4–Hydroxybenzoic Acid ($C_7H_6O_3$)

4–Hydroxybenzoic acid ($C_7H_6O_3$), which is a by-product of the PAHs sonication with a purity of $\geq$ 99.00%, [EC number: 202-804-9, Cat number: 24,014-1, CAS number: 99-96-7, Lot number: S79620-010, M_A: 138.12 g/mol], (50.00 g, Sigma-Aldrich) was used as standard.

4.4.1.16 1,4–Dioxane ($C_4H_8O_2$)

1,4–Dioxane ($C_4H_8O_2$), which is a by-product of the PAHs sonication with a purity of $\geq$ 99.50%, [HS code: 2932 99 00, EC number: 204-661-8, M_A:88.11 g/mol, d: 1.030-1.035 g/cm^3, EC Index number: 603-024-00-5, CAS number: 123-91-1], (glass bottle 250 ml, for analysis ENSURE ACS, ISO, Product number: 1096710250, Aldrich) was used as standard.

4.4.1.17 9,H–Fluorene–9,9–dimethanol ($C_{15}H_{14}O_2$)

9,H–Fluorene–9,9–dimethanol ($C_{15}H_{14}O_2$) (or fluorine-2-boronic acid), which is a by-product of the PAHs sonication with a purity of 98.00%, [CAS number: 4425-93-8, M_A: 226.27 g/mol, MDL number: MFCDO1321348, PubChem Substance ID: 24871428], (5.00 g, Product number: 477923-5G, Aldrich) was used as standard.

4.4.1.18 Dihydroxy Pyrene ($C_{10}H_{12}O_2$)

Dihydroxy pyrene ($C_{10}H_{12}O_2$) (or 2'hydroxy–5'–methylpropiophenone), which is a by-product of the PAHs sonication with a purity of 95.00%, [CAS number: 938-45-4, M_A: 164.20 g/mol, d: 1.070 g/ml, EC number: 213-342-2, MDL number: MFCDO1098830, PubChem Substance ID: 24884652], (10.00 g, Product number: 663719-10G, Aldrich) was used as standard.

4.4.1.19 Methyl–phenanthrene ($C_{17}H_{16}$)

Methyl–phenanthrene ($C_{17}H_{16}$) (or 9–Ethyl–10 methyl–phenanthrene), which is a by-product of the PAHs sonication [CAS number:17024-02-1, M_A: 220.317 g/mol], (50.00 mg, rare chemical library, Product number: S16637-1EA, Aldrich) was used as standard.

4.4.1.20 2–Ethyl–phenanthrene ($C_{16}H_{14}$)

2–Ethyl–phenanthrene ($C_{16}H_{14}$), which is a by-product of the PAHs sonication with a purity of 95.00%, [CAS number: 3674-74-6, M_A: 206.29 g/mol], (50.00 mg, rare chemical library, Product number: S301051-1EA, Aldrich) was used as standard.

4.4.2 Standard Chemicals used in the OMI ww and TI ww

4.4.2.1 Benzidine ($C_{16}H_{20}N_2$)

Benzidine ($C_{16}H_{20}N_2$), which is a standard chemical of OMI ww and TI ww sonications with a purity of ≥ 99.00%, [CAS number: 54827-17-7, HS code: 2921 59 90, EC number: 259-364-6, M_A: 240.34 g/mol], (GR for analysis, Product number: 1.08622.0001, Merck) was used as standard.

4.4.2.2 Absolute Ethanol (C_2H_5OH)

Absolute ethanol (C_2H_5OH), which is a standard chemical of OMI ww and TI ww sonications with a purity of ≥ 99.90%, [CAS number: 64-17-5, HS code: 2207 10 00, EC number: 200-578-6, M_A: 46.07 g/mol, d: 0.790 – 0.793 g/cm^3 (at 20°C)], (absolute for analysis EMSURE® ACS, ISO, Reag. Ph Eur grade, Product number: 1.00983.1000, Merck) was used as standard.

4.4.2.3 Citric Acid Anhydrous ($C_6H_8O_7$)

Citric acid anhydrous ($C_6H_8O_7$), which is a standard chemical of OMI ww and TI ww sonications with a purity of ≥ 99.50%, [CAS number: 77-92-9, HS code: 2918 14 00, EC number: 201-069-1, M_A: 192.12 g/mol, d: 1.665 g/cm^3 (at 18°C)], (anhydrous powder, suitable for use as excipient EMPROVE® exp Ph Eur, BP, JP, USP, E 330, FCC grade, Product number: 1.002415.000, Merck) was applied as standard.

4.4.2.4 Sodium Hydroxide (NaOH)

Sodium hydroxide (NaOH), which is a standard chemical of OMI ww and TI ww sonications with a purity of ≥ 98.00%, [CAS number: 1310-73-2, HS code: 2815 11 00, EC number: 215-185-5, M_A: 40.00 g/mol, d: 2.13 g/cm^3 (at 20°C)], (5 kg, plastic bottle, powder, suitable for use as excipient EMPROVE® exp Ph Eur, BP, FCC, JP, NF, E 524 grade, Product number: 1.06482.5000, Merck) was used as standard.

4.4.2.5 Hydrochloric Acid (HCl)

Hydrochloric acid (HCl) fuming 37.00%, which is a standard chemical of OMI ww and TI ww sonications with a purity of 37.00–38.00%, [Change/Lot: K34366314 510, HS code: 2806 10 00, d: 1.19 g/cm^3 (at 20°C)], (suitable for use as excipient EMPROVE® exp Ph Eur, BP, JP, NF grade, Product number: 1.00314.2500, Merck) was applied as standard.

4.4.2.6 p–Dimethileaminobenzaldehid ($C_9H_{11}NO$)

p–Dimethileaminobenzaldehid ($C_9H_{11}NO$), which is a standard chemical of OMI ww and TI ww sonications with a purity of $\geq$ 99.00%, [HS code: 2922 39 00, EC number: 202-819-0, CAS number: 100-10-7, M_A: 149.19 g/mol, d: 0.35 g/cm^3 (at 20°C)], (GR for analysis Reag. Ph Eur grade, Product number: 1.03058.1000, Merck) was applied as standard.

4.4.3 Standard Chemicals used for Sonication by-Products of OMI ww

4.4.3.1 2–Phenyl–phenol ($C_{12}H_{10}O$)

2–Phenyl–phenol ($C_{12}H_{10}O$), which is a by-product of OMI ww sonication with a purity of 95.00%, [Cat number: 606286, MDL number: MFCD01075578, M_A: 176.16 g/mol], (5.00 g, Aldrich) was used as standard.

4.4.3.2 3-Phenyl-phenol ($C_{12}H_{10}O$)

3-Phenyl-phenol ($C_{12}H_{10}O$), which is a by-product of OMI ww sonication with a purity of 85.00%, [Cat number: 26,225-0, CAS number: 580-51-8, Lot number: 08104PD040, M_A: 128.17 g/mol], (5.00 g, Aldrich) was used as standard.

4.4.4 Chemical Properties of Additives used through Sonication Process

4.4.4.1 Nitrogen Gas, $N_2(g)$

Pure $N_2(g)$ tube, gas amount=10.50 m^3 (at 15^{o}C), gas pressure=230 atm (at 15^{o}C), with a purity of 99.99% (Linde) was used to maintain $N_2(g)$ in PCI ww, OMI ww and TI ww before sonication experiments.

4.4.4.2 Air

Air pump, a velocity of around 150 ml/min, max capacity: 26,40 l, power: 108 W, pressure: 0.5 atm, minimum water depth: 3.5 cm, width: 23.5 cm, length: 26 cm, one outlet and 14 port diffuser, Item number: 206371, (Aquarium) was used to maintain air in PCI ww, OMI ww and TI ww before sonication experiments.

4.4.4.3 Oxygen Gas, $O_2(g)$

Pure $O_2(g)$ tube, gas amount=12.05 m^3 (at 15^{o}C), gas pressure=230 atm (at 15^{o}C), with a purity 99.99%, (Linde) was used to maintain $O_2(g)$ in PCI ww, OMI ww and TI ww before sonication experiments.

4.4.4.4 Hydrogen Peroxide (H_2O_2)

Hydrogen peroxide (H_2O_2), which is a chemical of PCI ww, OMI ww and TI ww sonication, with a purity of ≥ 30.00%, [HS code: 2847 00 00, M_A: 34.00 g/mol, d: 1.11 g/cm^3 (at 20°C)], (Perhydrol® for analysis EMSURE® ISO, Product number: 1.07209.1000, Merck) was used as a chemical in PCI ww, OMI ww and TI ww.

4.4.4.5 Titanium Dioxide (TiO_2)

Titanium (IV) oxide (TiO_2), which is a chemical of PCI ww, OMI ww and TI ww sonication, with a purity of ≥ 99.00%, [CAS number: 13463-67-7, HS code: 2823 00 00, EC number: 236-675-5, M_A: 79.87 g/mol, d: 4.20 g/cm^3 (at 20°C)], (for analysis

Reag. Ph Eur, Product number: 1.00808.1000, Merck) was used as a chemical in PCI ww, OMI ww and TI ww.

4.4.4.6 Sodium Chloride (NaCl)

Sodium chloride (NaCl), which is a chemical of PCI ww, OMI ww and TI ww sonication, with a purity of 99.50–100.50%, [CAS number: 7647-14-5, HS code: 2501 00 99, EC number: 231-598-3, M_A: 58.44 g/mol, d: 2.17 g/cm^3 (at 20°C)], (5000 g, suitable for use as excipient EMPROVE® exp Ph Eur,BP,USP, Product number: 1.06400.5000, Merck) was added as a chemical in PCI ww, OMI ww and TI ww.

4.4.4.7 Iron (II) Sulfate Heptahydrate ($FeSO_4.7H_2O$)

Iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$), which is a chemical of PCI ww, OMI ww and TI ww sonication, with a purity of > 99.00%, [CAS number: 7782-63-0, HS code: 2833 29 80, EC number: 231-753-5, M_A: 278.02 g/mol, d: 1.89 g/cm^3 (at 20°C)], (for analysis EMSURE® ACS, ISO, Reag. Ph Eur, Product number: 1.03965.1000, Merck) was used as a chemical in PCI ww, OMI ww and TI ww.

4.4.4.8 Iron (III) Chloride Hexahydrate ($FeCl_3.6H_2O$)

Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), which is a chemical of PCI ww, OMI ww and TI ww sonication, with a purity of > 99.00%, [CAS number: 10025-77-1, HS code: 2827 39 20, EC number: 231-729-4, M_A: 270.33 g/mol], (for analysis EMSURE® ACS, Reag. Ph Eur, Product number: 1.03943.1000, Merck) was used as a chemical in PCI ww, OMI ww and TI ww.

4.4.4.9 Sodium Bicarbonate ($NaHCO_3$)

Sodium bicarbonate ($NaHCO_3$), which is a chemical of PCI ww, OMI ww and TI ww sonication, with a purity of > 99.90%, [CAS number: 144-55-8, HS code: 2836 30 00, EC number: 205-633-8, M_A: 84.01 g/mol, d: 2.22 g/cm^3 (at 20°C)], (ACS, Reag, Ph Eur grade, Product number: 1.06329.1000, Merck) was used as a chemical in PCI ww, OMI ww and TI ww.

4.4.4.10 Butanol (C_4H_9OH)

Butanol (C_4H_9OH), which is a chemical of PCI ww, OMI ww and TI ww sonication, with a purity of ≥ 99.50%, [CAS number: 71-36-3, HS code: 2905 13 00, EC number: 200-751-6, M_A: 74.12 g/mol, d: 0.81 g/cm^3 (at 20°C)], (for analysis EMSURE® ACS, ISO, Reag. Ph Eur grade, Product number: 1.01990.2500, Merck) was added as a chemical in PCI ww, OMI ww and TI ww.

4.4.4.11 Sulfuric Acid (H_2SO_4)

Sulfuric acid (H_2SO_4), which is a chemical of PCI ww, OMI ww and TI ww sonication, with a purity of 95.00–98.00%, [CAS number: 7664-93-9, HS code: 2807 00 10, EC number: 231-639-5, M_A: 98.08 g/mol, d: 1.84 g/cm^3 (at 20°C)], (suitable for use as excipient EMPROVE® exp Ph Eur, BP, NF, Ph Franç grade, Product number: 1.00713.2500, Merck) was applied as a chemical in PCI ww, OMI ww and TI ww.

4.4.4.12 Sodium Hydroxide (NaOH)

Sodium hydroxide (NaOH), which is a chemical of PCI ww, OMI ww and TI ww sonication, with a purity of ≥ 99.00%, [CAS number: 1310-73-2, HS code: 2815 11 00, EC number: 215-185-5, EC index number: 011-002-00-6, M_A: 40.00 g/mol, d: 2.13 g/cm^3 (at 20°C)], (5.00 kg plastic bottle, pellets for analysis EMSURE® ISO grade, Product number: 1.06498.5000, Merck) was applied as a chemical in PCI ww, OMI ww and TI ww.

4.4.5 Determination of Acute Toxicity

4.4.5.1 Microtox Acute Toxicity Assay

Toxicity to the bioluminescent organism *Vibrio fischeri* was assayed using the Microtox measuring system according to DIN 38412 L34, L341, (1993). Microtox testing was performed according to the standard procedure recommended by the manufacturer (Lange, 1994). A specific strain of the marine bacterium, *Photobacterium phosphoreum* Microtox LCK 491 Kit (Dr. LANGE industrial measurement technique in Germany, 2010) were used for Microtox acute toxicity assay. DRLANGE LUMIXmini type luminometer (Dr. LANGE Company, 1996) was used for the microtox toxicity assay. Reductions in light intensity at 0., 5th, 15th and 30th min are chosen to measure the toxicity (EPS, 1992; Lange, 1994). All samples were serially diluted in 2.00% NaCI (w/v) and each assay was performed at pH=7.0 and a temperature of 15°C. NaCl (2.00%) was used as the control. Samples containing bacterial luminescence were measured for 0 min, 5 min, 15 and 30 min incubation times in a luminometer, respectively. Inhibition percentage (I %) values refer to decreasing activity in samples causing inhibitory effect of a test substances and/or a toxic wastewater during the light emission. Color correction was performed according to the DIN 38412 Instructions. The decrease in bioluminescence was indicated the toxic effect of the samples. Toxicity evaluation criteria for luminescent bacteria explained with the percent inhibition effect (H %). The decrease of bacterial luminescence due to the addition of toxic substances was calculated as follows in Eqs. (4.13), (4.14) and (4.15):

$$f_k = \frac{I_t}{I_0} \tag{4.13}$$

where;

f_k: Temporary correction factor determined from the control measurements.

I_0: Initial values of luminescence of control and test sample (0.50 ml bacterial suspension),

I_t: Values measured 0. 5th, 15th and 30th min after 0.5 ml of control or test sample was aded to 0.50 ml of bacterial suspension.

$$I_{ct} = \frac{avg\ f_k}{I_0} \tag{4.14}$$

where;

I_{ct}: I_0 value adjusted by the correction factor,

avg f_k: The average values of f_k.

$$\%\ Inhibition = \left[\frac{(I_{ct} - I_t)}{I_{ct}}\right] * 100 \tag{4.15}$$

Toxicity evaluation criteria for luminescent bacteria are presented in Table 4.12. If the percent inhibitory effect (H %) change between 0.00% and 5.00%, the effect is non-toxic. When H % is between 5.00% and 20.00%, the effect is possibly toxic, and when H % is between 20.00% and 90.00 the effect is toxic (Lange, 1994).

Table 4.12 Effect of the samples on the inhibition of luminescent bacteria (Lange, 1994).

Percent Inhibitory Effect (H %)	**Effect**
0% < H % < 5.00%	Non toxic
5.00% < H % < 20.00%	Moderate toxic
20.00% < H % < 90.00%	Toxic

4.4.5.2 Daphnia magna Acute Toxicity Test

Toxicity to test using 24 h born *Daphnia magna* as described in Standard Methods (2005). After preparing the test solution, experiments to carry out using 5 or 10 *Daphnids* introduced into the test vessel. These vessels to control with 100 ml of effective volume at 7.0-8.0 pH, providing a minimum DO concentration of 6.00 mg/l at an ambient temperature of 20-25°C. Young *Daphnia magna* to use in the test (in first start ≤ 24 h old). A 24 h exposure is generally accepted for a *Daphnia* acute toxicity test. Results to express as mortality percentage of the *Daphnids*. The immobile animals which do not able to move, to determine as dead *Daphnids*.

The results of *Daphnia magna* acute toxicity test was determined EC (mg/l) as following Eq. (4.16):

$$EC_{50} = D_L * \left[COD\ or\ PAH \right] \tag{4.16}$$

where;

EC_{50}: The effective concentration at 50.00% of inhibiton ratio (mg/l or ng/ml),

D_L: Inhibition ratio,

[COD or PAH]: The COD or PAH concentrations of sonicated sample (mg/l or ng/ml).

4.5 Reaction Kinetics

4.5.1 Pseudo Zero Order Reaction Kinetic

A pseudo zero-order reaction has a rate which is independent of the concentration of the reactant(s) (Capellos & Bielski, 1972). Increasing the concentration of the reacting species will not speed up the rate of the reaction. Pseudo zero-order reactions are typically found when a material that is required for the reaction to procede, such as a surface or a catalyst, is saturated by the reactants (Capellos & Bielski, 1972). The rate law for a pseudo zero-order reaction is as following Eq. (4.17):

$$r = k \tag{4.17}$$

where;

r: The reaction rate, and

k: The reaction rate coefficient with units of concentration/time.

If, and only if, this pseudo zero-order reaction 1) occurs in a closed system, 2) there is no net build-up of intermediates, and 3) there are no other reactions occurring, it can be shown by solving a mass balance for the system that Eq. (4.18):

$$r = -\frac{d[PAH]}{dt} = k \tag{4.18}$$

If this differential equation is integrated it gives an equation which is often called the integrated pseudo zero-order rate law, Eq. (4.19):

$$[PAH]_t = -k\,t + [PAH]_0 \tag{4.19}$$

where;

$[PAH]_t$: The concentration of PAH at a particular time, and

$[PAH]_0$: The initial concentration of PAH.

A reaction is zero order if concentration data are plotted versus time and the result is a straight line. The slope of this resulting line is the negative of the pseudo zero order rate constant (k). The half-life of a reaction describes the time needed for half of the reactant to be depleted (same as the half-life involved in nuclear decay, which is a first-order reaction). For a pseudo zero-order reaction the half-life is given by Eq. (4.20):

$$t_{\frac{1}{2}} = \frac{[PAH]_0}{2k} \tag{4.20}$$

4.5.2 Pseudo First Order Reaction Kinetic

A pseudo first-order reaction depends on the concentration of only one reactant (a unimolecular reaction) (Capellos & Bielski, 1972). Other reactants can be present, but each will be pseudo zero-order. The rate law for an elementary reaction that is pseudo first order with respect to PAH is Eq. (4.21):

$$r = -\frac{d[PAH]}{dt} = k\,[PAH] \tag{4.21}$$

where;

k: The pseudo first order rate constant, which has units of 1/time.

The integrated pseudo first-order rate law is Eq. (4.22):

$$\ln[PAH] = -kt + \ln[PAH]_0 \tag{4.22}$$

A plot of ln[PAH] vs. time *t* gives a straight line with a slope of – *k*. The half life of a pseudo first-order reaction is independent of the starting concentration and is given by Eq. (4.23):

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k} \tag{4.23}$$

4.5.3 Pseudo Second Order Reaction Kinetic

A pseudo second-order reaction depends on the concentrations of one second-order reactant, or two pseudo first-order reactants (Capellos & Bielski, 1972). For a pseudo second order reaction, its reaction rate is given by Eq. (4.24):

$$r = k\,[PAH]_0^{\,2} \quad or \quad r = k\,[PAH][PAH] \quad or \quad r = k\,[PAH]_t^{\,2} \tag{4.24}$$

The integrated pseudo second-order rate laws are respectively Eq. (4.25):

$$\frac{1}{[PAH]_t} = \frac{1}{[PAH]_0} + 2kt \tag{4.25}$$

The stoichiometric factor of 2 should not be included as a part of the rate constant for an elementary reaction of the type $2[PAH_1] \rightarrow [PAH_2]$. The proper definition of the rate law for pseudo second-order reactions is Eq. (4.26):

$$-\frac{d[PAH]}{dt} = 2k\,[PAH]^2 \tag{4.26}$$

This proper definition is used in most peer-reviewed literature, tables of rate constants, and simulation software (Capellos & Bielski, 1972) Eq. (4.27):

$$\frac{[PAH_1]_0}{[PAH_2]_0} = e^{([PAH_1]_0 - [PAH_2]_0)\,kt} \tag{4.27}$$

$[PAH_1]_0$ and $[PAH_2]_0$ must be different to obtain that integrated equation. The half-life equation for a pseudo second-order reaction dependent on one pseudo second-order reactant is Eq. (4.28):

$$t_{\frac{1}{2}} = \frac{1}{2\,k\,[PAH]_0} \tag{4.28}$$

For a pseudo second-order reaction half-lives progressively double. Another way to present the above rate laws is to take the log of both sides, Eq. (4.29):

$$\ln r = \ln k \quad + \quad 2 \ln \left[PAH\right] \tag{4.29}$$

4.6 Calculation of $[OH^{\bullet}]_{ss}$ Concentrations

If we assume that $OH^{\bullet}$ is the main species leading to sonodegradation of PAHs, the oxidation rate $V_{PAH\,/\,OH^{\bullet}}$ can be calculated using Eq. (4.30):

$$V_{PAH\,/\,OH^{\bullet}} = -\left(\frac{d[PAH]}{dt}\right)_{OH^{\bullet}} = k_{PAH\,/\,OH^{\bullet}}.\left[PAH\right]\left[OH^{\bullet}\right]_{ss} \tag{4.30}$$

where;

$V_{PAH\,/\,OH^{\bullet}}$: The oxidation rate of PAHs,

$k_{PAH\,/\,OH^{\bullet}}$: The pseudo second order reaction kinetic rate constant,

$[OH^{\bullet}]_{ss}$: The steady-state $OH^{\bullet}$ concentrations in PCI ww under ultrasound and

[PAH]: The PAH concentration.

The experimental rate of PAH sonodegradation $V_{PAH\,/\,US}$ is given with the Eq. (4.31):

$$V_{PAH\,/\,US} = \left(\frac{d[PAH]}{dt}\right)_{US} = k_{pf}\left[PAH\right] \tag{4.31}$$

where;

$V_{PAH\,/\,US}$: The experimental rate of PAH sonodegradation.

Therefore, Eq. (4.32):

$$k_{pf} = k_{PAH/OH^\bullet} \cdot \left[OH^\bullet\right]_{ss} \tag{4.32}$$

where;

k_{pf} : The experimental pseudo first order reaction kinetic rate constant.

It is assumed that the sonication process is 100% controlled by oxidation of PAHs with [$OH^\bullet$] at a frequency of 35 kHz. $[OH^\bullet]_{ss}$ are the calculated steady-state concentrations of $OH^\bullet$ in PCI ww during sonication of seventeen PAHs.

4.7 Statistical Analysis

Differences insensitivity scores between microorganisms were determined by a parametric t-test. The statistical package used for the analysis was SPSSWIN for Windows. The multiple regression analysis between *y* (dependent) and *x* (independent) variables was carried out using SPSSWIN for Windows Excel data analysis. The linear correlation was assessed with regression coefficient (R^2). The ANOVA (analysis of variance) test was performed in order to determine the statistical significance between *x* and *y* variables (Zar, 1984).

Analysis of variance (ANOVA) between experimental data was performed to detect the *F* and *p* values. In other words, the ANOVA test was used to test the differences between dependent and independent groups (Zar, 1984). The comparison between the actual variation of the experimental data averages and standard deviation was expressed in terms of *F* ratio. *F* was equal to “found variation of the data averages/expected variation of the data averages.” *p* reported the significance level. The linear correlations between the physicochemical properties of PCI ww, OMI ww and TI ww the acute toxicities of *Daphnia magna* and *Photobacterium phosphoreum* were determined with ANOVA tests. All results are reported at significance levels of p=0.01 and p=0.001. Regression analysis was applied to the experimental data in order to determine the regression coefficient (R^2) (STATGRAPHICS Centurion XV, software, 2005).

CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 Effect of Sonication Frequency on the PAHs and COD_{dis} Removals

Three different sonication frequencies (25 kHz, 35 and 132 kHz) was researched under ambient conditions (25°C), at constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication frequency for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww. Among the frequencies used in the sonication process (25 kHz, 35 and 132 kHz) it was found that a sonication frequency of 35 kHz is the optimum frequency for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww (Table 5.1).

Table 5.1 Effect of sonication frequency on the PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww at ambient conditions (25°C) (sonication power=640 W, sonication times=60 min, 120 and 150 min, initial total PAHs concentration in PCI ww=1378.77 ng/ml, initial COD_{dis} concentration in OMI ww=109444 mg/l, initial COD_{dis} concentration in TI ww=962.99 mg/l, n=3, mean values).

Sonication Frequency (kHz)	**PAHs Removal Efficiencies in PCI ww (%)**			**COD_{dis} Removal Efficiencies in OMI ww (%)**			**COD_{dis} Removal Efficiencies in TI ww (%)**		
	After			**After**			**After**		
	60 min	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**
25	43.09	52.21	75.87	10.67	39.56	56.43	26.40	45.39	69.11
35	**56.05**	**62.30**	**80.16**	**12.58**	**41.74**	**60.91**	**30.43**	**53.69**	**74.27**
132	51.42	57.66	78.64	11.10	40.34	59.85	28.31	51.56	73.07

Increasing the sonication frequency did not increase the number of free radicals, therefore a low number of free radicals did not escape from the bubbles and did not migrate (David, 2009). Explanation of such phenomenon is not yet fully understood, since a more energetic implosion of cavitation bubbles is expected to occur at low frequency rather than at high frequency because of a larger bubbles radius observed at low frequency (De Visscher et al., 1996; Dewulf et al., 2001). According to Minnaert (1933), the size of bubbles formed in water, under one atmosphere, is inversely proportional to the frequency of the wave (Burdin et al., 1999; Cum et al., 1992). However, the larger the bubble size, the greater the water vapour within the bubble, leading to a more important damping of the collapse at low frequency like 20–40 kHz (David, 2009). This damping induces a decreases in the temperature and pressure within the cavitation bubble at low frequency compared to a medium frequency (Burdin et al., 1999).

5.2 Effect of Sonication Power on the PAHs and COD_{dis} Removals

120–350–640 and 3000 W different sonication powers was researched under ambient conditions (25°C), at constant sonication frequency (35 kHz) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication power for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww. Among the powers used in the sonication process (120–350–640 and 3000 W) it was found that a sonication power (640 W) is the optimum power for maximum PAH and COD_{dis} removals in all three wastewaters (Table 5.2).

Table 5.2 Effect of sonication power on the PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww at ambient conditions (25°C) (sonication frequency=35 kHz, sonication time=60 min, 120 and 150 min, initial total PAHs concentration in PCI ww=1378.77 ng/ml, initial COD_{dis} concentration in OMI ww=109444 mg/l, initial COD_{dis} concentration in TI ww=962.99 mg/l, n=3, mean values).

Sonication Power (W)	**PAHs Rem. Eff. in PCI ww (%)**			**COD_{dis} Rem. Eff. in OMI ww (%)**			**COD_{dis} Rem. Eff. in TI ww (%)**		
	After			**After**			**After**		
	60 min	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**
120	8.04	12.17	25.24	9.41	18.32	24.54	9.14	15.30	22.47
350	26.12	30.09	45.67	10.04	29.85	47.76	17.66	29.08	40.54
640	**56.05**	**62.30**	**80.16**	**12.58**	**41.74**	**60.91**	**30.43**	**53.69**	**74.27**
3000	53.35	60.00	78.90	11.56	40.91	58.49	28.75	52.71	73.43

In general, when ultrasonic irradiation is used, the degradation ratio gradually becomes higher when the output power of the ultrasound is increased from 120 W to 640 W. The sono-degradation of pollutants increased with increasing applied power. As the power increased, the number of collapsing cavities also increased, thus leading to enhanced degradation rates, as reported by Busetti et al. (2006), Papadaki et al. (2004) and Psillakis et al. (2003, 2004). The vibration of sound in the cavitation area was increased with increasing applied power. More cavitation bubbles were produced during increasing applied power. However, the lifetime of this cavitation bubbles are shorter than the lifetime of cavitation bubbles at increasing power compared to a medium power. Thus resulting in low $OH^{\bullet}$ production and COD and PAH removals.

5.3 Effect of Sonication Time on the PAHs and COD_{dis} Removals

5–10–15–20–25–30–35–40–45–50–55–60–120 and 150 min sonication times was researched under ambient conditions (25°C), at constant sonication frequency (35 kHz) and constant sonication power (640 W) to determine the optimum sonication time for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww.

Among the sonication times used in the sonication process (0–60–120 and 150 min) it was found that 150 min sonication time is the optimum sonication time for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww (Table 5.3).

Table 5.3 Effect of sonication time on the PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww at ambient conditions (25°C) (sonication frequency=35 kHz, sonication power=640 W, initial total PAHs concentration in PCI ww=1378.77 ng/ml, initial COD_{dis} concentration in OMI ww=109444 mg/l, initial COD_{dis} concentration in TI ww=962.99 mg/l, n=3, mean values).

Sonication Time (min)	**PAHs Rem. Eff. in PCI ww (%)**	**COD_{dis} Rem. Eff. in OMI ww (%)**	**COD_{dis} Rem. Eff. in TI ww (%)**
0	0.00	0.00	0.00
5	9.12	2.17	2.32
10	19.25	3.75	4.07
15	21.28	4.33	6.80
20	27.39	4.79	8.44
25	30.11	5.01	9.67
30	33.78	5.54	10.29
35	35.46	6.25	13.65
40	37.80	7.01	17.15
45	38.17	8.66	20.81
50	46.43	9.73	24.33
55	49.50	11.08	28.01
60	56.05	12.58	30.43
120	62.30	41.74	53.69
150	**80.16**	**60.91**	**74.27**

Higher sonication times are needed for complete mineralization. Short sonication times did not provide high degradation yields for refractory PAHs since they were not exposed for a long enough time to ultrasonic irradiation. Moreover, the choice of solvent affected the degradation of PAHs under sonication which ultimately is expected to alter the effectiveness of ultrasonic extractions at long sonication times. The cavities are more readily formed when using solvents with low viscosity and low surface tension during long sonication times (Chakinala et al., 2008a, 2008b). Among the solvents used acetone and hexane have the highest surface tension and viscosity. The preliminary studies showed that solvents with high surface tension and viscosity generally have a higher threshold for cavitation resulting in fewer cavitation bubbles but more harsh conditions once cavitation is established resulting in higher temperatures and pressures upon bubble collapse (Rokhina et al., 2009). Higher vapor pressure leads to more solvent volatilizing into cavitation bubbles which are able to be dissociated by high temperature after 150 min sonication. Hexane and acetone have the highest vapor pressure among solvents. Thus, more hexane molecules migrate into cavitation bubbles leading to more molecules dissociating to generate radicals.

5.4 Effect of Sonication Volume on the PAHs and COD_{dis} Removals

25–50–100–150–250–500 and 1000 ml different sonication volumes was researched under ambient conditions (25^{o}C), at constant sonication frequency (35 kHz), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication volume for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww. Among the sonication volumes used in the sonication process (25–50–100–150–250–500 and 1000 ml) it was found that the PAH and COD_{dis} yields are close to each other in volumes of 50–100–150–250–500 and 1000 ml. However, the optimum sonication volume for maximum PAH and COD_{dis} removals in PCI ww, OMI ww and TI ww was recorded as 500 ml. A significant correlation between yields and sonication volumes was obtained (ANOVA, F=12.67, F=14.88, F=15.78, R^2=0.83, R^2=0.84, R^2=0.84, p=0.05 for PCI ww, OMI ww and TI ww) (Table 5.4).

Table 5.4 Effect of sonication volume on the PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww at ambient conditions (25°C) (sonication frequency=35 kHz, sonication power=640 W, sonication time=60 min, 120 and 150 min, initial total PAHs concentration in PCI ww=1378.77 ng/ml, initial COD_{dis} concentration in OMI ww=109444 mg/l, initial COD_{dis} concentration in TI ww=962.99 mg/l, n=3, mean values).

Sonication Volume (ml)	**PAHs Rem. Eff. in PCI ww (%)**			**COD_{dis} Rem. Eff. in OMI ww (%)**			**COD_{dis} Rem. Eff. in TI ww (%)**		
	After			**After**			**After**		
	60 min	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**
25	50.48	55.25	79.39	8.28	38.14	55.46	24.26	49.38	73.82
50	51.30	56.03	79.56	9.39	39.22	56.41	25.10	50.61	73.64
100	52.45	58.55	78.32	10.60	40.69	57.83	27.54	51.49	74.57
150	53.77	59.76	78.93	11.32	41.53	59.88	28.33	52.48	74.46
250	54.62	60.20	79.31	12.47	42.50	60.25	29.27	53.14	73.93
500	**56.05**	**62.30**	**80.16**	**12.58**	**41.74**	**60.91**	**30.43**	**53.69**	**74.27**
1000	52.24	59.18	78.10	10.51	40.21	58.33	28.48	53.50	72.36

In this study, even if the difference between the seven volumes is very big, there is a slight decrease of sono-degradation yields of PAHs and COD_{dis} yields in PCI ww, OMI ww and TI ww samples, respectively, at high volumes. The main reason for this effect may be the homogeneous agitation given both by magnetic stirring and the sonication waves. Under these conditions, the wastewater move homogenous to the most active sonication zone. Some studies showed that when the volume gets larger, the solution cannot be mixed as effectively as in a smaller volume and the wastewater cannot move to the most active sonication zone:

David (2009) mentioned that the volume of the solution should be kept as small as possible, depending on the affective volume of sonicator in order to keep the solution in homogeneous turbulence throughout sonication. Kidak et al. (2009) determined that when the volume gets larger, the solution cannot be mixed as effectively as in a smaller volume and sonication yields dereased. In our study, the maximum PAHs and COD_{dis} removal efficiencies were observed at 500 ml sonication volume. PAH sand COD_{dis} removal efficiencies were not significantly varied between 25 and 500 ml sonication volumes. Significant correlations between PAHs, COD_{dis} yields and sonication volumes was not observed (R^2=0.48, R^2=0.43, R^2=0.37, F=3.45, F=2.78, F=3.78, p=0.05 for PCI ww, OMI ww and TI ww, respectively). Therefore, the sono-degradation rates of pollutants were accelerated with active reactive radicals ($O^\bullet$, $OH^\bullet$, $OOH^\bullet$…etc.) in cavitation solution at long (150 min) sonication times.

5.5 Effect of Sonication Temperature on the PAHs and COD_{dis} Removals

25°C, 30 and 60°C sonication temperatures was researched at constant sonication frequency (35 kHz), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 to 150 min) to determine the optimum sonication temperatures for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww. Among the sonication temperatures used in the sonication process (25°C, 30 and 60°C) it was found that 30°C and 60°C sonication temperatures are the optimum sonication temperatures for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww (Table 5.5).

Table 5.5 Effect of sonication temperature on the PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww (sonication frequency=35 kHz, sonication power=640 W, sonication time= 60 min, 120 and 150 min, initial total PAHs concentration in PCI ww=1378.77 ng/ml, initial COD_{dis} concentration in OMI ww=109444 mg/l, initial COD_{dis} concentration in TI ww=962.99 mg/l, n=3, mean values).

Sonication Temperature (°C)	**PAHs Rem. Eff. in PCI ww (%)**			**COD_{dis} Rem. Eff. in OMI ww (%)**			**COD_{dis} Rem. Eff. in TI ww (%)**		
	After			**After**			**After**		
	60 min	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**
25	56.05	62.30	80.16	12.58	41.74	60.91	30.43	53.69	74.27
30	44.05	61.22	89.94	15.47	42.29	62.57	42.39	67.34	81.53
60	46.50	67.37	92.48	17.77	46.81	66.83	48.08	64.48	84.92

Increased temperatures most likely facilitated bubble formation due to an increase of the equilibrium vapor pressure. This beneficial effect was compensated by the fact that bubbles contained more vapor and consequently reduced the maximum temperature obtained during bubble collapse. Furthermore, increased temperatures probably encouraged degassing of the liquid phase, thus reducing the number of gas nuclei available for bubble formation and the destruction rate of pollutants increased (Psillakis et al., 2004). Furthermore, increased solution temperature allows PAH molecules to move faster into the cavitation bubble (i.e., increase diffusivity) (Wang, J. et al., 2006a). At higher temperatures more molecules will benefit from the temperature enhanced diffusivity and this may result in increase in removal rates for PAHs at long sonication times (Wang, J. et al., 2006b).

5.6 Effect of Sonication Intensity on the PAHs and COD_{dis} Removals

12.73–16.63–22.64–32.60–50.93 and 90.54 W/cm^2 sonication intensities was researched at ambient conditions (25^oC), constant sonication frequency (35 kHz), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 to 150 min) to determine the optimum sonication intensity for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww. Among the sonication intensities used in the sonication process (12.73–16.63–22.64–32.60–50.93 and 90.54 W/cm^2) it was found that a sonication intensity of 90.54 W/cm^2 is the optimum sonication intensity for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww (Table 5.6).

Sonication intensities was calculted by dividing the sonication power to the sonication areas of the wastewater samples.

example 1.

r=2 cm

Sonication intensity= (Power / Area) = (640 W / 12.56 cm^2) = 50.93 W/cm^2

example 2.

r=3.5 cm

Sonication intensity= (Power / Area) = (640 W / 38.49 cm^2) = 16.63 W/cm^2

Table 5.6 Effect of sonication intensiy on the PAHs and COD$_{dis}$ removals in PCI ww, OMI ww and TI ww at ambient conditions (25^{o}C) (sonication frequency=35 kHz, sonication power=640 W, sonication time= 60, 120 and 150 min, initial total PAHs concentration in PCI ww=1378.77 ng/ml, initial COD$_{dis}$ concentration in OMI ww=109444 mg/l, initial COD$_{dis}$ concentration in TI ww=962.99 mg/l, n=3, mean values).

Sonication Intensity (W/cm^2)	**PAHs Rem. Eff. in PCI ww (%)**			**COD$_{dis}$ Rem. Eff. in OMI ww (%)**			**COD$_{dis}$ Rem. Eff. in TI ww (%)**		
	After			**After**			**After**		
	60 min	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**
12.73	34.21	43.40	65.81	5.15	23.21	36.54	17.32	44.39	63.76
16.63	39.23	48.56	68.77	7.47	25.20	38.39	21.26	45.30	65.81
22.64	41.37	50.54	70.37	8.49	26.79	41.16	23.67	46.51	68.03
32.60	45.72	57.08	75.54	10.41	38.42	46.43	26.52	48.48	70.69
50.93	53.57	60.43	79.29	12.46	40.48	59.57	29.85	52.62	73.58
90.54	**56.05**	**62.30**	**80.16**	**12.58**	**41.74**	**60.91**	**30.43**	**53.69**	**74.27**

Since the formation of cavitation bubbles and the extent of bubble collapse depend on the sound intensity various sound intensities were compared for their impacts on the PAHs and COD$_{dis}$ removals. COD$_{dis}$ removal is caused by the acoustic cavitation during sonication and a certain sound intensity is needed to generate cavitation, the so called threshold. High sound intensity is needed to cause acoustic cavitation in the medium, which then causes COD$_{dis}$ removal. The cavitation threshold depends on the medium viscosity, density, purity, temperature, pressure, ultrasonic frequency and gas contents amongs others (Benabdallah El-Hadj et al., 2007).

In these studies, it was found that PAHs removals reached a maximum at about 90.54 W/cm^2 and then decrease upon increasing the intensity further. The observation could be interpreted with a significant increase in number of bubbles, close to the emitting surface, caused by sharply increasing the power intensity. The considerable amount of bubbles may coalesce to form large bubbles, which would cavitate less violently than that of tiny bubbles. Thus, though the collapse of single cavity is becoming more violent, the number of cavitation events decreases due to a decrease in power dissipated into the system and hence overall intensity of cavitation decreases (Sivakumar & Pandit, 2001).

As the intensity increased the number of collapsing cavities also increased. Thus leading to enhanced degradation rates, as reported by Papadaki et al. (2004) and Psillakis et al. (2004). An increase in ultrasonic intensity will lead to greater sonochemical effects in the collapsing bubble. The collapse of bubbles in the reaction reactor occurred more rapidly, thus increasing the production of $OH^{\bullet}$ at higher ultrasonic intensities. It has been shown that increasing the ultrasonic intensity increases the degradation rate of organic compounds (Papadaki et al., 2004). Furthermore, the pulsation and collapse of bubbles in the reaction cell occur more rapidly, the number of cavitation bubbles increases thus producing a higher concentration of $OH^{\bullet}$ at higher ultrasonic intensities. These $OH^{\bullet}$ react with PAHs in the solution. Therefore, the increase in the sonodegradation of PAHs could be explained by increasing the ultrasonic intensities arise from the enhancement of radical yields (Psillakis et al., 2004).

5.7 Effect of Sonication Density on the PAHs and COD$_{dis}$ Removals

0.24–0.70–1.28 and 6.00 W/ml sonication densities was researched at ambient conditions (25^{o}C), at constant sonication frequency (35 kHz), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum sonication density for maximum PAHs and COD$_{dis}$ removals in PCI ww, OMI ww and TI ww. Among the sonication density used in the sonication process (0.24–0.70–1.28 and 6.00 W/ml) it was found that a sonication density of 1.28 W/ml is the optimum specific energy for maximum PAHs and

COD_{dis} removals in PCI ww, OMI ww and TI ww (Table 5.7). The sonication densities were calculated by dividing the sonication power to the sonicated sample volumes.

example 1.

v=500 ml

Sonication density= (Power / Volume) = (640 W / 500 ml) = 1.28 W/ml

Table 5.7 Effect of sonication density on the PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww at ambient conditions (25°C) (sonication frequency=35 kHz, sonication power=640 W, sonication time=60 min, 120 and 150 min, initial total PAHs concentration in PCI ww=1378.77 ng/ml, initial COD_{dis} concentration in OMI ww=109444 mg/l, initial COD_{dis} concentration in TI ww=962.99 mg/l, n=3, mean values).

Sonication Densities (W/ml)	**PAHs Rem. Eff. in PCI ww (%)**			**COD_{dis} Rem. Eff. in OMI ww (%)**			**COD_{dis} Rem. Eff. in TI ww (%)**		
	After			**After**			**After**		
	60 min	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**
0.24	41.05	45.13	67.40	8.61	33.20	50.22	20.37	40.82	61.19
0.70	49.84	51.47	75.33	10.08	38.45	54.38	25.41	46.16	68.23
1.28	**56.05**	**62.30**	**80.16**	**12.58**	**41.74**	**60.91**	**30.43**	**53.69**	**74.27**
6.00	52.31	58.18	78.35	11.74	40.36	59.82	28.67	51.37	72.14

Sonication density (W/ml) is referred to power intensity (W/cm^2), for the optimization studies because the former directly gives an idea about actual power dissipated in the given volume of the solution and in ultrasonic bath two factors influence the extent of degradation: (1) the liquid height, and (2) liquid volume (Sivakumar & Pandit, 2001). The sonication density could be promoted with increasing sonication power during cavitation process. Thus enhanced the sono-degradation of pollutant in cavitation solution.

5.8 Effect of Specific Energy (E_s) on the PAHs and COD_{dis} Removals

2.49–3.12–4.15–5.19–24.93 and 31.16 kWh/kg COD in influent specific energy ranges was researched in ambient conditions (25^{o}C), at constant sonication frequency (35 kHz), constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum specific energy for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww. Among the specific energy used in the sonication process (2.49–3.12–4.15–5.19–24.93 and 31.16 kWh/kg COD in the influent) it was found that a specific energy of 3.12 kWh/kg COD in influent was the optimum specific energy for maximum COD_{dis} removals in PCI ww, OMI ww and TI ww (Table 5.8). In this study it is important to note that the COD removals obtained at specific energies > 3.12 kWh/kg COD exhibited similar yields. Therefore, in order to minimize the electricity costs, a specific of 3.12 kWh/kg COD was chosen for maximum COD yields at all wws.

The specific energy was calculated according to the Eq. (4.3) given in section 4:

$$(kWh / kg\, COD_0) = \frac{Sonicator\ Power(W) * Time(h) * (1\, kj / 1000\, j)}{V(l) * COD_0(g / l) * (1\, kg / 1000 g)} \qquad (4.3)$$

The specific energy was calculated by two different ways: (1) By keeping the ultrasonic power constant and exposing it at different durations, (2) by application of different powers at constant process time. In this study, the specific energy was calculated by dividing the (constant power x increasing sonication times) to the (constant initial COD_{dis} x inreasing sonication volumes of wastewater samples).

example 1.

V=500 ml

Specific energy = E_s = [(640 W*2.5 h*1 kj/1000 j) / (0.5 l*1.027g/l*1 kg/1000g)]

= 3.12 kWh / kg COD_0

example 2.

V=300 ml

Specific energy = E_s = [(640 W*2.5 h*1 kj/1000 j) / (0.3 l*1.027g/l*1 kg/1000g)]

= 4.15 kWh / kg COD_0

example 3.

V=50 ml

Specific energy = E_s = [(640 W*2.5 h*1 kj/1000 j) / (0.05 l*1.027g/l*1 kg/1000g)]

= 31.16 kWh / kg COD_0

Table 5.8 Effect of specific energy on the PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww at ambient conditions (25°C) (sonication frequency=35 kHz, sonication power=640 W, sonication time=60 min, 120 and 150 min, initial total PAHs concentration in PCI ww=1378.77 ng/ml, initial COD_{dis} concentration in OMI ww=109444 mg/l, initial COD_{dis} concentration in TI ww=962.99 mg/l, n=3, mean values).

Specific Energy (kWh/kg COD in influent)	**PAHs Rem. Eff. in PCI ww (%)**			**COD_{dis} Rem. Eff. in OMI ww (%)**			**COD_{dis} Rem. Eff. in TI ww (%)**		
	After			**After**			**After**		
	60 min	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**	**60 min**	**120 min**	**150 min**
2.49	47.70	56.65	77.33	9.97	39.32	57.89	26.11	49.75	70.43
3.12	**56.05**	**62.30**	**80.16**	**12.58**	**41.74**	**60.91**	**30.43**	**53.69**	**74.27**
4.15	51.99	59.93	79.01	10.31	38.54	60.27	28.35	53.24	74.06
5.19	52.49	58.27	80.66	11.33	40.97	59.93	28.40	51.56	73.07
24.93	53.20	61.01	79.72	11.25	40.19	59.74	29.06	54.87	74.26
31.16	54.27	60.35	80.29	12.19	41.43	60.07	29.15	53.29	73.49

Sonochemical decomposition of organic compounds is resulted from the formation, growth and collapse of high-energy cavitation bubbles, which releasing large quantities of energy over a small location. At low frequencies, the implosions of stable cavitation bubbles create high energy waves and micro-jetting effects together with the inside-bubble pyrolysis phenomenon, which explains the reductions of COD_{dis} or PAHs. Sonication is a high energy process and its efficient usage is very important by means of cost-effectiveness (Kidak et al., 2009; Zhang, G. et al., 2008). Sonication energy consumption could be reduced during COD_{dis} and PAHs removals while specific energy is the main parameter to describe the ultrasonic energy consumption during COD_{dis} removal, which is defined as ultrasonic power per unit of sonicated wastewater. High sonication power and long sonication time increased the specific energy during sonication process.

5.9 Sonication of PCI ww

Raw wastewaters taken from the influent of the aeration unit of a PCI ww treatment plant in Izmir were analyzed. The characterization of PCI ww was shown in Table 5.9 for minimum, medium and maximum values. All measurements were carried out three times and the results given as the means of triplicate samplings with standard deviation (SD) values.

Table 5.9 Characterization values of PCI ww (n=3, mean values ± SD)

Parameters	**Values**		
	Minimum	**Medium**	**Maximum**
pH	6.00 ± 0.21	6.80 ± 0.24	7.50 ± 0.26
DO (mg/l)	1.57 ± 0.06	1.78 ± 0.06	2.18 ± 0.08
ORP (mV)	24.82 ± 0.87	28.20± 0.99	34.12 ± 1.20
TSS (mg/l)	273.06 ± 9.56	310.30 ± 10.86	375.47 ± 13.14
TVSS (mg/l)	220.53 ± 7.72	250.60 ± 8.78	303.23 ± 10.61
COD_{total} (mg/l)	1298.12 ± 45.43	1475.20 ± 51.63	1785.36 ± 62.48
COD_{dis} (mg/l)	904.54 ± 31.64	1027.43 ± 35.95	1243.78 ± 43.51
BOD_5 (mg/l)	514.26 ± 17.99	584.09 ± 20.44	707.80 ± 24.80
BOD_5/COD_{dis}	0.46 ± 0.02	0.57 ± 0.02	0.70 ± 0.03
TOC (mg/l)	547.54 ± 19.15	620.81 ± 21.74	751.43 ± 26.30
Total N (mg/l)	13.60 ± 0.48	15.40 ± 0.54	18.60 ± 0.65
NH_4-N (mg/l)	1.90 ± 0.07	2.20 ± 0.08	2.70 ± 0.10
NO_3-N (mg/l)	1.60 ± 0.06	1.80 ± 0.06	2.20 ± 0.08
NO_2-N (mg/l)	0.040 ± 0.001	0.046 ± 0.001	0.056 ± 0.002
Total P (mg/l)	9.30 ± 0.33	10.60 ± 0.37	12.80 ± 0.45
PO_4-P (mg/l)	6.10 ± 0.21	6.80 ± 0.24	8.30 ± 0.29
Oil (mg/l)	181.80 ± 6.36	206.50 ± 7.23	250.32 ± 8.75
Influent PAHs (ng/ml)	1378.77 ± 48.26	1816.40 ± 63.57	2250.21 ± 78.76

5.9.1 Effect of Increasing Sonication Times on the Removals of COD$_{dis}$, TOC and PAHs in PCI ww

5.9.1.1 Effect of Increasing Sonication Times on the Removals of COD$_{dis}$ and TOC in PCI ww

56.05%, 62.30% and 80.16% COD$_{dis}$ removals were found at an initial COD$_{dis}$ concentration of 1027.43 mg/l after 60 min, 120 and 150 min sonication times, respectively, at 25°C ambient conditions at pH=7.0 (Figure 5.1). The maximum COD$_{dis}$ removal efficiency was 80.16% after 150 min sonication time at pH=7.0 and at 25°C. A significant linear correlation between COD$_{dis}$ yields and increasing sonication time was observed (R^2=0.81, F=16.30, p=0.01).

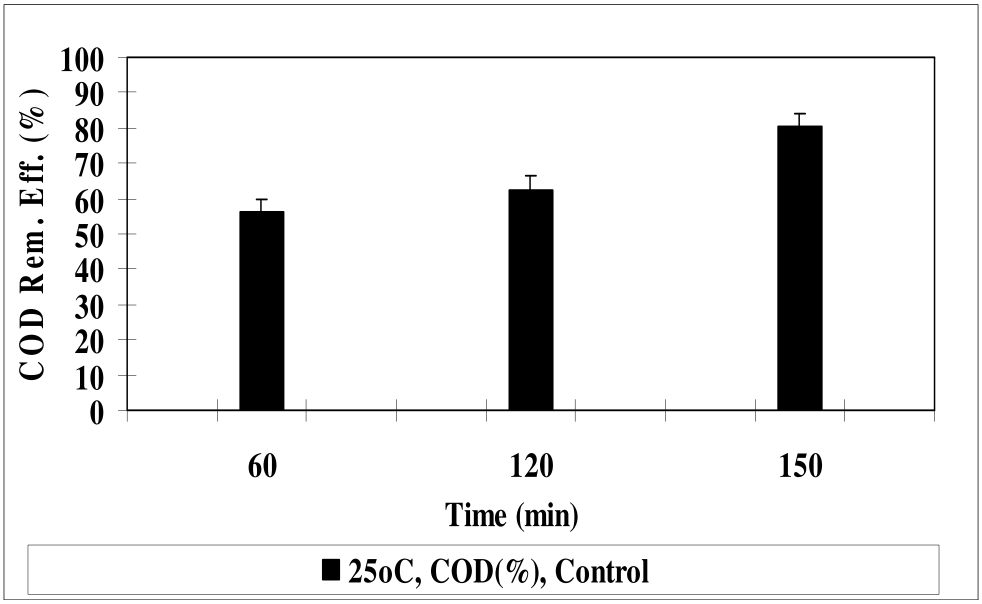


Figure 5.1 Effect of increasing sonication times on the COD$_{dis}$ removal efficiencies in PCI ww at 25°C (ambient conditions) (sonication power=640 W, sonication frequency 35 kHz).

The treatment by sonication converts COD$_{dis}$ to much smaller sonodegraded compounds. In such cases it is obvious that higher sonication times are needed for complete mineralization. Short sonication times (60 min) did not provide high degradation yields for refractory COD since they were not exposed for a long enough time to ultrasonic irradiation. Therefore, a decrease in the percentage of remaining COD_{dis} was expected at longer sonication times due to sufficient radical reactions through cavitation. The formation of hydroxylated by products is observed under ultrasonic irradiation; it is suggested that $OH^{\bullet}$ is an important species for sonodegradation of PCI ww at 35 kHz and at 640 W. COD_{dis} was not completely removed under the ultrasonic action even with a long sonication time (150 min). These results underline the fact that degradation products of COD are recalcitrant toward sonochemical treatment. This is due to the fact that the intermediate products have very low probabilities of making contact with $OH^{\bullet}$, which react mainly at the interface of the bubble. Thus, the sonochemical action that gives rise to products bearing more hydroxyl (or carboxylic) groups is of low efficiency toward COD_{dis} abatement.

55.39%, 62.74% and 78.37% TOC yields were observed at an initial TOC concentration of 620.81 mg/l after 60 min, 120 and 150 min sonication, respectively, at pH=7.0 and at 25°C ambient conditions. The maximum TOC removal efficiency was 78.37% after 150 min sonication time at pH=7.0 and at 25°C (Figure 5.2).

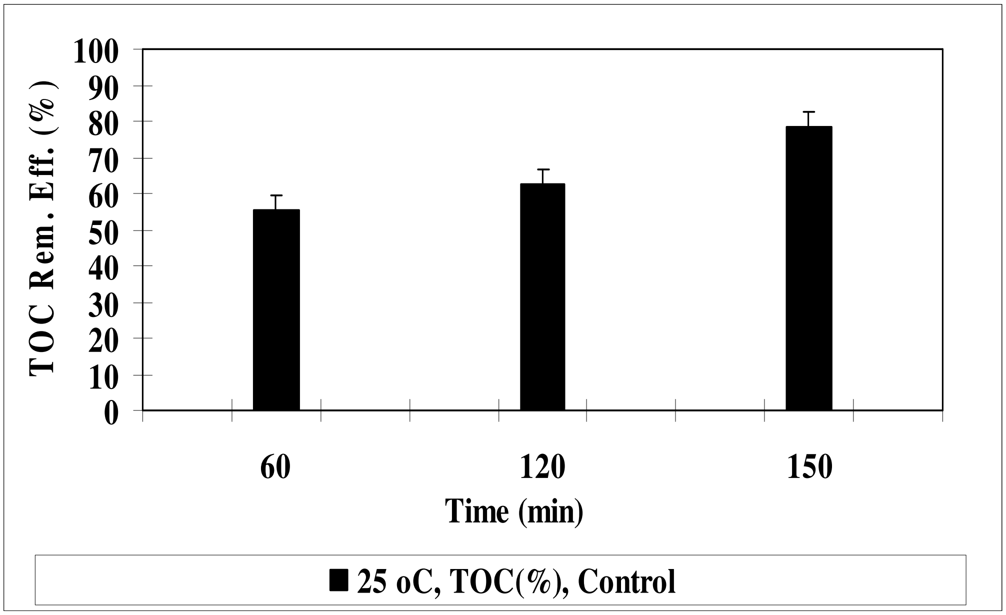


Figure 5.2 Effect of increasing sonication times on the TOC removal efficiencies in PCI ww at 25°C (ambient conditions) (sonication power=640 W, sonication frequency 35 kHz).

A significant linear correlation between TOC yields and increasing sonication time was observed (R^2=0.80, F=14.21, p=0.01). TOC removals have similar properties with COD_{dis} removal at sonication process. The treatment by sonication converts TOC to much smaller sonodegraded compounds. Short sonication time (e.g., 60 min) did not provide high degradation yields for TOC since they were not exposed for a long enough time to ultrasonic irradiation. Therefore, a decrease in the percentage of remaining TOC was attended at longer sonication times (i.e., 150 min) due to sufficient radical reactions through cavitation.

5.9.1.2 Effect of Increasing Sonication Times on the PAHs Removal Efficiencies in PCI ww at 25^{o}C Ambient Conditions

Raw PCI ww samples were sonicated at an ambient temperature of 25^{o}C and at pH=7.0 and at increasing sonication times (60 min, 120 and 150 min). 54.92%, 61.33% and 79.65% total PAHs removals were observed in 1378.77 ng/ml influent total PAHs concentration after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25^{o}C. The maximum total PAHs removal efficiency was 79.65% after 150 min sonication time at pH=7.0 and at 25^{o}C. A significant linear correlation between PAHs yields and increasing sonication time was observed (R^2=0.71, F=11.34, p=0.01) (Figure 5.3).

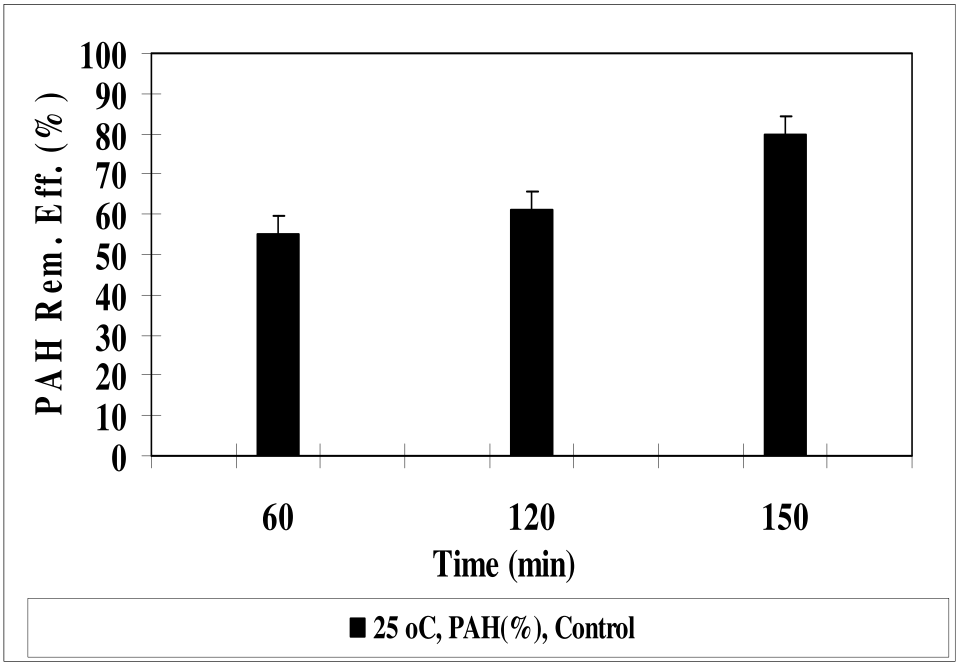


Figure 5.3 Effect of increasing sonication times on the total PAHs removal efficiencies in PCI ww at 25°C (ambient conditions) (sonication power=640 W, sonication frequency 35 kHz).

Seventeen PAHs (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR, BbF, BkF, BaP, IcdP, DahA and BghiP) in PCI ww were determined with GC-MS in raw ww before sonication experiments at 25°C ambient conditions. The GC-MS chromatogram of PAHs in PCI ww were shown before sonication process in Figure 5.4 while the GC-MS chromatogram of PAHs in PCI ww were demonstrated in Figure 5.5 after 150 min sonication time at 25°C.

High removal efficiencies were found for PAHs with high benzene rings. 88.94% BkF, 66.03% BaP, 62.62% IcdP, 77.74% DahA and 78.72% BghiP yields were obtained for PAHs with 4 and 5 benzene rings after 150 min sonication time at 25°C (Table 5.10).

Table 5.10 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments after 60 min, 120 and 150 min sonication time at 25°C (sonication power =640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAH concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**Inf. $^{(A)}$ T=0 min PAHs (ng/ml) ± SD**	**Eff. $^{(B)}$T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
NAP	1012.93 ± 35.45	206.20 ± 7.22	27.30	30.49	70.21
ACL	50.20 ± 1.76	10.22 ± 0.36	52.29	58.40	73.77
ACT	66.82 ± 2.34	13.60 ± 0.48	51.48	57.49	87.04
FLN	55.57 ± 1.95	11.31 ± 0.40	52.03	58.11	81.09
PHE	125.58 ± 4.40	25.56 ± 0.90	48.80	54.50	79.35
ANT	7.48 ± 0.26	1.52 ± 0.05	54.51	60.87	90.86
CRB	14.20 ± 0.50	2.89 ± 0.10	54.15	60.47	64.86
FL	19.36 ± 0.68	3.94 ± 0.14	53.87	60.17	83.52
PY	15.54 ± 0.54	3.16 ± 0.11	54.08	60.39	72.46
BaA	0.55 ± 0.02	0.11 ± 0.004	54.89	61.30	90.25
CHR	2.68 ± 0.09	0.55 ± 0.02	54.77	61.17	83.73
BbF	0.80 ± 0.03	0.16 ± 0.006	54.87	61.28	94.52
BkF	0.80 ± 0.03	0.16 ± 0.006	54.87	61.28	88.94
BaP	0.07 ± 0.003	0.02 ± 0.0007	54.91	61.32	66.03
IcdP	1.09 ± 0.04	0.22 ± 0.008	54.86	61.26	62.62
DahA	4.58 ± 0.16	0.93 ± 0.03	54.67	61.05	77.74
BghiP	0.51 ± 0.02	0.10 ± 0.004	54.89	61.30	78.72

$^{(A)}$ Inf.= influent, $^{(B)}$ Eff. = effluent.

70.21% NAP, 87.04% ACT, 90.25% BaA, 83.73% CHR and 94.52% BbF removals were observed for PAHs with one and three benzene rings, respectively, at 25°C after 150 min sonication time. In this study, no significant difference in yields between PAHs with three (ANT, FL, PY), five (BbF, BkF) and six rings (DahA, BghiP) was observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times (R^2=0.96, F=14.36 p=0.001) (Tables 5.10 and 5.11).

Table 5.11 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml).

PAHs	CAS-No	MF	Benzene Ring No	MW	T_M	T_B	S_W (25°C)	V_P (25°C)	H (25°C)	log K_{OA} (25°C)	log K_{OW}	IPC
NAP	91-20-3	$C_{10}H_8$	2	128	80	218	31.00	$8.50x10^{-2}$	$4.40x10^{-4}$	-	3.36	1012
ACL	208-96-8	$C_{12}H_8$	3	152	93	280	16.10	$6.68x10^{-3}$	$1.14x10^{-4}$	6.34	3.94	50.00
ACT	83-32-9	$C_{12}H_{10}$	3	154	93	279	3.90	$2.15x10^{-3}$	$1.84x10^{-4}$	6.52	3.92	66.82
FLN	86-73-7	$C_{13}H_{10}$	3	166	115	295	1.69	$6.00x10^{-4}$	$9.62x10^{-5}$	6.90	4.18	55.57
PHE	85-01-8	$C_{14}H_{10}$	3	178	99	340	1.15	$1.21x10^{-4}$	$3.35x10^{-5}$	7.68	4.46	12.55
ANT	120-12-7	$C_{14}H_{10}$	3	178	215	340	$4.34x10^{-2}$	$2.67x10^{-6}$	$5.56x10^{-5}$	7.71	4.45	7.47
CRB	86-74-8	$C_{12}H_9$	3	167	246	355	1.80	$7.50x10^{-7}$	$1.16x10^{-7}$	8.03	3.72	14.19
FL	206-44-0	$C_{16}H_{10}$	4	202	108	384	0.26	$9.22x10^{-6}$	$8.86x10^{-6}$	8.76	5.16	19.36
PY	129-00-0	$C_{16}H_{10}$	4	202	151	404	0.135	$4.50x10^{-6}$	$1.19x10^{-5}$	8.81	4.88	15.54
BaA	56-55-3	$C_{18}H_{12}$	4	228	84	438	$9.40x10^{-3}$	$2.10x10^{-7}$	$1.20x10^{-5}$	10.28	5.76	$55.00x10^{-2}$
CHR	218-01-9	$C_{18}H_{12}$	4	228	258	448	$2.00x10^{-3}$	$6.23x10^{-9}$	$5.23x10^{-6}$	10.30	5.81	$26.80x10^{-2}$
BbF	205-99-2	$C_{20}H_{12}$	5	252	168	-	$1.50x10^{-3}$	$5.00x10^{-7}$	$6.57x10^{-7}$	11.34	5.78	$79.00x10^{-2}$
BkF	207-08-9	$C_{20}H_{12}$	5	252	217	480	$8.00x10^{-4}$	$9.70x10^{-10}$	$5.84x10^{-7}$	11.37	6.11	$80.00x10^{-2}$
BaP	50-32-8	$C_{20}H_{12}$	5	252	177	495	$1.62x10^{-3}$	$5.49x10^{-9}$	$4.57x10^{-7}$	11.56	6.13	$75.00x10^{-3}$
DahA	53-70-3	$C_{22}H_{14}$	5	278	270	524	$2.49x10^{-3}$	$1.00x10^{-10}$	$1.23x10^{-7}$	12.59	6.75	$4.578x10^{-3}$
BghiP	191-24-2	$C_{22}H_{12}$	6	276	278	> 500	$2.60x10^{-4}$	$1.00x10^{-10}$	$3.31x10^{-7}$	12.55	6.63	$5.130x10^{-3}$
IcdP	193-39-5	$C_{22}H_{12}$	6	276	164	536	$1.90x10^{-4}$	$1.25x10^{-10}$	$3.48x10^{-7}$	12.43	6.70	$10.93x10^{-2}$

naphthalene (NAP), acenaphthylene (ACL), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[*a*]anthracene (BaA), chrysene (CHR), benz[*b*]fluoranthene (BbF), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g/mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg/l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 /mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng/ml).

Although, Park et al. (2000) reported that lower molecular weight (2-, 3- and 4-ring) PAHs were found to be degraded more rapidly than the heavier (5-6 ring) compounds in this study high removal efficiencies were found for PAHs with high benzene rings after long sonication time (150 min) at 25°C ambient temperature (Table 5.10). In other words, although DahA and BghiP were the most hydrophobic types of PAHs with low Henry's law constants, vapor pressures, solubilities and high octanol-water coefficients, a significant correlation was not observed between the removal percentages of the these PAHs and their physicochemical properties aforementioned after long sonication times and at low temperatures such as 25°C. Treatment by sonication converts PAHs with multiple benzene rings to much smaller compounds. It is obvious that higher sonication times are needed for complete mineralization. Short sonication times did not provide high degradation yields for refractory PAHs since they were not exposed for a long enough time to ultrasonic irradiation. Therefore, a decrease of the percent remaining PAHs was expected at longer sonication times due to high temperature and radical reactions from cavitation**.**

Although, ANT and PHE contained similar benzene rings (3) the PHE have higher removal yields than ANT at high sonication times (Table 5.10). This could be attributed to higher solubility, water pressure, Henry's law constant and low octanol / water partition coefficient of PHE compared to ANT (Table 5.11). This is contrast to the study performed by David (2009) which reported that the geometry of the chemical structure of PAHs affected the degradation efficiency of PAHs with a straight structure ANT which was more easily degraded than one with a branched structured PHE. Moreover, the choice of solvent affected the degradation of PAHs under sonication which ultimately is expected to alter the effectiveness of ultrasonic extractions at long sonication times. High PHE yields compared to ANT could be attributed to the type of solvent used. The cavities are more readily formed when using solvents with low viscosity and low surface tension during long sonication times (Chakinala et al., 2008a; 2008b). The preliminary studies showed that solvents with high surface tension and viscosity generally have a higher threshold for cavitation resulting in fewer cavitation bubbles but more harsh conditions once cavitation is established resulting in higher temperatures and pressures upon bubble collapse. In this study, among the solvents used acetone and hexane have the highest surface tension and viscosity. Higher cavitation bubbles resulting in fiercer cavitation conditions, was a reason for less PHE remaining with acetone after 150 min sonication time. The vapor pressure of the solvent is another important factor affecting the cavitation (Rokhina et al., 2009). Higher vapor pressure leads to more solvent volatilizing into cavitation bubbles which are able to be dissociated by high temperature after 150 min sonication time. Hexane and acetone have the highest vapor pressure among solvents (Suslick, 1986). Thus, more hexane molecules migrate into cavitation bubbles leading to more molecules dissociating to generate radicals. As a result, more radical reactions of PHE occurred resulting in a lower percent remaining with hexane after 150 min sonication time.

The results found in this study were stronger in comparison with the study performed by Psillakis et al. (2004). They found 74.00%, 72.00% and 76.00% PHE, NAP and ACL removal rates, respectively, at a temperature 40^{o}C, power 450 W and frequency of 28 kHz after 98 min sonication time. Similarly, in a study performed by Little et al. (2002). 0.60 ng/ml PHE was found to be recalcitrant to sonochemical removal at 22^{o}C at an ultrasound frequency of 30 kHz and power 320 W after 135 min sonication time. However, increasing the liquid bulk temperature to 40^{o}C led to about 56.00% removal at the same operational conditions. In this study, 79.65% total PAHs removal was observed at 25^{o}C after 150 min sonication time. The total PAHs yield is higher than the yield obtained by 56.00% at 22^{o}C as mentioned above.

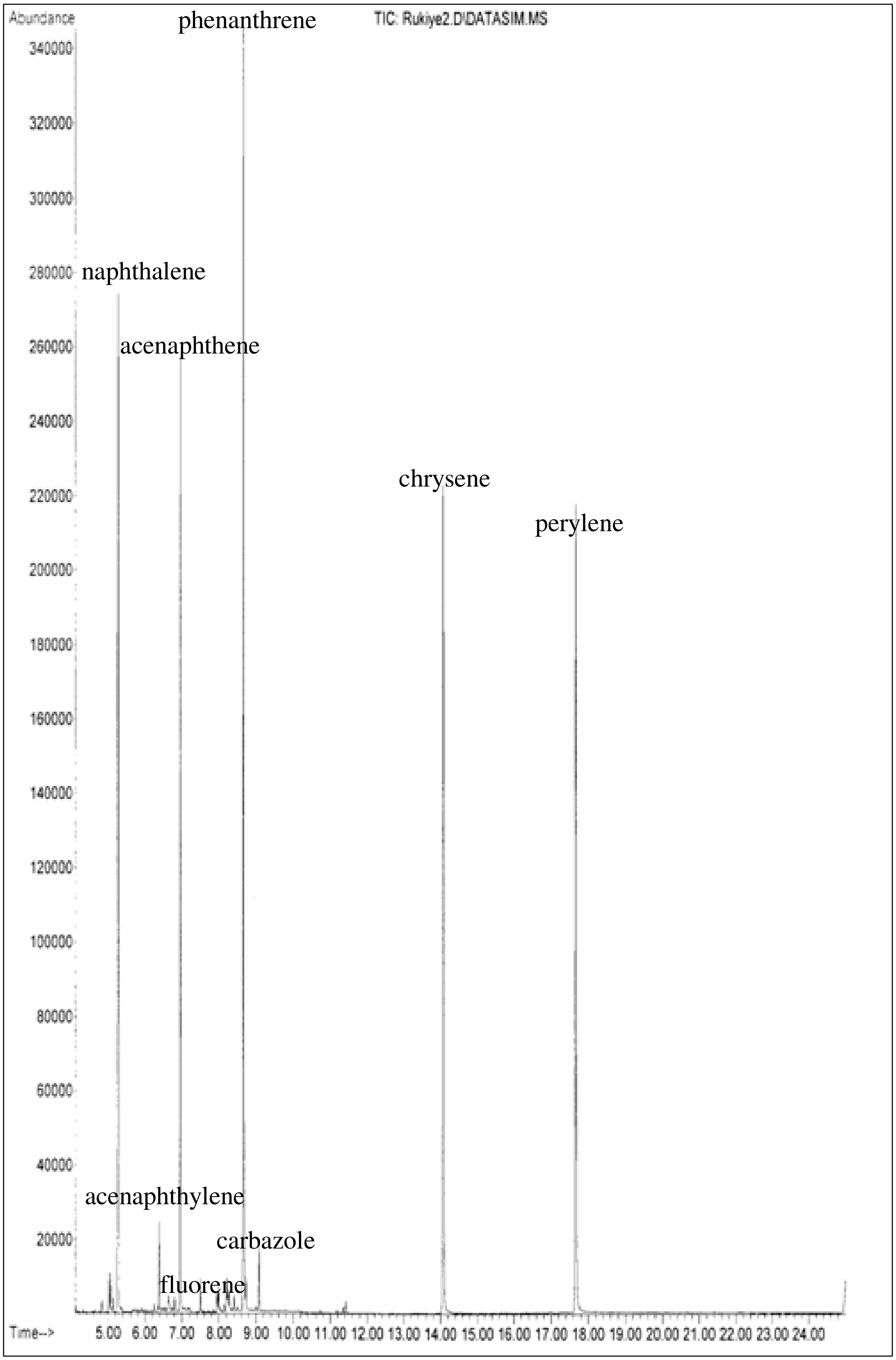


Figure 5.4 The GC-MS chromatogram of PAHs in PCI ww before sonication experiments at 25°C.

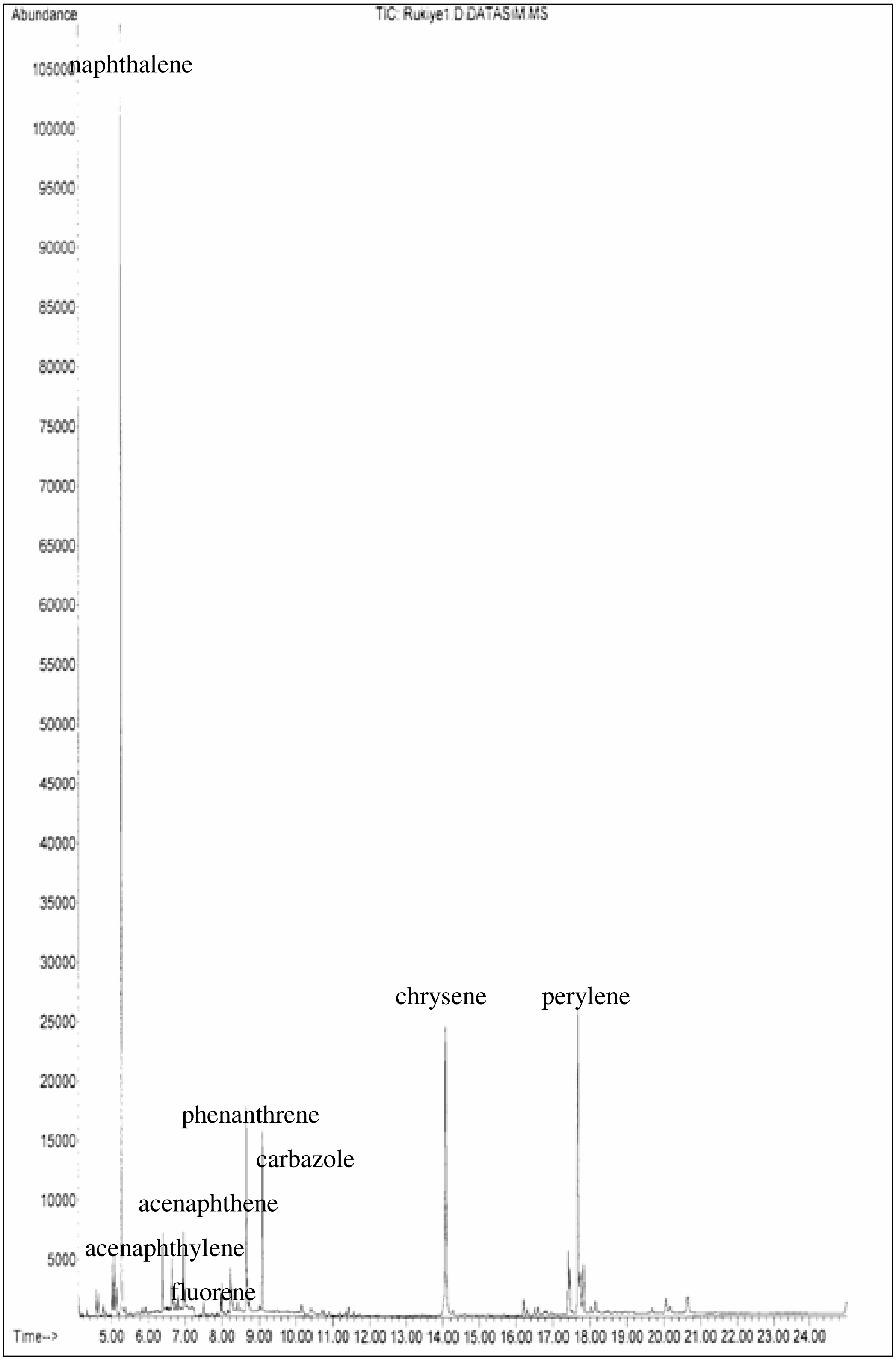


Figure 5.5 The GC-MS chromatogram of PAHs in PCI ww after 150 min sonication time at 25°C.

The PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww were measured with HPLC after 120 min sonication at 25°C (Table 5.12).

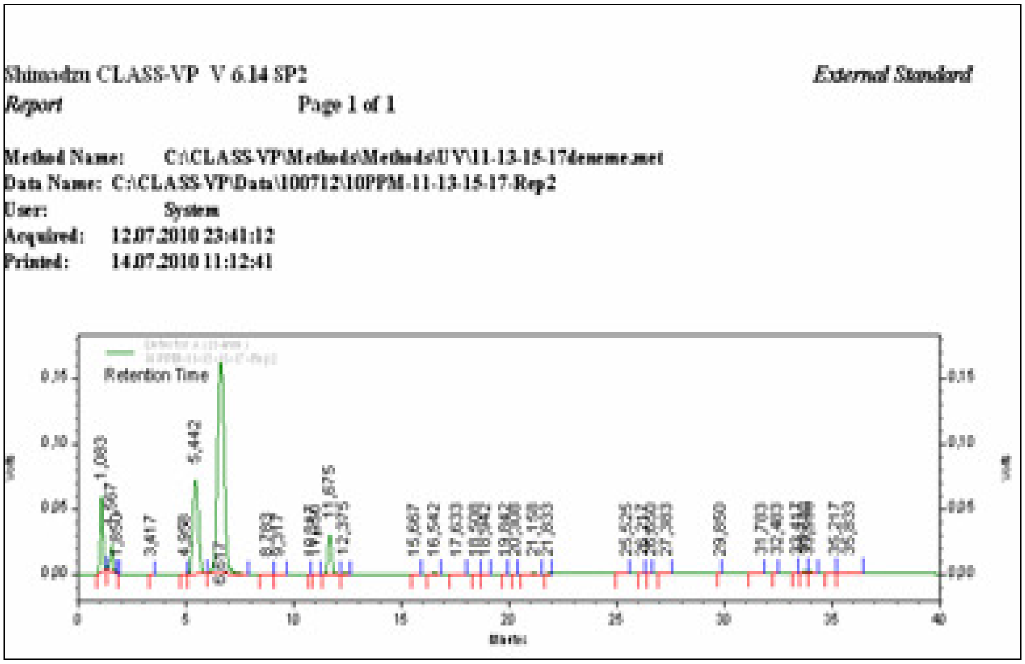
Table 5.12 The measurements of PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww with HPLC after 120 and 150 min sonication at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs Intermediates	**PAH_0 (ng/ml)**	**120 min**			**150 min**
		PAH (ng/ml)	**PAHR (%)**	**PAHI (ng/ml)**	**PAHIR (%)**
1–Methylnaphthalene	1378.77	533.18	61.33	320.24	76.77
9–Hydroxyfluorene	1378.77	533.18	61.33	205.85	85.07
9,10–Phenanthrenequione	1378.77	533.18	61.33	78.16	94.33
Benzoic acid	1378.77	533.18	61.33	174.57	87.34
1,2,3–Thiadiazole–4–carboxylic acid	1378.77	533.18	61.33	77.58	94.37

PAH_0: Initial total PAHs concentration (ng/ml), PAH: Total PAHs concentration (ng/ml) after 120 min sonication time, PAHR: Total PAHs removal efficiency (%) after 120 min sonication time, PAHI: PAHs intermediates concentration (ng/ml) after 120 min sonication time, PAHIR: removal of PAHs intermediates (%) after 150 min sonication time.

As shown in Table 5.12, the initial total PAHs concentration of 1378.77 ng/ml decreased to 533.18 ng/ml after 120 min sonication time at 25°C. From 1378.77 ng/ml initial PAHs concentration 320.24 ng/ml 1–methylnaphthalene, 205.85 ng/ml 9–hydroxyfluorene, 78.16 ng/ml 9,10–phenanthrenequione, 174.57 ng/ml benzoic acid, 77.58 ng/ml 1,2,3–thiadiazole–4–carboxylic acid were produced after 120 min sonication time at 25°C. It was found that the initial PAHs cleaved to the inter-metabolites mentioned above (Table 5.12). After 120 min sonication time the remaining PAHs concentration was found to be high (522.37 ng/ml). The low removal efficiency of the total PAHs (61.33%) could be attributed to the studied low temperature (25°C). From 1378.77 ng/ml total PAH 855 ng/ml total PAHs intermetabolites were produced after 120 min sonication time. The PAHs intermediates namely, 1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid were sonodegraded with yields of 76.77%, 85.07%, 94.33%, 87.34% and 94.37%, respectively, after 150 min sonication time at 25°C (Table 5.12).

The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww after 120 min sonication time at 25°C, was shown in Figure 5.6.



Shimadzu CLASS-VP V 6.14 SP2 *External Standard*
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Figure 5.6 The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww after 120 sonication time at 25°C (sonication power =640 W, sonication frequency=35 kHz).

5.9.2 Effect of Increasing Sonication Temperature on the Removals of COD$_{dis}$, TOC and PAHs in PCI ww

5.9.2.1 Effect of Increasing Sonication Temperature on the Removals of COD$_{dis}$ and TOC in PCI ww

At the beginning of the studies the raw PCI ww samples were sonicated at 30°C and 60°C at a pH=7.0 at increasing sonication times from 5 min up to 60 min to determine the lowest sonication time for maximum COD$_{dis}$ removal efficiencies. The lowest sonication time was determined as 60 min for the maximum COD$_{dis}$ removals (Table 5.13).

Table 5.13 Effect of sonication time on the COD$_{dis}$ removals in PCI ww, at 30°C and 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD$_{dis}$ concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml) (n=3, mean values ± SD).

Time (min)	**30°C**		**60°C**	
	COD$_{dis}$ (mg/l)	**Rem. Eff. (%)**	**COD$_{dis}$ (mg/l)**	**Rem. Eff. (%)**
0	1027.43 ± 35.96	0.00	1027.43 ± 35.96	0.00
5	950.20 ± 33.26	7.52	932.83 ± 32.65	9.21
10	818.95 ± 28.66	20.29	831.45 ± 29.10	19.07
15	772.48 ± 27.04	24.81	808.75 ± 28.31	21.28
20	738.96 ± 25.86	28.08	746.27 ± 26.12	27.37
25	731.95 ± 25.62	28.76	720.68 ± 25.22	29.86
30	694.78 ± 24.32	32.38	685.60 ± 24.00	33.27
35	668.42 ± 23.40	34.94	665.98 ± 23.31	35.18
40	635.13 ± 22.23	38.18	645.92 ± 22.61	37.13
45	624.08 ± 21.84	39.26	640.29 ± 22.41	37.68
50	597.06 ± 20.90	41.89	548.35 ± 19.20	46.63
55	568.27 ± 19.89	44.69	526.80 ± 18.44	48.73
60	537.64 ± 18.82	47.67	476.70 ± 16.70	53.60

44.05%, 61.22% and 89.94% COD_{dis} removals were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Figure 5.7). An increase of 9.78% in COD_{dis} yield was obtained after 150 min sonication time at 30°C, compared to the control (E=80.16% COD_{dis} at pH=7.0 and at 25°C) (Figure 5.7). 46.50%, 67.37% and 92.48% COD_{dis} removals were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.7). The contribution of 60°C temperature on COD_{dis} removals were 5.07% and 12.32% after 120 and 150 min sonication, respectively, compared to the control (E=62.30% and E=80.16% COD_{dis} after 120 and 150 min sonication times at pH=7.0 at 25°C). The maximum COD_{dis} removal was 92.48% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing sonication temperature was observed (R^2=0.93, F=15.43, p=0.01) (Figure 5.7).

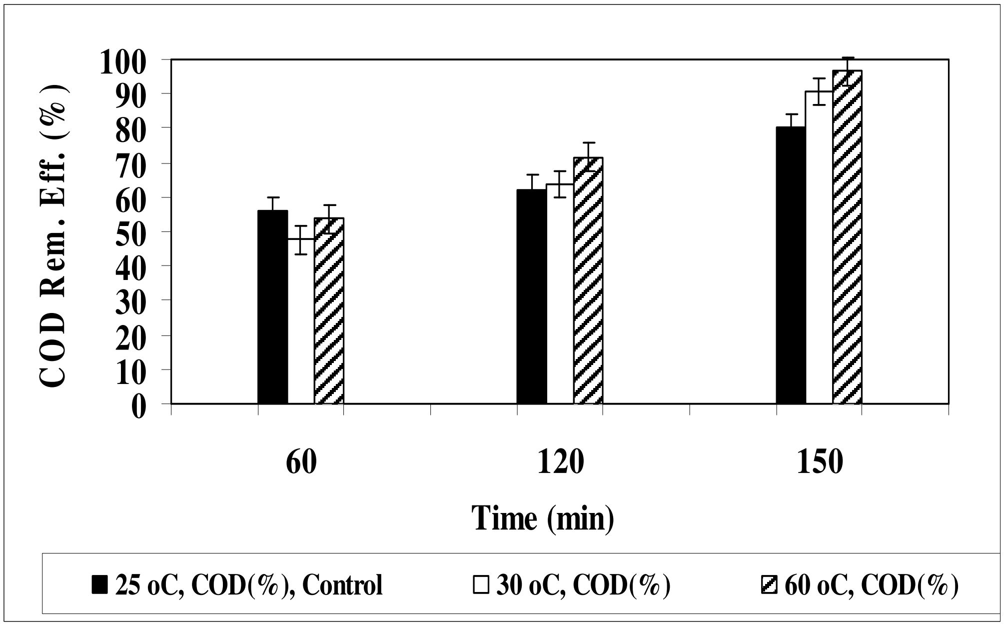


Figure 5.7 Effect of increasing temperatures on the COD_{dis} removal efficiencies in PCI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

Increasing temperatures (from 25°C to 30°C and to 60°C) increased the COD_{dis} removal of PCI ww after sonication process since sonodegradation reaction rates in cavitation process increased with increasing temperature during sonication at increasing sonication times. As a result, increasing temperature increased the COD_{dis} removal efficiency in PCI ww after sonication experiments.

47.70%, 63.38% and 90.89% TOC removals were measured after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Figure 5.8). An increase of 12.52% in TOC removal was found after 150 min sonication time at 30°C, compared to the control (E=78.37% TOC at pH=7.0 and at 25°C). A significant linear correlation between TOC yields and increasing sonication temperature was observed (R^2=0.95, F=17.78, p=0.01) (Figure 5.8).

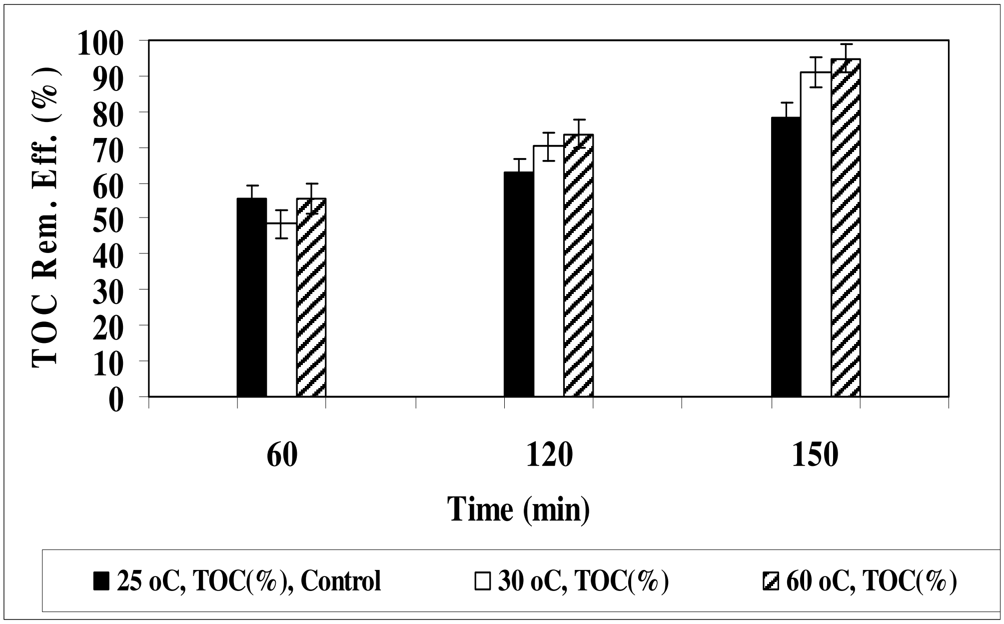


Figure 5.8 Effect of increasing temperatures on the TOC removal efficiencies in PCI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

49.50%, 70.00% and 94.23% TOC removals were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.8). The contribution of 60°C temperature to the TOC removals were 7.26% and 15.86% after 120 and 150 min sonication times, respectively, compared to the control (E=62.74% and 78.37% TOC after 120 and 150 min sonication times at pH=7.0 and at 25°C). The maximum TOC removal efficiency was 94.23% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TOC yields and increasing sonication temperature was observed (R^2=0.94, F=17.11, p=0.01) (Figure 5.8).

Increasing temperatures (30°C and 60°C) increased the TOC removals in PCI ww after sonication process. Sonodegradation reaction in cavitation process was rapidly performed with increasing temperatures at long sonication times such as 150 min. The treatment by sonication converts COD_{dis} and TOC to much smaller sonodegraded compounds. Low sonication temperature (25°C) did not provide high degradation yields for COD_{dis} and TOC.

5.9.2.2 Effect of Increasing Temperature on the Removal of PAHs in PCI ww at Increasing Sonication Times

Raw PCI ww samples were sonicated in a sonicator at 30°C and 60°C during 60 min, 120 and 150 min of sonication times at pH=7.0. Similar total PAH removal yields were found at 25°C (E=54.92% total PAHs at pH=7.0) and 60°C (E=54.21% total PAHs at pH=7.0) after 60 min of sonication time (Figure 5.9). In other words, increasing the temperature from 25°C to 30°C and 60°C did not contribute to the PAHs removal after 60 min of sonication time. The total PAHs removal decreased slightly at a temperature of 30°C with the same sonication time (Figure 5.9). Similarly, the total PAHs removals at 30°C remained at the same level as 25°C after 120 min of sonication time. Increasing the temperature from 25°C to 60°C increased the total PAHs removal efficiency after 120 and 150 min sonication times (Figure 5.9). In general, as the sonication time increased from 60 min to 150 min, the total PAHs removal increased. The maximum total PAHs removal efficiency was 96.90% after 150 min sonication at pH=7.0 and at 60°C. A significant linear correlation between total PAHs yields and increasing sonication temperature was observed (R^2=0.83, F=10.41, p=0.01) (Figure 5.9).

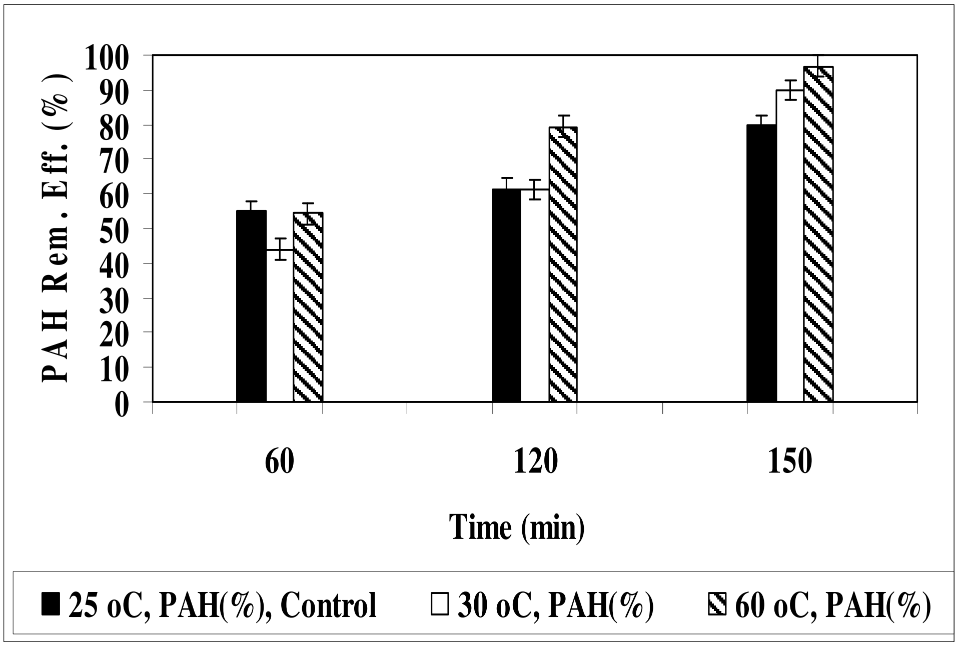


Figure 5.9 Effect of increasing temperature on the total PAHs removal efficiencies in PCI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

Removal efficiencies in seventeen PAHs were measured in the influent and in the effluent of the sonication experiments after 60 min, 120 and 150 min sonication times at 30^{o}C (Table 5.14). As seen in Table 5.14, all the removal yields of individual PAHs increased as the sonication time increased from 60 min to 150 min at a temperature of 60^{o}C. The yields for all individual PAHs were above 91.00% except for BbF (86.21%) after 150 min of sonication time at a temperature of 60^{o}C (Table 5.14). This showed that sonication at high temperature increased the yields in all PAHs species.

Table 5.14 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments after 60 min, 120 and 150 min sonication times at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**Inf. (A) T=0 min PAHs (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
NAP	2164.51 ± 75.76	614.16 ± 21.50	21.76	61.53	98.48
ACL	53.02 ± 1.86	2.76 ± 0.10	44.02	73.77	97.12
ACT	71.83 ± 2.51	3.34 ± 0.12	43.25	72.67	94.16
FLN	59.04 ± 2.07	2.89 ± 0.10	43.77	73.41	96.00
PHE	143.28 ± 5.02	8.71 ± 0.31	40.75	79.04	96.34
ANT	7.54 ± 0.26	0.31 ± 0.01	46.11	76.80	91.72
CRB	14.41 ± 0.50	0.65 ± 0.02	45.77	76.31	97.85
FL	19.78 ± 0.69	0.85 ± 0.03	60.51	75.93	95.41
PY	15.81 ± 0.55	0.67 ± 0.02	60.70	74.21	70.69
BaA	0.55 ± 0.02	0.02 ± 0.0007	46.47	67.32	92.24
CHR	2.69 ± 0.09	0.11 ± 0.004	46.36	77.16	95.35
BbF	0.80 ± 0.03	0.03 ± 0.001	46.46	67.31	86.21
BkF	0.80 ± 0.03	0.03 ± 0.001	46.46	79.30	93.17
BaP	0.07 ± 0.003	0.003 ± 0.0001	46.49	71.36	97.77
IcdP	1.09 ± 0.04	0.04 ± 0.001	46.44	67.28	97.98
DahA	4.60 ± 0.16	0.19 ± 0.007	46.26	67.02	96.60
BghiP	0.51 ± 0.02	0.02 ± 0.0007	46.47	61.33	96.45

(A) Inf.= influent, (B) Eff. = effluent.

The results of this study showed that the PAHs removal was not dependent on the ring numbers of benzene for the individual PAHs species. Therefore, it can be concluded that a correlation between the removal of the PAHs and water solubility, Henry's law constants and vapor pressure, was not observed at 60^{o}C and the difference is not significant (R^2=0.54, F=3.34, P=0.001) (Table 5.15). It was found that the PAHs degradation is a function of long sonication time (150 min) and high temperature (60^{o}C). A high correlation was found between PAHs yields, time and temperature (R^2=0.97). This correlation is also significant (F=17.78 p=0.001). The two experimental conditions (640 W sonication power and 35 kHz sonication frequency) employed in this study influenced the important physical parameters related to cavitation bubbles such as the extent of radical production from the bubble, the thickness of the liquid shell surrounding the bubble, the concentration of the PAHs in the interfacial region and extent of radical scavenging in the medium (Chakinala et al., 2008a; 2008b). For this reason, most probably, a significant difference was not observed between the lower molecular weight PAHs (e.g. those with two, three or four aromatic rings) and the higher molecular weight, more hydrophobic PAHs for their individual removals (R^2=0.82, F=13.67, p=0.001) at 60^{o}C. On the other hand, low-frequency ultrasound is expected to induce destructive effects for hydrophobic solutes, since they can easily diffuse near cavitation bubbles and undergo pyrolytic destruction inside the collapsing bubble or hydroxylation and thermal decomposition at its interfacial sheath (Chakinala et al., 2008a; 2008b Rokhina et al., 2009).

Given that all PAHs with high molecular used in this study are relatively non-volatile, their ability to migrate towards the bubble and rapidly decompose at the interface is likely to be dictated by their hydrophobicity. It appears that the more hydrophobic PAHs are all readily susceptible to sonochemical degradation and high removal yields (86.00-98.00%) is achieved within 150 min of irradiation with the conditions under consideration (Table 5.14).

Table 5.15 Pysical and chemical properties of PAHs in this study (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml).

PAHs	**CAS-No**	**MF**	**MW**	**T_M**	**T_B**	**S_W (25°C)**	**V_P (25°C)**	**H (25°C)**	**log K_{OA} (25°C)**	**log K_{OW}**	**IPC**
FLN	86-73-7	$C_{13}H_{10}$	166	115	295	1.69	$6.00x10^{-4}$	$9.62x10^{-5}$	6.90	4.18	55.57
PHE	85-01-8	$C_{14}H_{10}$	178	99	340	1.15	$1.21x10^{-4}$	$3.35x10^{-4}$	7.68	4.16	12.55
FL	206-44-0	$C_{16}H_{10}$	202	108	384	0.26	$9.22x10^{-6}$	$8.86x10^{-6}$	8.76	5.16	19.36
PY	129-00-0	$C_{16}H_{10}$	202	151	404	$1.35x10^{-1}$	$4.50x10^{-6}$	$1.19x10^{-5}$	8.81	4.88	15.54
CHR	218-01-9	$C_{18}H_{12}$	228	258	448	$2.00x10^{-3}$	$6.23x10^{-9}$	$5.23x10^{-6}$	10.30	5.81	$2.68x10^{-1}$
BbF	205-99-2	$C_{20}H_{12}$	252	168	-	$1.50x10^{-3}$	$5.00x10^{-7}$	$6.57x10^{-7}$	11.34	5.78	$7.90x10^{-1}$
IcdP	193-39-5	$C_{22}H_{12}$	276	164	536	$1.94x10^{-3}$	$1.25x10^{-10}$	$3.48x10^{-7}$	12.43	6.7	$10.93x10^{-2}$
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	$2.49x10^{-4}$	$1.00x10^{-10}$	$1.23x10^{-7}$	12.59	6.75	$45.78x10^{-2}$
BghiP	191-24-2	$C_{22}H_{12}$	276	278	> 500	$2.67x10^{-4}$	$1.00x10^{-10}$	$3.31x10^{-7}$	12.55	6.63	$51.30x10^{-2}$

fluorene (FLN), phenanthrene (PHE), fluoranthene (FL), pyrene (PY), chrysene (CHR), benz[*b*]fluoranthene (BbF), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g/mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg/l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 /mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng/ml)

Among the PAHs studied, only in the case of PY increasing the temperature did not influence its removal (Table 5.14). The yield of PY decreased slightly as increasing the temperature from 120°C to 150°C while the removals of PHE, BghiP and the rest of the PAHs increased. The slight decrease in degradation rate observed for PY may be due to the increased solution temperature. For PY, an increased solution temperature might imply a slightly higher adsorption on the air-water interface and an increased diffusivity. These factors act to affect the slight accumulation of PY on the interface in different ways. As the temperature increased, the increased diffusivity may contribute to more available PY at the subsurface for adsorption. Thus, a slight increase in PY removal efficiency was observed from 25°C to 60°C (Tables 5.14 and 5.15). The decrease in removal efficiency at 150°C may be due to less favorable adsorption resulting in reduced accumulation on the interface. Although, the effects of increasing temperature on the sonolytic removal efficiencies were also examined for all PAHs, in this section only PHE and BghiP are discussed.

The removal yields of PHE and BghiP increased with increasing temperature. For partitioning into the bubble, the increased solution temperature will allow PHE and BghiP molecules to more easily enter the cavitation bubble (i.e., increase diffusivity). At higher temperatures this effect will be enhanced and this may be the cause of the increase in removal rates for PHE and BghiP at 150°C.

The results of this study showed that although a strict correlation between the remaining percentage of the aforementioned PAHs and physicochemical properties was observed after 30 min, 60 and 120 min sonication times (R^2=0.89, P=4.89, p=0.001), a significant correlation was not observed between the remaining percentages of PAHs and their properties after 150 min sonication time (R^2=0.45, p=16.56, P=0.01) and over 90.00% removal rates of the all PAHs was achieved. Furthermore, it becomes evident that a larger hydrophobicity resulted in smaller reaction kinetic constants of the PAHs. Low initial PAHs concentrations led to low reaction rates and also to smaller residual concentrations. The coefficient of the correlation between the residual concentration and the total initial concentration of the single PAHs was strong and highly significant (R^2=0.85, $p < 0.001$).

Several investigators have reported contradictory findings regarding the temperature effect. In certain reaction systems for instance, the net effect of an increase in T_o and consequently T_{max}, is an increase in degradation rates. This occurs up to the point at which the cushioning effect of the vapor begins to dominate the system and further increases in liquid temperature result in reduced reaction rates. The fact that removal decreases with increasing liquid temperature is believed to be associated with the effect of temperature on both the bubble formation energy threshold and the intensity of bubble implosion. The maximum temperature (T_{max}) obtained during the bubble collapse is given as follows Eq. (5.1):

$$T_{\max} = T_o \left(\frac{P}{P_o}\right)(\gamma - 1) \tag{5.1}$$

where, T_o is the liquid bulk temperature, P_o is the vapor pressure of the solution, P is the liquid pressure during the collapse and γ is the specific heat ratio (i.e. the ratio of constant pressure to constant volume heat capacities). Increased temperatures are likely to facilitate bubble formation due to an increase of the equilibrium vapor pressure; nevertheless, this beneficial effect is compensated by the fact that bubbles contain more vapor which cushions bubble implosion and consequently reduces $T_{max.}$ In addition to this, increased temperatures are likely to favor degassing of the liquid phase, thus reducing the number of gas nuclei available for bubble formation (Psillakis et al., 2004).

In order to detect the effect of increasing sonication time on the yields of less hydrophobic PAHs with low benzene rings (PHE, ANT, CHR, BbF and PY) and more hydrophobic PAHs with high benzene yields (DahA and BghiP) the raw PCI ww samples were sonicated at a temperature of 60°C at increasing sonication times (from 60 to 120 min and 150 min). The increase in temperature to 60°C will increase the kinetic reaction to a point at which the cushioning effect of the vapor in the bubble begins to dominate the system. Since the PAHs are relatively non-volatile, the degradation reaction took place in the gas-liquid film between the cavitating bubble and the bulk liquid mixture. As the reaction temperature increased, the rate of diffusion of PAHs from the bulk liquid phase to the reaction zone was accelerated. An increase in temperature up to 60^{o}C improved the intensity of the cavitation, thus increasing the amount of free radicals produced within the bubble. It was suggested that these free radicals were required for the degradation reaction to occur and that they diffuse from the vapor cavity to the gas-liquid film where reaction ensues. As the rates of the counter diffusing reactants became comparable, a further increase in temperature (up to 80–90^{o}C) had little or no effect on the reaction (i.e. the percent change in PAHs concentration reached a plateau as a function of temperature).

The results of the study showed that as the sonication time was increased the yields of BghiP, CHR, ANT and BbF increased while the destruction yields of DahA, PHE and PY decreased after 150 min sonication time (Figure 5.10). The effect of sonication time on the BghiP, CHR, ANT and BbF removals was significant for 150 min sonication time at 60^{o}C (R^2=0.98, F=14.56, $p < 0.01$). No significant correlation was found between the DahA, PHE and PY yields and 150 min sonication time at 60^{o}C (R^2=0.58, F=6.39, $p < 0.01$). The treatment by sonication converts PAHs with multiple benzene rings to much smaller compounds. In such cases it is obvious that higher sonication times are needed for complete mineralization. Short sonication times (60 min) did not provide high degradation yields for refractory PAHs since they were not exposed for a long enough time to ultrasonic irradiation (Figure 5.10).

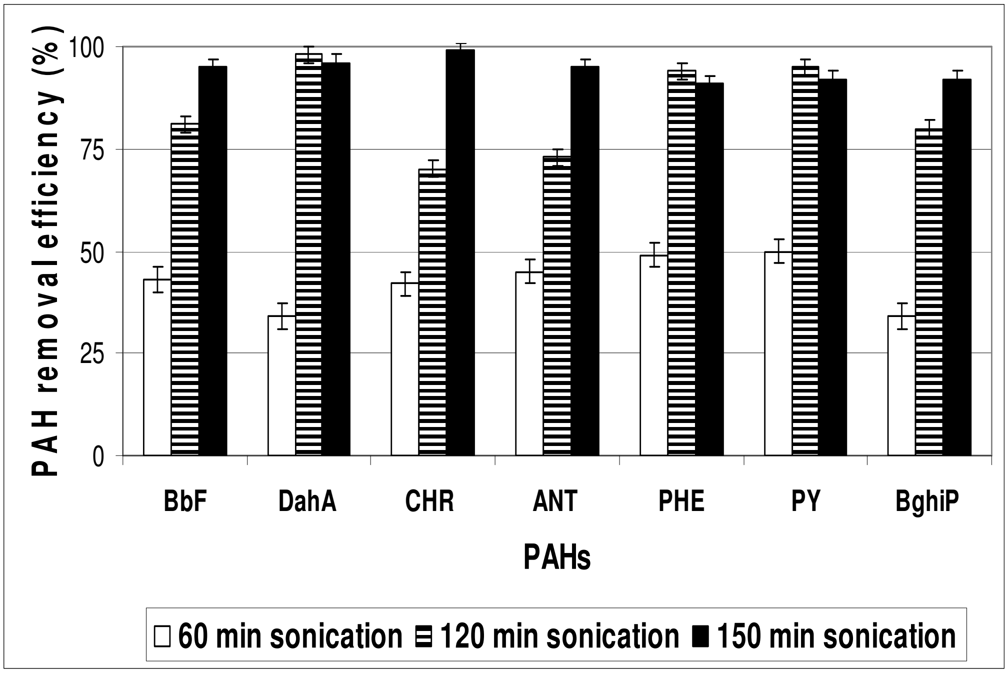


Figure 5.10 Effect of increasing sonication time on PAHs removal efficiencies at 60°C (sonication power=640 W, sonication frequency=35 kHz).

Therefore, a decrease in the percentage of remaining PAHs was expected at longer sonication times due to sufficient radical reactions through cavitation. It was found that the yields in PAHs with high benzene rings (DahA and BghiP; E=90.00–92.00%) were as high as the PAHs with lower benzene rings (BbF, CHR, PHE, PY and ANT; E=92.00–95.00%). In order to explain this, it is important to mention some of the physical/chemical properties of these compounds. Table 5.16 shows the Henry's law constant, the pseudo second-order reaction rate constant for reaction with $OH^{\bullet}$ ($k_{OH}{}^{\bullet}$), the solubility and the octanol–water partitioning coefficient (K_{OW}) of these seven PAHs. The solubilities of DahA and BghiP are approximately 15 times lower than for CHR and BbF, 100 times lower than for ANT and 10000 times lower than for PHE (Table 5.16). Moreover, the Henry's law constant of DahA and BghiP are also lower than ANT, PY, BbF and CHR. Given the lower solubilities and the low Henry's law constant of DahA and BghiP and following the studies on non-volatile, hydrophobic compounds (Benabdallah El-Hadj et al., 2007; Quesada-Penate et al., 2009), we would expect lower degradation yields for DahA and BbF compared to ANT and CHR. However, the data in Figure 5.10 does not agree with this supposition. There are two possible explanations for the enhancement in the yields for DahA and BghiP: (1) They have high removals as the ANT, PY, BbF and CHR, via the $OH^{\bullet}$ pathway (hydroxylation) and/or (2) DahA and BghiP accumulate at the interface of the liquid gas phase to a greater degree than the other PAHs by a subsequent entrapment of the pollutant vapor in the cavitation bubble (pyrolysis). Reported second order reaction rate constants for the DahA and BghiP listed in Table 5.16, are lower than those of the other PAHs. Therefore, suggestion (1) can be ignored. The thickness of the liquid shell surrounding the bubble, in which temperature rises, is higher for hydrophobic organics like PAHs. In this shell, in principle, the thermal penetration depth in the bulk medium varies directly with the bubble size and the thickness of liquid layer around the bubble that gets heated up is larger for saturated medium. Finally, the extent of pyrolysis in the liquid shell depends on the thickness of this shell and concentration of the pollutant molecules in it.

Table 5.16 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml).

PAHs	**CAS-No**	**MF**	**MW**	T_M	T_B	S_W	**V_P (25°C)**	**H (25°C)**	**log K_{OA} (25°C)**	**Log K_{OW}**	**SORKC**	**IPC**
PHE	85-01-8	$C_{14}H_{10}$	178	99	340	1.15	$1.21x10^{-4}$	$3.35x10^{-5}$	7.68	4.46	23.40	125.58
ANT	120-12-7	$C_{14}H_{10}$	178	215	340	$4.34x10^{-2}$	$2.67x10^{-6}$	$5.56x10^{-5}$	7.71	4.45	28.20	3.63
PY	129-00-0	$C_{16}H_{10}$	202	151	404	$1.35x10^{-1}$	$4.50x10^{-6}$	$1.19x10^{-5}$	8.81	4.88	15.60	14.49
CHR	218-01-9	$C_{18}H_{12}$	228	258	448	$2.00x10^{-3}$	$6.23x10^{-9}$	$5.23x10^{-6}$	10.30	5.81	12.50	2.32
BbF	205-99-2	$C_{20}H_{12}$	252	168	-	$1.50x10^{-3}$	$5.00x10^{-7}$	$6.57x10^{-7}$	11.34	5.78	9.50	0.23
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	$2.49x10^{-3}$	$1.00x10^{-10}$	$1.23x10^{-7}$	12.59	6.75	7.60	5.42
BghiP	191-24-2	$C_{22}H_{12}$	276	278	> 500	$2.60x10^{-4}$	$1.00x10^{-10}$	$3.31x10^{-7}$	12.55	6.63	6.90	0.58

phenanthrene (PHE), anthracene (ANT), pyrene (PY), chrysene (CHR), benz[*b*]fluoranthene (BbF), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g / mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg / l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 / mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; SORKC: Second order reaction kinetic constant (ng/ml.s); IPC: Initial PAH concentration (mean, ng / ml).

If the pollutant is hydrophobic in nature, characterized by low solubility in water, it tends to partition between the bulk medium and bubble interface (Quesada-Penate et al., 2009). The bubble–bulk interface also has a hydrophobic character, and hence, the concentration of the hydrophobic pollutant molecules in this region is much higher than the bulk. Therefore, hydrophobic PAHs concentrations were high in the interfacial region between bubble and bulk. The PAHs transfer process from the PCI ww to the cavitational bubbles and the removal of PAHs are jointly controlled by the hydrophobicity of PAHs. Increasing hydrophobicity by low Henry's law constants induces destructive effects for hydrophobic PAHs, since they can easily diffuse near the cavitation bubbles and undergo pyrolytic destruction inside the collapsing bubble (Rae et al., 2005). Given that PAHs with high molecular weights (Table 5.16) in PCI ww have the ability to migrate towards the bubble, rapid decomposition at the interface is likely to be dictated by their hydrophobicity. It appears that the more hydrophobic DahA is readily susceptible to sonochemical degradation and nearly complete removal (99.00%) is achieved within 150 min of irradiation at 60^oC (Figure 5.10). On the other hand, the hydrophobicity of an organic compound can be described fairly well by its octanol–water partition coefficient and water solubility. The higher octanol–water partition coefficient of hydrophobic PAHs results in higher PAHs removal although there are a few exceptional cases. In the exceptional cases, such as the yields of CHR and BbF, the vapor pressure and/or the reactivity of PAHs with intermediates (i.e. free radicals, atoms and active molecules) generated in situ in bulk liquid, play a simultaneous role, at least to a certain extent. Although, the BbF is more hydrophobic (having higher octanol–water partition coefficient) than that of CHR its removal efficiency is lower than that of CHR. This could be explained as follows: the hydrophobicity of BbF is higher with low Henry's law constant (log P_{OW}=5.98 at 25^oC) compared to CHR with high Henry's law constant (log P_{OW}=5.71 at 25^oC), but its vapor pressure (V_P, $5.00x10^{-7}$ mm Hg at 25^oC) is low compared to CHR (V_P, $6.23x10^{-9}$ mm Hg at 25^oC) (Table 5.16). Hence, the yield of BbF is lower compared to CHR after 150 min sonication (Figure 5.10). A significant linear relationship was found between the hydrophobic PAHs yields and the Henry's law constants and the solubilities of these PAHs (R^2=0.96, F=14.67, p=0.001) while the relationship between vapor pressure and the PAHs removals was not significant (R^2=0.65, F=7.95, p=0.001).

Although, the BbF, DahA, CHR and ANT removals increased at increasing sonication times among the PAHs studied it was found that PHE, PY and BghiP concentrations decreased as the sonication time increased from 60 to 120 min while the concentration of these PAHs increased after 150 min sonication (Figure 5.10). The reason of this could be explained by the ultimate destruction of these PAHs after 120 min sonication. This sonication time could be accepted as the optimum time for the maximum degradation of PHE, PY and BghiP to the inter-metabolites.

5.9.2.2.1 Produced Metabolites from PHE, PY and BghiP PAHs in PCI ww

With the increase of sonication time to 150 min PHE was removed with an efficiency of 96.34% since this PAH degraded to the by-products NAP, p-hydroxy-benzoic acid and FLN (Table 5.17). PY was degraded to di–hydroxy pyrene and to benzoic acid while BghiP degraded to pyrene di-hydrodiol and to benzoic acid (Table 5.17)

Table 5.17 By-products of PHE, PY and BghiP at a frequency of 35 kHz after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**Initial PAHs Conc. (ng/ml)**	**Sonication Metabolites (ng/ml)**
PHE	125.58	naphthalene: 51; p–hydroxybenzoic acid:8.90; fluorene: 39
PY	14.49	di–hydroxy pyrene: 5.10; benzoic acid: 3.90
BghiP	0.58	benzoic acid: 0.05; pyrene di–hydrodiol: 0.32

Free radical and pyrolysis reactions produce different products, with relative abundances depending on the nature of the solute and its concentration. For example, Adewuyi (2001; 2005a, 2005b) found that FLN and benzoic acid are the sonication metabolites of PHE and methyl radicals ($CH_3^{\bullet}$) formed from the pyrolysis of solvent-hexane. Dewulf et al. (2001) found that sonolysis of simple hydrocarbons creates the same kind of products associated with very high-temperature pyrolysis. $CH_3^{\bullet}$ and ethyl ($CH_3CH_2^{\bullet}$) radicals are expected to be formed when hexane is decomposed sonochemically as a solvent (Rae et al., 2005). $CH_3^{\bullet}$ has also been shown to form during the pyrolysis of acetone molecules. These alkyl radicals then react with PHE to form different types of methyl- and ethyl-phenanthrene by-products. In our study, although $CH_3^{\bullet}$ and $CH_3CH_2^{\bullet}$ were not measured the metabolites found from the sonication of PHE (FL, NAP and benzoic acid) agree with the results found by older and more recent research as reported by Rae et al. (2005) (Table 5.17). The mechanism of pyrolysis of PHE had two pathways: (1) Loss of one carbon in PHE and yielding CH_4 and FLN and (2) fragmentation resulting in a four carbon fragment and NAP. Therefore, FLN is an indication of a pyrolysis by-product formed from the PHE due to high-temperature reactions in or near a cavitation bubble as reported by Adewuyi (2001). In our study, CH_4, H_2 and CO_2 gases were identified in the headspace of the sonicator reactor. The GC spectra of these gases are illustrated in (Figure 5.11).

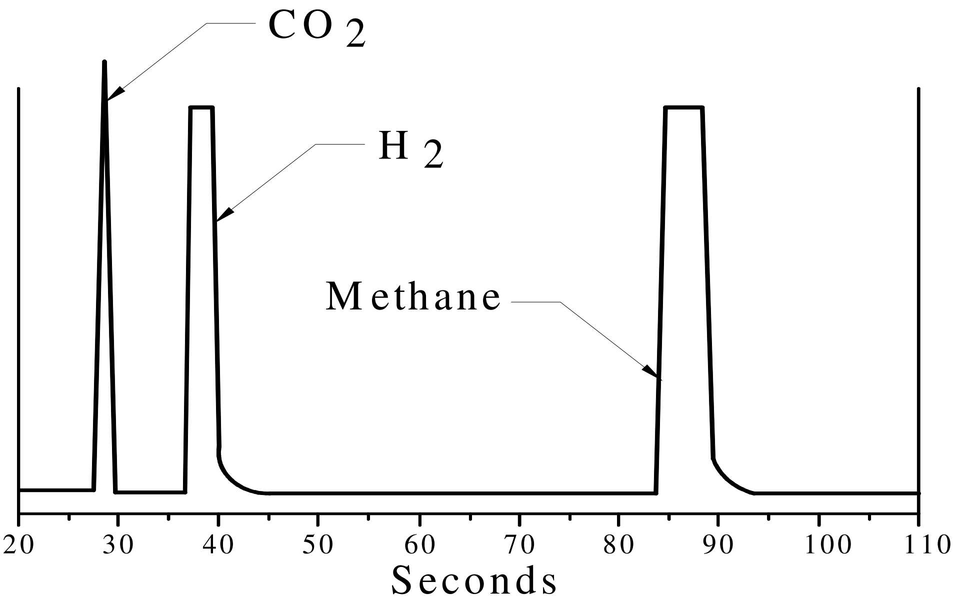


Figure 5.11 $CH_4(g)$, $H_2(g)$ and $CO_2(g)$ spectra measured in the headspace of the sonicator by GC (sonication power=640 W, sonication frequency=35 kHz).

The increasing of PAHs concentrations after 150 min sonication time could be attributed to the re-formation of the PHE, PY and BghiP from the by-products (Figure 5.10). We suspected that the increase of PHE with longer sonication time may be due to the re-formation of PHE from the by-products mentioned above and from the FLN. The FLN formed during the sonication of PHE may be attacked by $CH_3^{\bullet}$ to regenerate PHE as reported by Adewuyi (2001). Cyclization reactions of PHE with methyl- or ethyl-naphthalene may also contribute to the re-formation of PHE. A radical mechanism proposed by David (2009) showed PHE formation from pyrolysis of 9,9–dimethyl–fluorene at 800°C by a free radical ring expansion process. Wu & Ondruschka (2005) also reported NAP and benzene formation during PHE pyrolysis at < 900°C. Furthermore, Little et al. (2002) studied PHE pyrolysis at 700 and 850°C and reported that NAP is one of the pyrolysis products of PHE. Therefore, the NAP by-product detected in this study may be direct pyrolysis products of PHE. Similarly, PY yields increased after 120 min sonication time since the PY degraded to di–hydroxy pyrene and to benzoic acid (Table 5.17). Then we suspected that PY reproduced from the hydroxy-pyrene since the PY yields decreased. Similarly, the yield of BghiP increased after 120 min sonication time with sonodegradation to its by-products namely, benzoic acid and pyrene di-hydrodiol at 63°C (Table 5.17). However, the yields of the BghiP decreased after 150 min sonication time. This could be explained by the re-formation of BghiP from pyrene di-hydrodiol and benzoic acid (Table 5.17).

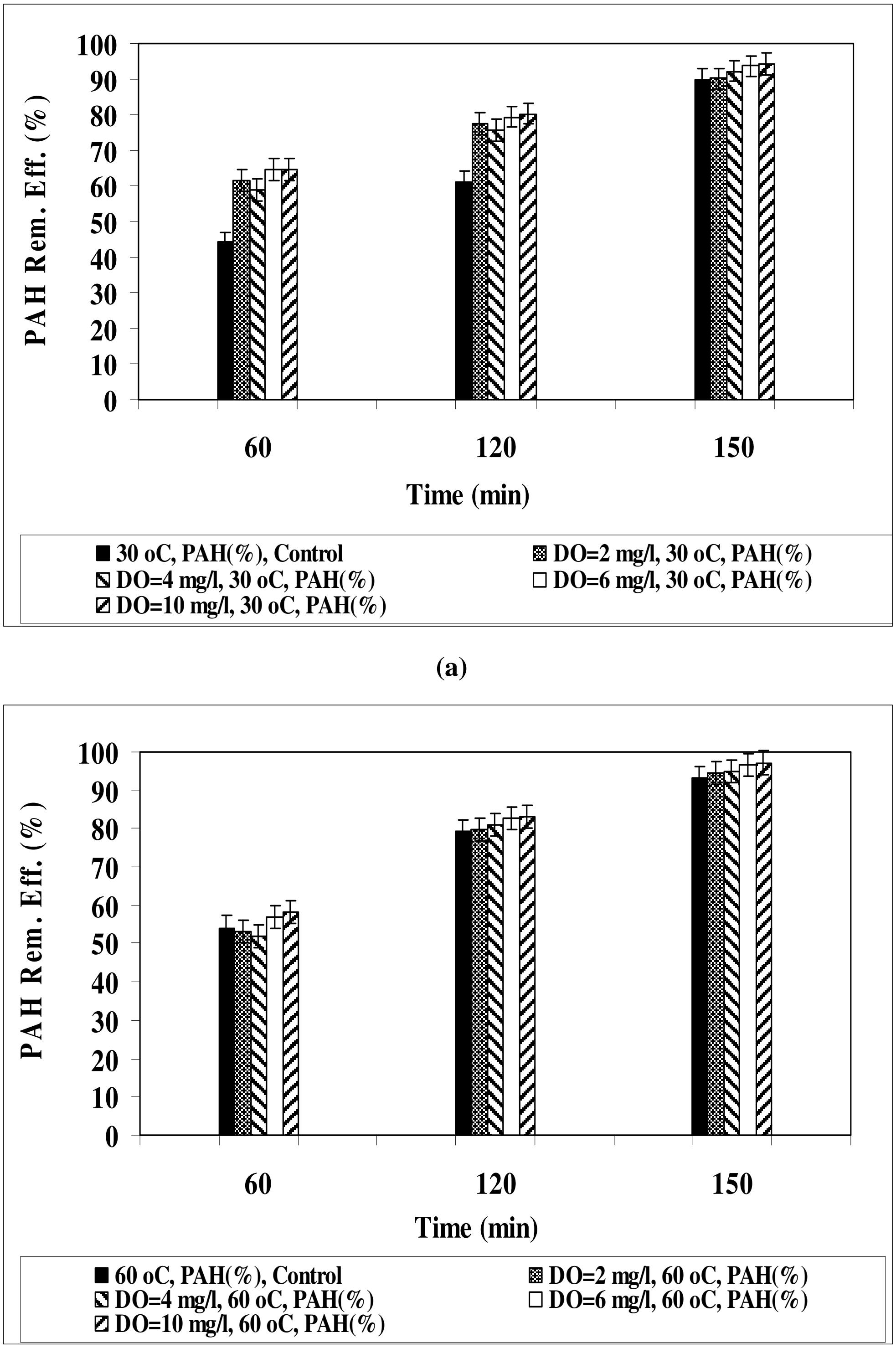
In this study, the presence of CH_4, H_2 and CO_2 gases indicated not only the destruction of the PAHs but also confirmed the mechanism ‘‘pyrolysis” with degassing of the medium throughout sonication. The results given above are consistent with our results. When PHE is sonicated in an organic solvent, it is expected that a certain number of PHE molecules will migrate into the gaseous cavitation bubbles. Then PHE molecules are available to migrate towards the cavitation bubble interfaces or volatilize into the cavitation bubbles to react under pyrolysis thus leading to a lower percentage remaining (Adewuyi, 2001). In addition, at higher concentrations of PHE, the solute is more likely to compete for reaction with $CH_3^{\bullet}$, which could also contribute to the loss of PHE (Little et al., 2002).

It was observed that the PAHs with multiple benzene rings were also degradable with high yields, even though some studies demonstrated that sonication is not effective for PAHs with a large number of benzene rings (Psillakis et al., 2004). The PAHs yields obtained in our study are high in comparison to the removal performances of PAHs in the studies given below. In the study by Laughrey et al. (2001) 77.00% PAHs removal efficiency was observed for the sonochemical degradation of 50.00 μg/l of initial PAHs mixture concentration (NAP, ACL and PHE) in water after 120 min sonication time, at 40°C, at 150 W and at 24 kHz. Benabdallah El-Hadj et al. (2007) found 31.00-34.00% and 44.00-50.00% PAHs removals in mesophilic (35°C) and thermophilic (55°C) conditions for NAP and PY at 20 kHz and at 70 W, after 110 min sonication time, before anaerobic digestion. The yields obtained in the aforementioned studies are low in comparison to the removal performances of PAHs found in this study. It was observed that the PAHs with high benzene rings were also degradable with high yields, even though some studies demonstrated that sonication is not effective for PAHs with high benzene rings (Laughrey et al., 2001).

5.9.3 Effect of DO Concentrations on the Removal of PAHs in PCI ww at Increasing Sonication Times and Temperatures

The raw PCI ww samples were oxygenated with increasing DO concentrations (2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l) with pure O_2 before the sonication experiments. 90.22%, 92.27%, 93.77% and 94.32% total PAHs removal efficiencies were measured in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO concentrations, respectively, after 150 min of sonication time at pH=7.0 and at 30^{o}C (Figure 5.12a). Only 4.00, 6.00 and 10.00 mg/l DO concentrations increased the total PAHs removal efficiencies from 90.11% to 92.27-94.32% in comparison to the non-oxygenated samples (control, E=90.11% total PAHs at pH=7.0) at a temperature of 30^{o}C and a sonication time of 150 min. In other words, the effect of increasing DO concentrations on the total PAHs removals was found to be insignificant at a temperature of 30^{o}C and a sonication time of 150 min. The total PAHs yields also increased significantly (from 45.34% to 64.66% and from 62.40% to 80.34%) after 60 and 120 min sonication times, respectively, compared to the control at all DO concentrations for the same temperature.

94.67%, 95.00%, 96.79% and 97.23% total PAHs removal efficiencies were obtained in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO at pH=7.0 and at 60^{o}C after 150 min sonication time (Figure 5.12b). As shown, the total PAHs removal efficiencies increased as the sonication time increased. However, the PAHs yields did not show a significant increase at increasing DO concentrations compared to the control (DO=0.00 mg/l while E=96.90% total PAHs at pH=7.0 and at 60^{o}C). The maximum total PAHs removal efficiency was 97.23% after 150 min sonication time in DO=10.00 mg/l at 60^{o}C. Increasing the temperature also did not increase the total PAHs removal efficiencies at increasing DO (ANOVA, F=2.51, p=0.001) (Figure 5.12b).



(a)

(b)

Figure 5.12 Effect of increasing DO concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

Table 5.18 shows removal efficiencies for seventeen PAHs in the presence of 10.00 mg/l DO at 60°C after 60 min, 120 and 150 min sonication times since the maximum total PAHs removals was obtained at a DO concentration of 10.00 mg/l.

Table 5.18 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments in DO=10.00 mg/l concentration after 60 min, 120 and 150 min sonication times at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml n=3, mean values ± SD).

PAHs	**Inf.** [(A)] **T=0 min PAHs (ng/ml) ± SD**	**Eff.** [(B)] **T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
NAP	1871.45 ± 65.50	455.54 ± 15.94	31.52	65.04	98.66
ACL	52.30 ± 1.83	1.94 ± 0.07	55.88	79.87	97.46
ACT	70.56 ± 2.47	2.33 ± 0.08	51.15	78.82	94.85
FLN	58.16 ± 2.04	2.03 ± 0.07	55.64	79.52	96.47
PHE	138.78 ± 4.86	6.20 ± 0.22	52.69	75.31	96.77
ANT	7.52 ± 0.26	0.21 ± 0.007	59.87	80.71	92.70
CRB	14.35 ± 0.50	0.45 ± 0.02	57.55	82.25	98.10
FL	19.68 ± 0.50	0.59 ± 0.02	61.30	81.90	95.95
PY	15.74 ± 0.55	0.47 ± 0.02	57.48	79.15	96.20
BaA	0.55 ± 0.02	0.02 ± 0.0007	56.20	73.18	93.16
CHR	2.69 ± 0.09	0.08 ± 0.003	50.10	75.04	95.90
BbF	0.80 ± 0.03	0.02 ± 0.0007	59.66	71.17	87.84
BkF	0.80 ± 0.03	0.02 ± 0.0007	58.19	83.17	93.98
BaP	0.07 ± 0.003	0.002 ± 0.0001	65.22	83.22	98.04
IcdP	1.09 ± 0.04	0.03 ± 0.001	58.18	85.15	98.22
DahA	4.60 ± 0.16	0.13 ± 0.005	52.01	82.91	97.01
BghiP	0.51 ± 0.02	0.01 ± 0.0004	51.20	83.19	96.87

(A) Inf.= influent, (B) Eff. = effluent.

The yield of 2 and 3-ring PAHs removals was almost 96.47% for FLN and 96.77% for PHE, respectively, in raw PCI ww samples containing 10.00 mg/l DO at 60^{o}C after 150 min of sonication. The removal efficiencies of four ring PAHs (CHR, BkF, BaP and IcdP) were also higher (efficiency varied between 93.98 and 98.22%) in the samples oxygenated with 10.00 mg/l DO at 60^{o}C in comparison to the PAHs containing few benzene rings after 150 min sonication time. Similarly, around 96.87-97.01% removal efficiencies were obtained for PAHs with five rings BghiP, DahA (Table 5.18).

The PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww were measured with HPLC in DO=10.00 mg/l after 120 min sonication time at 25^{o}C (Table 5.19).

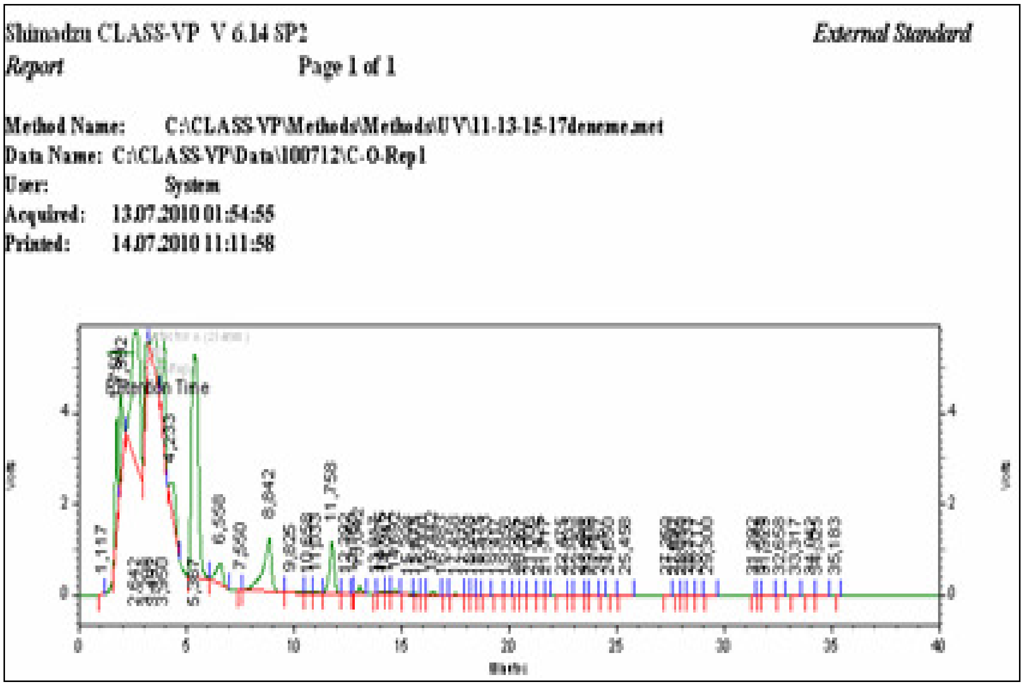
Table 5.19 The measurements of PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww with HPLC in DO=10.00 concentration mg/l after 120 and 150 min sonication times at 25^{o}C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs Intermediates	**PAH_0 (ng/ml)**	**120 min**			**150 min**
		PAH (ng/ml)	**PAHR (%)**	**PAHI (ng/ml)**	**PAHIR (%)**
1–Methylnaphthalene	1378.77	413.63	70.00	274.24	80.11
9–Hydroxyfluorene	1378.77	413.63	70.00	176.07	87.23
9,10–Phenanthrenequione	1378.77	413.63	70.00	55.29	95.99
Benzoic acid	1378.77	413.63	70.00	129.88	90.58
1,2,3–Thiadiazole–4–carboxylic acid	1378.77	413.63	70.00	48.26	96.50

PAH_0: Initial total PAHs concentration (ng/ml), PAH: Total PAHs concentration (ng/ml) after 120 min sonication time, PAHR: Total PAHs removal efficiency (%) after 120 min sonication time, PAHI: PAHs intermediates concentration (ng/ml) after 120 min sonication time, PAHIR: removal of PAHs intermediates (%) after 150 min sonication time.

As shown in Table 5.19, the initial total PAHs concentration of 1378.77 ng/ml decreased to 413.63 ng/ml in DO=10.00 mg/l after 120 min sonication time at 25°C. From 1378.77 ng/ml initial PAHs 274.24 ng/ml 1–methylnaphthalene, 176.07 ng/ml 9–hydroxyfluorene, 55.29 ng/ml 9,10–phenanthrenequione, 129.88 ng/ml benzoic acid and 48.26 ng/ml, 1,2,3–thiadiazole–4–carboxylic acid were produced after 120 min sonication time at 25°C. It was found that the initial PAHs sono-degraded to the inter-metabolites as mentioned above (Table 5.19). After 120 min sonication time the remaining PAHs concentration was found to be high (695.03 ng/ml). The initial PAHs concentration of 1378.77 ng/ml converted to 683.74 ng/ml PAHs intermetabolites in question as aforementioned. The low removal efficiency of the total PAHs (70.00%) could be attributed to the studied low temperature (25°C) although, DO increased the PAH yields at 60°C. The PAHs intermediates namely, 1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid were sonodegraded with yields of 80.11%, 87.23%, 95.99%, 90.58% and 96.50%, respectively, in DO=10.00 mg/l after 150 min sonication time at 25°C (Table 5.19).

The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww in DO=10.00 mg/l after 120 min sonication time at 25°C, was given in Figure 5.13.



Shimadzu CLASS-VP V 6.14 SP2 External Standard
Report Page 1 of 1

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Data Name: C:\CLASS-VP\Data\100712\C-O-Rep1
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Acquired: 13.07.2010 01:54:55
Printed: 14.07.2010 11:11:58

Figure 5.13 The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) performed in PCI ww in DO=10.00 mg/l concentration after 120 min sonication time at 25^{o}C (sonication power=640 W, sonication frequency=35 kHz).

O_2 mediates the rate of mineralization of PAHs. The higher DO content of PCI ww resulted in faster rates of PAHs degradation through sonication, supporting the hypothesis that increased oxygenation was largely responsible for the enhanced PAHs degradation. Although, O_2 exposure is an important factor in PAHs degradation it was reported that saturating the solutions cause decreases in $O_2H^\bullet$ production resulting in low PAHs yields. In the presence of O_2, the reactive radicals ($O^\bullet$, $OH^\bullet$, $OOH^\bullet$) will be produced by a series of reactions and thus contribute to the removal of the PAHs (Wheat & Tumeo, 1997). Although, O_2 and air have similar ratios of specific heats and thermal conductivity, the highest formation rate of H_2O_2, which was induced from the recombination of reactive radicals ($OH^\bullet$ and $O_2H^\bullet$) was observed under O_2 (Kojima et al., 2005). In oxygenated solutions, the $O_2H^\bullet$ formed by; Eq. (5.2)

$$H^\bullet + O_2 \quad \rightarrow \quad O_2H^\bullet \tag{5.2}$$

will decay with generation of H_2O_2. However, the production of the $O_2H^\bullet$ increases the oxidation process due to further formation of H_2O_2 by its recombination reaction (Kojima et al., 2005) Eq. (5.3):

$$O_2H^\bullet + O_2H^\bullet \quad \rightarrow \quad H_2O_2 + O_2 \tag{5.3}$$

The O_2 dissolved in water contributes to the effective formation of many oxidants such as $OH^\bullet$ and $O^\bullet$ by pyrolysis of O_2. At the same time, these oxidants may further react to produce $O_2H^\bullet$ (Laughrey et al., 2007; Suslick, 2000). On the other hand, the maximum temperature produced in collapsing cavitation bubble was higher by sonication in Ar than O_2, because of high specific heat ratio of Ar (Kojima et al., 2005) and O_2.With the combination of O_2 and Ar, it is considered that many oxidants such as O_3 and $O^\bullet$ were produced by stronger pyrolytic effect arising from the presence of O_2 in addition to $OH^\bullet$ typically formed by thermal decomposition of H_2O. Moreover, it is also considered that production of $OH^\bullet$ was accelerated by the reaction of $O_2H^\bullet$ and H_2O with oxidants O_3 and $O^\bullet$ (Ince et al., 2009). Hence, it is assumed that more reactive species in Ar/O_2 were formed compared with those in O_2/N_2 and in Ar. Lawton & Show (2009) reported that the decomposition of dichlorinated groups in the Ar/O_2 mixture was the highest due to the coupled effects of pyrolysis and radical reaction.

As aforementioned aqueous phase sonolysis is likely to result in the formation of H_2O_2 which may be formed through the recombination of $OH^\bullet$ at the gas–liquid interface and/or in the solution bulk. Moreover, if the solution is saturated with O_2, (H_2O) and more $OH^\bullet$ are formed in the bubble, the recombination of the former at the interface and/or in the solution bulk results in the formation of additional H_2O_2 (Wu & Ondrucschka, 2005). It was found that PAHs mainly decomposed at the gas–liquid interface through both $OH^\bullet$ oxidation and pyrolytic reactions (for instance, CH_4 and CO_2 were identified as the primary pyrolysis by-products) rather than in the solution bulk (David, 2009) (Figure 5.11). This was attributed to the fact that the PAHs, in this study, although less water soluble and non-volatile molecules, tended to accumulate at the gas–liquid interface. Furthermore, it was also found that the concentration of H_2O_2 formed during PAHs sonication experiments was substantially lower than that formed during water sonication in the absence of PAHs.

In order to verify the generation of H_2O_2, sonication tests in the absence of PAHs were carried out. As shown in Figure 5.14 the H_2O_2 concentration accumulated in deionized water (pH=6.93) increased with an increase of O_2 dosage from 2.00 up to 6.00 mg/l. The yield of H_2O_2 reached a value as high as 84.00 mg/l under sonication after 150 min in deionized H_2O whereas the H_2O_2 production was only 9.00 mg/l in wastewaters containing PAHs. This H_2O_2 level could only remove some less hydrophobic PAHs with low yields in comparison with the total amounts of PAHs removed with a mean yield of 95.00% after 150 min sonication time at 60°C. Since H_2O_2 production is an indicator of the presence of $OH^\bullet$ through sonication a low H_2O_2 concentration shows that $OH^\bullet$ did not contribute to the sonolysis of PAHs.

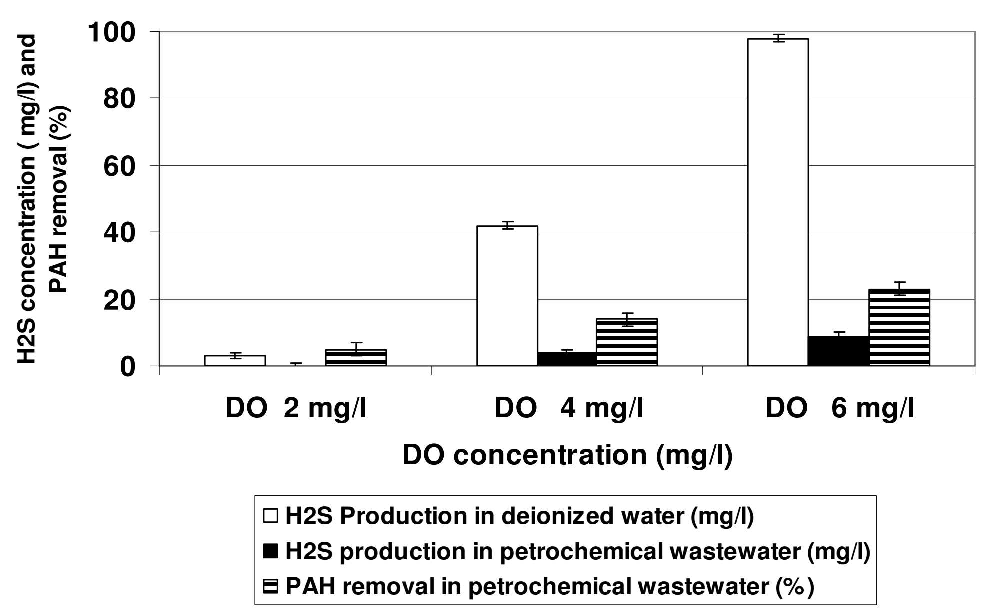


Figure 5.14 Effect of DO (2.00 mg/l, 4.00 and 6.00 mg/l) on H_2S production in deionized water and PCI ww containing PAHs after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz).

Consequently, it reveals that the hydrophobic PAHs in wastewater were principally sono-degraded mainly by way of pyrolytic reaction, deduced from the cavitation, while $OH^{\bullet}$ made a minor contribution to the removal of PAHs. Throughout the studies some gaseous by-products were observed in the headspace of the sonication reactor. 38.21-45.35% CO_2 and 11.20-15.43% CH_4 were measured after 10 min of sonication time in all the hydrophobic PAHs studied in the headspace of the sonicator reactor (Figure 5.15). The theoretical total carbon amount of initial total PAHs for $CH_4(g)$ and $CO_2(g)$ shows that the carbon balance reaches about 12.26-18.37% and 31.11-49.60%, respectively. It can be assumed that these gases are primarily formed as soon as more hydrophobic PAHs penetrate the cavitation bubbles in order to be pyrolyzed. The presences of these products indicate that the destruction of PAHs was performed via pyrolytic mechanism**.**

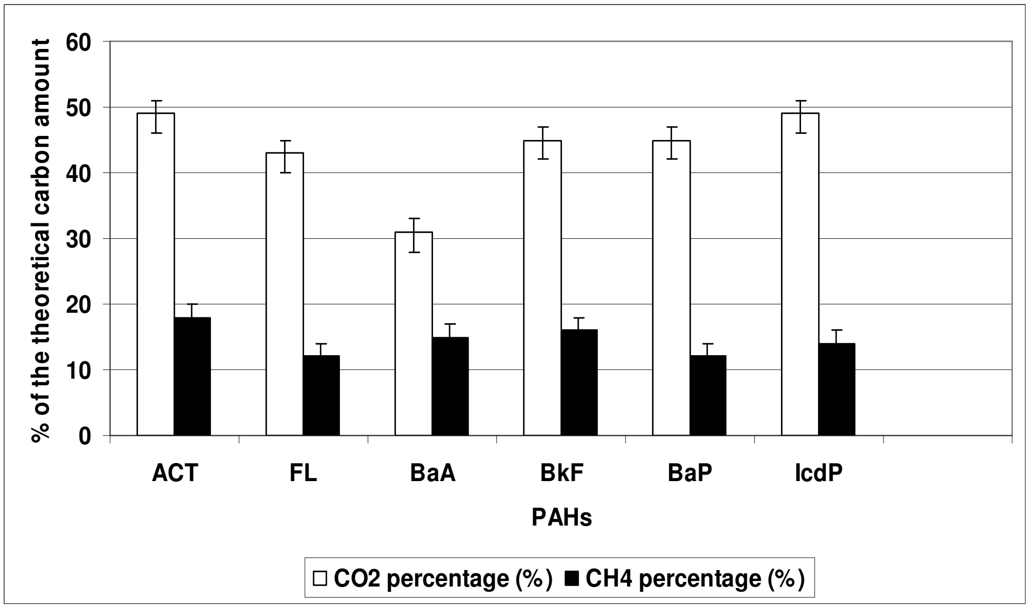
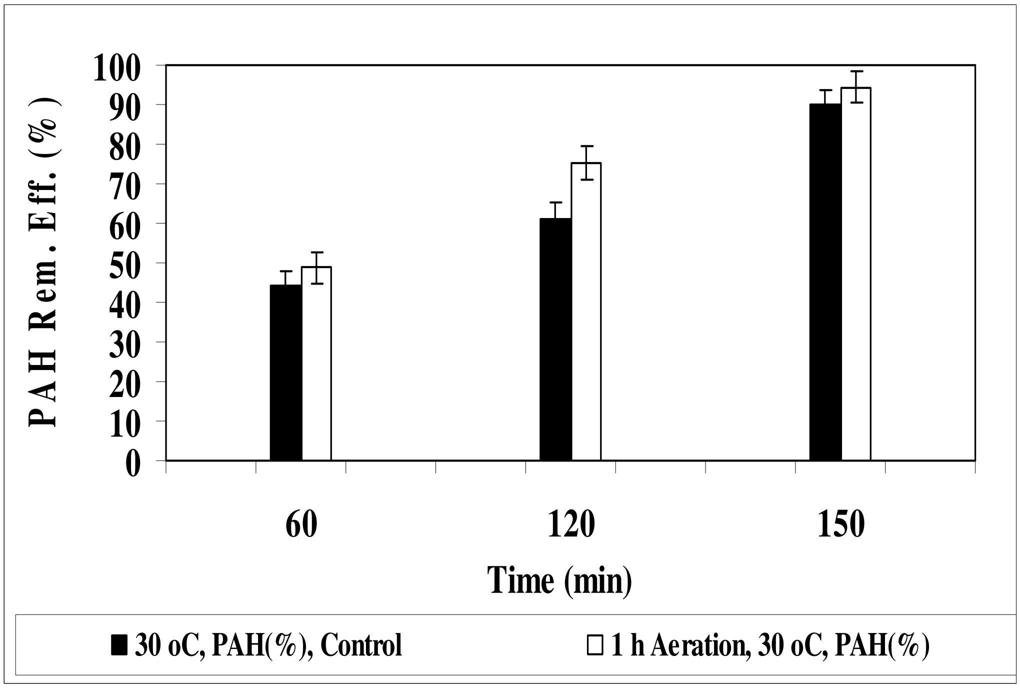


Figure 5.15 Theoretical carbon percentage based on CH_4 and CO_2 produced throughout sonication of PAHs after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz).

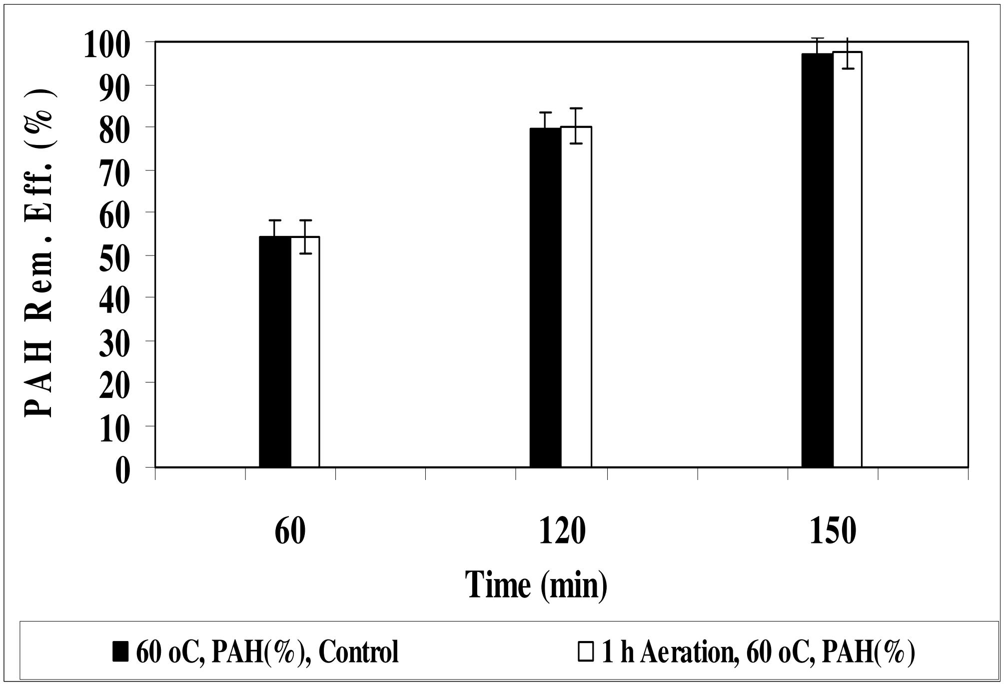
5.9.4 Effect of Aeration on the Removal of PAHs in PCI ww at Increasing Sonication Time and Temperature

PCI ww were aerated for 1 h with an air pump before the sonication experiments. 48.95%, 75.39% and 94.48% total PAHs yields were measured under 1 h aeration after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Figure 5.16a). The contribution of aeration were 3.61%, 12.99% and 4.37% to the total PAHs yields after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control (E=45.34%, 62.40% and 90.11% total PAHs after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C) (Figure 5.16a).

54.21%, 80.16% and 97.62% total PAHs removals was obtained under 1 h aeration at 60°C after 60 min, 120 and 150 min sonication times, respectively, while the control has a yield of 96.90% after 150 min sonication time (Figure 5.16b). Aeration did not increase the total PAHs yields after 60 and 120 min sonication times compared to the control at 60°C. The maximum total PAHs yield was 97.62% after 150 min sonication time under 1 h aeration at 60°C. The contribution of aeration to the total PAHs removal was not significant at 60°C (R^2=0.45, F=4.56, p=0.01) (Figure 5.16b).



(a)



(b)

Figure 5.16 Effect of 1 h aeration on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

The aeration contributed only to the removals of less hydrophobic PAHs (Table 5.20). The yields in BbF, BkF and BaP increased from 62.15-67.21% to 93.94-97.99% with 1 h aeration after 150 min sonication time at 60°C. Air in the aqueous solution was reported to play a very important role in the generation of highly oxidative $OH^{\bullet}$ enhancing the decomposition of less hydrophobic PAHs (Kojima et al., 2005). In the presence of air, reactive radicals such as $O^{\bullet}$, $OH^{\bullet}$ and $O_2H^{\bullet}$ will be produced by a series of reactions and may participate in the decomposition reaction of the less hydrophobic PAHs. These PAHs are degraded with hydroxylation reactions since the $OH^{\bullet}$ ions concentrations increased from $23x10^{-21}$ up to $8x10^{-7}$ ng/ml after 120 min sonication time under 1 h aeration. However, aeration did not contribute to the yields of more hydrophobic PAHs. The removals of IcdP, DahA and BghiP remained around 76.18-79.80% after 150 min sonication time at 60°C (Table 5.20). This reveals that the more hydrophobic PAHs in PCI ww were principally destroyed by way of pyrolytic reaction, deduced from the cavitation inside the bubble and/or at the interfacial region (Chakinala et al., 2008a, 2009b; Rae et al., 2005). It was reported that the contribution of aeration was not so effective on the sonication of PAHs with high benzene rings (De Visscher et al., 1996). Pysical and chemical properties of PAHs in this study was demonstrated in Table 5.21.

Table 5.20 Influent and effluent PAHs concentrations and maximum PAHs removal efficiencies after 60 min, 120 and 150 min sonication times under 1 h aeration at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml) (n=3, mean values± SD).

PAHs	**Inf. T=0 min PAHs (ng/ml) ± SD**	**Eff. T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
BbF	0.20±0.03	0.03±0.003	62.15	79.21	94.57
BkF	0.40±0.06	0.03±0.003	64.15	80.21	93.84
BaP	0.11±0.02	0.002±0.0003	67.21	79.30	97.99
IcdP	1.86±0.25	0.04±0.004	54.12	62.17	76.18
DahA	4.64±0.63	0.14±0.02	53.83	63.75	77.94
BghiP	0.50±0.07	0.02±0.002	54.17	69.24	79.80

Table 5.21 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml).

PAHs	**CAS-No**	**MF**	**MW**	T_M	T_B	S_W **(25°C)**	V_P **(25°C)**	**H (25°C)**	**log** K_{OA} **(25°C)**	**log** K_{OW}	**IPC**
BbF	205-99-2	$C_{20}H_{12}$	252	168	-	$1.50x10^{-3}$	$5.00x10^{-7}$	$6.57x10^{-7}$	11.34	5.78	$7.90x10^{-1}$
BkF	207-08-9	$C_{20}H_{12}$	252	217	480	$8.00x10^{-4}$	$9.70x10^{-10}$	$5.84x10^{-7}$	11.37	6.11	$8.00x10^{-1}$
BaP	50-32-8	$C_{20}H_{12}$	252	177	495	$1.62x10^{-3}$	$5.49x10^{-9}$	$4.57x10^{-7}$	11.56	6.13	$7.50x10^{-2}$
IcdP	193-39-5	$C_{22}H_{12}$	276	164	536	$1.94x10^{-3}$	$1.25x10^{-10}$	$3.48x10^{-7}$	12.43	6.70	$10.93x10^{-2}$
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	$2.49x10^{-4}$	$1.00x10^{-10}$	$1.23x10^{-7}$	12.59	6.75	$45.78x10^{-2}$
BghiP	191-24-2	$C_{22}H_{12}$	276	278	> 500	$2.67x10^{-4}$	$1.00x10^{-10}$	$3.31x10^{-7}$	12.55	6.63	$51.30x10^{-2}$

benz[*b*]fluoranthene (BbF), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g/mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg/l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 /mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng/ml)

In this study, it was found that, under pyrolytic conditions, the H_2O_2 formation from the reactive radicals ($OH^\bullet$ and $O_2H^\bullet$) decreased trough sonication of more hydrophobic IcdP, DahA and BghiP. The studies including the H_2O_2 generation in deionized water showed that H_2O_2 accumulated in deionized water (pH=2.0) and increased up to 148 mg/l with 1 h aeration after 120 min sonication time at 30^{o}C (Table 5.22).

Table 5.22 H_2O_2 production, $OH^\bullet$ ion concentrations through sonication of BbF, BkF, BaP, IcdP, DahA and BghiP before and after 120 min sonication time at 30^{o}C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**H_2O_2 Production (mg/l)**					**$OH^\bullet$ Concentration (ng/ml)**		**PAH ***
				Deionized Water				
	BS	**BS**	**AS-1**	**BS**	**AS-1**	**BS**	**AS-1**	
BbF	4.00	178	5.00	148	148	23.00×10^{-21}	8.00×10^{-7}	92.00
BkF	4.00	178	5.00	148	148	23.00×10^{-21}	8.00×10^{-7}	90.00
BaP	5.00	178	5.00	148	148	23.00×10^{-21}	8.00×10^{-7}	89.00
IcdP	5.00	178	5.00	148	148	23.00×10^{-21}	4.00×10^{-20}	47.00
DahA	5.00	178	5.00	148	148	23.00×10^{-21}	5.00×10^{-19}	56.00
BghiP	5.00	178	5.00	148	148	23.00×10^{-21}	6.00×10^{-20}	56.00

*: PAH removal efficiency; BS: Before sonication; AS-1: After 120 min sonication

The yield of H_2O_2 decreased to a value as low as 5.00 mg/l from 178 mg/l under sonication of less hydrophobic PAHs after 150 min sonication time, whereas it could only cause the destruction of some less hydrophobic PAHs (BbF, BkF and BaP) with a yield of 67.00-92.00% in comparison with the more hydrophobic PAHs removed (IcdP, DahA and BghiP) with a yield of (47.00-56.00%) (Table 5.22). The H_2O_2 concentration did not change for more hydrophobic PAHs before and after 120 and 150 min sonication times and remained between 4.00-5.00 mg/l. These differences could be explained by the differences in their physicochemical properties and their destruction ways. For example, the hydrophobicity of a more hydrophobic PAH "BghiP" is higher with low Henry's law constant (log P_{OW}=5.98 at 25^{o}C) compared to a less hydrophobic PAH "BbF" with high Henry's law constant (log P_{OW}=5.71 at 25°C) and low vapor pressure (V_P, 5.00x10^{-7} mm Hg at 25°C) and octanol water coefficients properties (Table 5.21). The PAHs containing high benzene rings were removed with low efficiencies compared to the low benzene ring PAHs (BkF, BaP) since their solubilities, Henry's law constant (5.84x10^{-7} and 4.57x10^{-7} atm m^3 /mol at 25°C) and vapor pressures (9.70x10^{-10} and 5.49x10^{-9} mm Hg at 25°C) are low. The low removal efficiencies in more hydrophobic PAHs (IcdP, DahA) could probably be attributed to their non-hydroxylated sonication mechanism since the $OH^{\bullet}$ ions produced through aeration are not favor for their sono-degradation (Mendez-Arriaga et al., 2008; Psillakis et al., 2004). A non-hydroxylated pathway was observed in the work of Psillakis et al. (2004) with aeration in the removal of some more hydrophobic PAHs (IcdP, DahA) at low frequency. In the presence of more hydrophobic PAHs (IcdP, DahA) more aeration inside the bubble dissolves into the medium during oscillations with a consequent rise in the intensity of collapse and radical production. Higher concentration at the bubble interface raises the partial pressure of the more hydrophobic PAHs (IcdP, DahA) which leads to entrapment of these PAHs into the cavitation bubble, resulting in pyrolytic sono-decomposition during the transient collapse of the bubble (Sivasankar & Moholkar, 2009a). The less hydrophobic (BkF, BaP) PAHs could not be destroyed under aerated sonication process since it can not be removed in hydroxylated mediums containing $OH^{\bullet}$ ions as high as 12.00x10^{-8} ng/ml (Goskonda et al., 2002). The more hydrophobic BghiP could not be destroyed in hydroxylated mediums containing $OH^{\bullet}$ ions as high as 23.00x10^{-21} and 8.00x10^{-7} ng/ml (Table 5.22). The destruction way of this PAH was mainly pyrolysis (Goskonda et al., 2002).

The effect of air on the removal of short chain, less hydrophobic, PAHs could be explained as follows: the hydroperoxyl radicals ($O_2H^{\bullet}$) formed by Eq. (5.4);

$$H^{\bullet} + Air \quad \rightarrow O_2H^{\bullet} \tag{5.4}$$

will decay with generation of H_2O_2 as follows (De Visscher et al., 1996; Dewulf et al., 2001; Rae et al., 2005) in Eqs. (5.3), (5.5), (5.6) and (5.7).

$$O_2 \rightarrow 2O^\bullet \tag{5.5}$$

$$O^\bullet + H_2O \rightarrow 2OH^\bullet \tag{5.6}$$

$$2OH^\bullet \rightarrow H_2O_2 \tag{5.7}$$

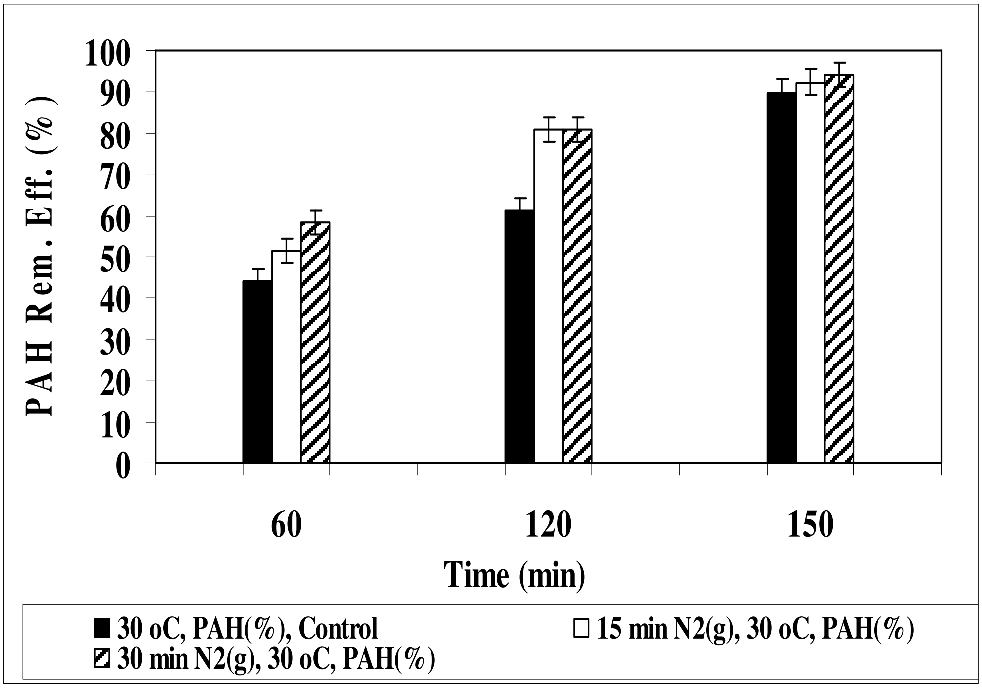
In the presence of air, reactive radicals such as $O^\bullet$, $OH^\bullet$ and $O_2H^\bullet$ will be produced by a series of reactions and may participate in the decomposition reaction of the PAHs. In aerated solutions, the $O_2H^\bullet$ formed by Eq. (5.3) given in the section "effect of DO on the sonication of PAHs" and will decay with the generation of H_2O_2 (See Eq. 5.3 in DO section). Air in aqueous solution of less hydrophobic PAHs was reported to play a very important role in the generation of highly oxidative $OH^\bullet$, enhancing its decomposition (Goskonda et al., 2002). The effect of air on the removal of short chain, less hydrophobic, PAHs could be explained as follows: In aerated solutions, $O_2H^\bullet$ formed by Eq. (5.4);

The production of the $O_2H^\bullet$ increases the oxidation process due to further formation of H_2O_2 by its recombination reaction (Kojima et al., 2005; Mendez-Arriaga et al., 2008; Naddeo et al., 2007, 2010; Olson & Barbier, 1994; Tuziuti et al., 2006; Yim et al., 2001, 2002, 2003). This was attributed to increase $OH^\bullet$ entering to the bulk solution. It has been speculated that the rate of $OH^\bullet$ formation in the gas phase is higher in an oxygenated atmosphere. Since in this study it was studied at low frequency (35 kHz) longer collapse times for the bubbles $OH^\bullet$ have more time to recombine before being ejected from inside the bubble into the bulk liquid than at higher frequencies (Park et al., 2000). This implies that $OH^\bullet$ reacts with less hydrophobic PAHs primarily in the bulk solution and that the number of $OH^\bullet$ capable of reaching the bulk at 35 kHz. It is clear that the destruction yields of less hydrophobic PAHs increases significantly up to 99.00% with an increase of aeration from 1 h up to 2 h (Kojima et al., 2005). This observation may be partially ascribed to the generation of $OH^\bullet$, resulted from dissociation of molecular O_2 (in the air) in the bubble, which is likely to recombine to form H_2O_2 at the gas–liquid interface of the bubbles as given in Eqs. (5.5), (5.6) and (5.7).

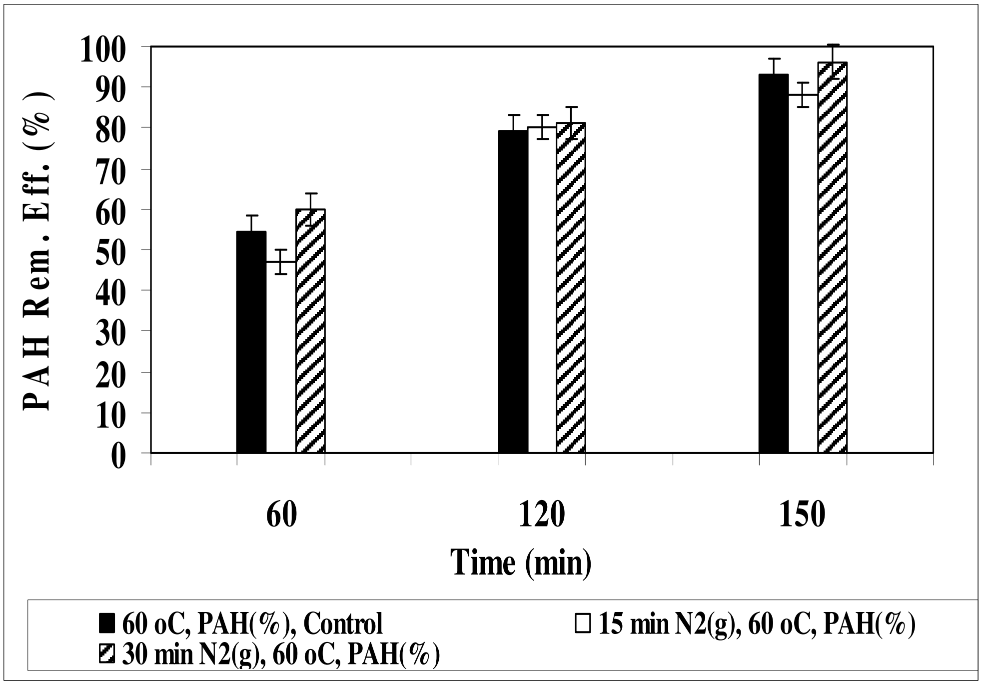
As a conlusion the more hydrophobic PAHs in PCI ww were principally destructed by way of pyrolytic reaction, deduced from the cavitation. Psillakis et al. (2003, 2004) reported that hydropholic compounds like IcdP, DahA and BghiP were degraded directly via pyrolytic reactions occurring inside the bubble and/or at the interfacial region or indirectly via radical reactions occurring at the interface and/or in the solution bulk of aerated solutions (Laughrey et al., 2001). It was reported that the contribution of aeration was not so effective on the sonication of PAHs with high benzene rings (Park et al., 2000). However, the destruction of less hyrophobic PAHs also involve the participation of $OH^{\bullet}$ and possibly H atoms which are formed from the water dissociation within the bubble and migrate towards the interface and the solution bulk in oxygenated environments.

5.9.5 Effect of $N_2(g)$ on the PAHs Removal Efficiencies in PCI ww Versus Sonication Times and Temperatures

15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) was sparged in PCI ww before sonication experiments. Maximum 92.46%, 94.16% and 88.33%, 96.27% total PAHs removal efficiencies were found under 15 and 30 min of $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging at 30°C and 60°C, respectively, after 150 min sonication time at pH=7.0 (Figure 5.17a-b). An increase of 6.08-13.18% and 18.51-18.71% in total PAHs yields were obtained under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging after 60 and 120 min sonication times while no significant increase in PAHs removals were observed after 150 min sonication time at pH=7.0, compared to the control [without $N_2(g)$ E=90.11% for total PAHs after 150 min sonication at pH=7.0 and at 30°C] (Figure 5.17a). The contribution of 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging on the PAHs removals are significant at low sonication times (60 and 120 min) and temperature (30°C) (R^2=0.84, F=13.09, p=0.001). $N_2(g)$ sparging did not significantly affect the PAHs removals compared to the control (E=96.90% total PAHs at pH=7.0) at 60°C at all sonication times (R^2=0.32, F=1.34, p=0.001) (Figure 5.17b).



(a)



(b)

Figure 5.17 Effect of increasing N_2(g) sparging on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

Similar to the results of Kojima et al. (2005) 15 and 30 min N_2(g) (3.00 and 6.00 mg/l N_2) sparging did not contribute to the PAHs removals at 60 and 120 min sonication times at 60^{o}C with the exception of 15 and 30 min N_2(g) (3.00 and 6.00 mg/l N_2) sparging after 120 min sonication time at 30^{o}C. This could be attributed to the benzene ring-opening reactions of PAHs and other intermediates as well as the degradation of by-products throughout N_2(g) sparging at low temperature.

The individual PAHs removals increased from 58.48-59.91% up to 71.79-96.91% after sonication time as long as 150 min sonication time. A significant correlation between PAHs removals and long sonication time was observed when 30 min N_2(g) (6.00 mg/l N_2) is sparged at 60^{o}C (R^2=0.86, F=17.98, p=0.001) (Table 5.23).

Table 5.23 Maximum removal efficiencies in some PAHs measured in the influent and in the effluent of the sonication experiments under 30 min N_2(g) (6.00 mg/l N_2) sparging after 60 min, 120 and 150 min sonication times at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml n=3, mean values ± SD).

PAHs	**Inf. $^{(A)}$ T=0 min PAHs (ng/ml) ± SD**	**Eff. $^{(B)}$ T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
FL	19.84 ± 0.69	0.80 ± 0.03	58.48	76.06	89.04
BaA	0.55 ± 0.02	0.02 ± 0.0007	59.87	80.94	92.39
BbF	0.80 ± 0.03	0.03 ± 0.001	59.86	80.91	96.91
BaP	0.07 ± 0.003	0.003 ± 0.0001	59.91	62.99	68.24
IcdP	1.09 ± 0.04	0.04 ± 0.001	59.83	68.88	78.49
DahA	4.60 ± 0.16	0.18 ± 0.006	59.57	63.53	71.79
BghiP	0.51 ± 0.02	0.02 ± 0.0007	59.88	64.94	74.60

(A) Inf.= influent, (B) Eff. = effluent.

In this study, it was found that N_2(g) sparging increased the yields of less hydrophobic PAHs. 89.04% FL, 92.39% BaA and 96.91% BbF maximum PAHs yields were obtained after 150 min sonication time at 60^oC for less hydrophobic PAHs with four benzene rings when 30 min N_2(g) (6.00 mg/l N_2) was sparged to the PCI ww (Table 5.23). The yields obtained for more hydrophobic PAHs namely BaP, IcdP, DahA and BghiP were significantly lower (68.24-78.49%) than that of less hydrophobic PAHs after 150 min sonication time at 60^oC. The PAHs containing high benzene rings were removed with low efficiencies compared to the low benzene ring PAHs since their solubilities, Henry's law constant and vapor pressures are low.

In the presence of more hydrophobic PAHs more N_2(g) inside the bubble dissolves into the medium during oscillations with a consequent rise in the intensity of collapse and radical production. Higher concentration at the bubble interface raises the partial pressure of the more hydrophobic PAHs which leads to entrapment of these PAHs into the cavitation bubble, resulting in pyrolytic sono-decomposition during the transient collapse of the bubble (Sivasankar et al., 2007; Sivasankar & Moholkar, 2008, 2009a).

A non-hydroxylated pathway was observed in the work of Psillakis et al. (2003) with N_2(g) sparging in the removal of some more hydrophobic PAHs at low frequency. The low removal efficiencies in more hydrophobic PAHs could probably be attributed to their non-hydroxylated sonication mechanism since the $OH^\bullet$ ions produced through N_2(g) sparging are not favor for their sono-degradation (Mendez-Arriaga et al., 2008; Psillakis et al., 2004).

H_2O_2 which is preferentially formed by the recombination of $OH^\bullet$ issue from the sonolysis of H_2O can be used as a good indicator of the $OH^\bullet$ production. The H_2O_2 measurement during acoustic cavitation, in absence and in the presence of PCI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the PAHs treatment by sonication in PCI ww decreases with increasing sonication time at 60^oC. In the absence of PCI ww (in deionized water) the H_2O_2 was accumulated and its concentration was measured as 187.00 mg/l, whereas this level was only 9.00 mg/l in PCI ww after 150 min sonication time in samples containing N_2 (Table 5.24). The $OH^\bullet$ ion concentrations also increased from $10.00x10^{-62}$ to $43.00x10^{-7}$ mg/l after 150 min sonication time in PCI ww containing less hydrophobic FL, BaA and BbF. This showed that hydroxylation is the main mechanism for the removal of less hydrophobic PAHs. In other words, $OH^\bullet$ is the major process for complete degradation of less hydrophobic PAHs.

Table 5.24 Effect of 30 min N_2(g) (6.00 mg/l N_2) sparging on H_2O_2 production and $OH^\bullet$ ion concentrations in PCI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	187.00	0.00
H_2O_2 concentration (mg/l) for less hydrophobic PAHs (60°C) after 30 min sonication	198.00	$10.00x10^{-52}$
H_2O_2 concentration (mg/l) for more hydrophobic PAHs (60°C) after 30 min sonication	4.00	$10.00x10^{-62}$
H_2O_2 concentration (mg/l) for less hydrophobic PAHs (60°C) after 120 min sonication	108.00	$2.00x10^{-22}$
H_2O_2 concentration (mg/l) for more hydrophobic PAHs (60°C) after 120 min sonication	4.00	$10.00x10^{-62}$
H_2O_2 concentration (mg/l) for less hydrophobic PAHs (60°C) after 150 min sonication	9.00	$43.00x10^{-7}$
H_2O_2 concentration (mg/l) for more hydrophobic PAHs (60°C) after 150 min sonication	4.00	$10.00x10^{-62}$

In PCI ww the most sonogenerated $OH^\bullet$ reacted with 89.00-97.00% less hydrophobic PAHs removals and radical recombination to produce H_2O_2 (Gogate et al., 2004). The $OH^\bullet$ ion concentrations remained constant around $10.00x10^{-62}$ mg/l after 150 min sonication in PCI ww containing more hydrophobic BaP, IcdP, DahA and BghiP. No increase in $OH^\bullet$ ion concentrations was observed throughout sonication of more hydrophobic PAHs. This showed that hydroxylation is not the main mechanism for the removal of more hydrophobic PAHs. This indicates that the main process for the destruction of more hydrophobic PAHs is pyrolysis.

Since the sonooxidation of more hydrophobic BaP, IcdP, DahA and BghiP comprised 0.11%, 0.10%, 0.09% and 0.08% of the total sonodegradation process, $OH^\bullet$ is not the major process for complete degradation of these PAHs (Table 5.25).

Table 5.25 Effect of 30 min N_2(g) (6.00 mg/l N_2) sparging on $[OH^\bullet]_{ss}$ concentrations and on the percentage of PAHs oxidation with $OH^\bullet$ ratio to conventional sonodegradation for seven PAHs after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml n=3, mean values).

PAHs	**$k_{PAH/OH^\bullet}$ [a]**	**k_{pf} [b]**	**$[OH^\bullet]_{ss}$ [c]**	**$V_{PAH/OH^\bullet}$ [d]**	**$V_{PAH/US}$ [e]**	**$V_{PAH/OH^\bullet} / V_{PAH/US}$ [f]**
FL	3.98×10^{10}	0.167	43.00×10^{-7}	9.88×10^{-5}	1.09×10^{-4}	0.98
BaA	3.22×10^{10}	0.147	43.00×10^{-7}	8.96×10^{-6}	0.91×10^{-5}	0.87
BbF	3.08×10^{10}	0.108	43.00×10^{-7}	7.70×10^{-6}	0.80×10^{-5}	0.77
BaP	2.85×10^{10}	0.099	10.00×10^{-62}	4.54×10^{-6}	0.39×10^{-5}	0.11
IcdP	2.08×10^{10}	0.069	10.00×10^{-62}	3.89×10^{-8}	0.23×10^{-7}	0.10
DahA	1.34×10^{10}	0.030	10.00×10^{-62}	1.99×10^{-10}	0.18×10^{-8}	0.09
BghiP	0.67×10^{10}	0.012	10.00×10^{-62}	0.99×10^{-11}	0.08×10^{-8}	0.08

a: PAHs oxidation rate constant (ng/ml . s); b: Experimental pseudo first order reaction of PAHs, (1/min); c: Steady-state $[OH^\bullet]$ concentrations, (ng/ml); d: PAHs oxidation rate (ng/ml.min); e: Experimental rate of PAHs sonodegradation (ng/ml.min); f: The percentage of PAHs oxidation with $OH^\bullet$ ratio to conventional sonodegradation ratio ($V_{PAH/OH^\bullet} / V_{PAH/US}$)

In other words, in this study, the contribution of $OH^\bullet$ is minor for the ultimate sonodegradation of more hydrophobic PAHs. The formation of by-products (hydroxylated compounds namely phenanthrenediols) for possible $OH^\bullet$ oxidation was not observed in HPLC. Similar results were obtained in the studies performed by Lindsey & Tarr (2000b), Wen et al. (2003), Wu & Ondruschka (2005). Since the sonooxidation of less hydrophobic FL, BaA and BbF comprised 0.87% and 0.77%

and 79.00% of the total sonodegradation process, $OH^{\bullet}$ is the major process for complete degradation of these PAHs. The contribution of the pyrolysis to the destruction of these PAHs is not significant.

Different suggestions were reported on the effect of N_2(g) sparging on PAHs removals: Dissolved N_2 present in aqueous solution might scavenge the free radical attacks to PAHs (David, 2009). Some studies showed that the PAHs are degraded in a N_2(g) sparged system with high concentrations of $OH^{\bullet}$ scavenger through sonication (Psillakis et al., 2004). Sparging of N_2(g) could change the temperature within the cavitation site or other properties of the cavitation process. Gasses with lower thermal conductivity values such as N_2 (18.70 mW/mol.K) increase the temperature inside the cavitation bubble upon collapse because they will allow less heat to the surrounding (Psillakis et al., 2004). The ratio of the specific heat at constant pressure and constant volume (C_p/C_v) plays a role in determining the maximum size of the cavitation bubble (Papadaki et al., 2004; Psillakis et al., 2004). Since the C_p/C_v ratio of N_2(g) is high (1.543) the bubble diameter increase during cavitation process resulting in high $OH^{\bullet}$ ions (Mendez-Arriaga et al., 2008; Psillakis et al., 2003). In this study it was found that N_2(g) increase the $OH^{\bullet}$ ions through sonication of less hydrophobic PAHs by increasing the temperature and bubble diameter as reported by Sivasankar & Moholkar (2009).

The benefit of N_2(g) sparging in enhancing the sonochemical activity is reported (Laughrey et al., 2001; Naddeo et al., 2010). Sparging of N_2(g) changed the temperature within the cavitation site and the variations of chemical properties of the system resulting in high PAHs removals (Laughrey et al., 2001). The mechanism affecting the yield of PAHs removals through sonication was explained as follows: N_2(g) sparging changed the temperature within the cavitation site and the variations of chemical properties of the system resulting in high PAHs removals at 30°C (De Bel et al., 2009). Gases with lower thermal conductivity (18.40 mW/mol.K) values such as N_2(g) increased the temperature up to 49°C inside the cavitation bubble upon collapse because they allowed less heat to the surroundings such as 37°C (Dewulf et al., 2001; Psillakis et al., 2004; Van Lersel, 2008). The ultrasonic degradation of

PAHs in aqueous solution is strongly affected by the average specific heat ratio of the gas dissolved in the solution, since the degradation is considered to proceed in local hot-spots formed by adiabatic collapsing bubbles (Kojima et al., 2005). The ratio of the specific heat at constant pressure and constant volume (C_p/C_v) plays a role in determining the maximum size of the cavitation bubble (Papadaki et al., 2004). The specific heat (C_p) of $N_2(g)$ is 1.0397 J /g.K (Psillakis et al., 2004). The (Cp/Cv) ratios of $N_2(g)$ is 1.543. It is unlikely that any significant change in the cavitation process occured due to sparging with $N_2(g)$. The $N_2(g)$ or its sonolysis product may scavenge a fraction of the reactive radicals (Mendez-Arriaga et al., 2008). The greater the ratio, the greater the radius of the bubble before collapse. Significant changes in the cavitation process, due to changes in the chemical properties of PAHs occurred due to sparging with $N_2(g)$. The PAHs degradation in $N_2(g)$ sparged systems suggests that a non-oxygen dependent, non-hydroxyl radical pathway also exists more hydrophobic PAHs . This pathway is most likely pyrolysis occurring in the gas phase (Dewulf et al., 2001).

It was found that $N_2(g)$ bubbles produce the highest number of $OH^\bullet$ in the sonication of less hydrophobic PAHs. Since the intensity of collapse of $N_2(g)$ bubbles indicated by the temperature peaks attained at the collapse of these bubbles as reported by Sivasankar & Moholkar (2009). Although, some researchers mentioned that the trend of $N_2(g)$ in production of $OH^\bullet$ is low through hydroxylation reaction (Mendez-Arriaga et al., 2008; Psillakis et al., 2004) in a medium containing more hydrophobic PAHs the dissolved $N_2(g)$ slowly diffuses into the cavitation bubble during oscillations, as result of which the equilibrium of the bubble grows. This gas cushions the transient collapse of the bubble, the temperature and pressure peaks attained in the bubble reduce, resulting in the reduction of $OH^\bullet$ production. This affects negatively the degradation of PAHs occurring through hydroxylation. In the presence of more hydrophobic PAHs more $N_2(g)$ inside the bubble dissolves into the medium during oscillations with consequent rise in the intensity of collapse and radical production. Higher concentration at the bubble interface raises the partial pressure of the pollutant that leads to higher evaporation and subsequent entrapment of the pollutant into the cavitation bubble, which under goes pyrolytic decomposition at the extreme conditions reached during the transient collapse of the bubble (Hung & Hoffmann, 1998). Sivasankar & Moholkar (2009) mentioned that the presence of N_2(g) has a negative effect on the formation of H_2O_2 and on the degradation of PAHs during sonication under air. The HNO_2 formed may be the scavenger of $OH^\bullet$, which eventually leads to the suppression in H_2O_2 production.

In this study, high total PAHs removals were found with N_2(g) sparging in comparison with the other literature data. For example, in Laughrey et al. (2001) 80.00% total PAHs removals were found at 20°C under 30 min of N_2(g) (6.00 mg/l N_2) sparging at 20 kHz, and at 70 W, after 120 min sonication time. The PAHs yields reached higher than that found by Laughrey et al. (2001) under similar operational and sonicational conditions. 87.00% total PAHs removal was found for initial 0.90 μg/l total PAHs concentration at 400 W and at 24 kHz under 25 min N_2(g) (5.00 mg/l N_2) sparging at 60°C after 150 min sonication time. Different suggestions were reported on the effect of N_2(g) sparging on PAH removals: Dissolved N_2 present in aqueous solution might scavenge the free radicals, inhibiting the free radical attack to PAHs (David, 2009). These results agree with the data obtained for less hydrophobic PAHs. On the other hand, a non-hydroxylated pathway was observed in the work of Psillakis et al. (2003) with N_2(g) sparging resulting in a non-complete removal of NAP, ACL and PHE at low frequency. The low removal efficiencies in more hydrophobic PAHs could be probably attributed to their non-hydroxylated sonication mechanism.

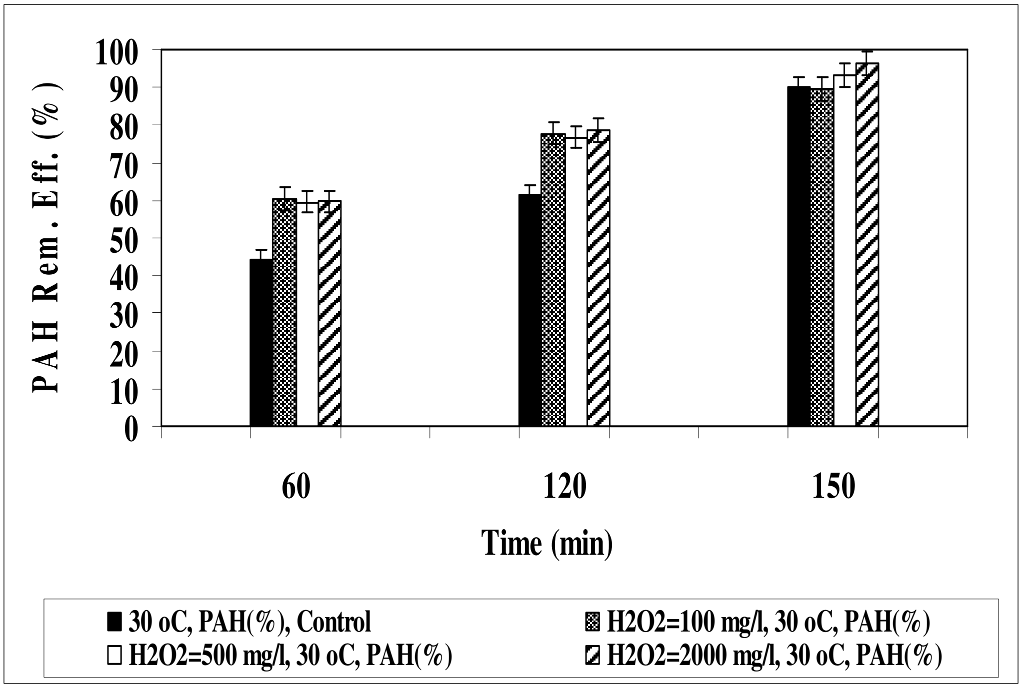
5.9.6 Effect of H_2O_2 Concentrations on the Removal of PAHs in PCI ww at Increasing Sonication Times and Temperatures

100 mg/l, 500 and 2000 mg/l H_2O_2 were added in PCI ww before the sonication experiments. 89.63%, 93.28% and 96.46% total PAHs removals were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, at pH=7.0 and at 30°C after 150 min sonication time (Figure 5.18a). An increase of 3.17% and 6.35% in total PAHs removals were measured in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without H_2O_2 while E=90.11% total PAHs at pH=7.0 and at 30°C). Although, a correlation between

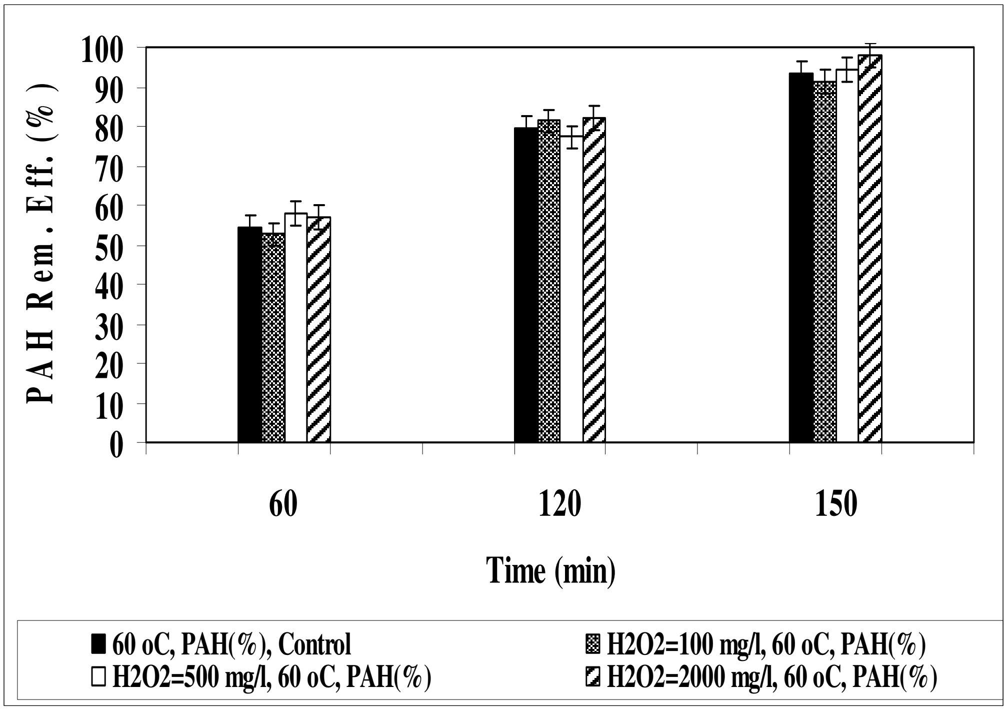
PAHs removals and H_2O_2 concentrations is observed, this relationship is not significant at pH=7.0 and at 30°C after 60 and 120 min sonication times at 30°C (R^2=0.80, F=2.87, p=0.001) (Figure 5.18a).

91.33%, 94.19% and 98.04% total PAHs removal efficiencies were obtained in 100 mg/l, 500 and 2000 mg/l H_2O_2 at 60°C after 150 min sonication time at pH=7.0 (Figure 5.18b). No significant increase in total PAHs yields was obtained by increasing the H_2O_2 concentrations compared to the control (E=96.90% for total PAHs at pH=7.0) at 60°C (R^2=0.40, F=3.87, p=0.001). The PAH yields in the samples containing H_2O_2 and non containing (control) samples were around 52.61–57.90% and 77.22-82.19%, respectively, at 60°C after 60 and 120 min sonication times at pH=7.0. The maximum total PAHs removal efficiency was 98.04% after 150 min sonication time in H_2O_2=2000 mg/l at pH=7.0 and at 60°C (Figures 5.18b).

It was reported that this oxidant elevates the extent of PAHs removal through acustic cavitation (Chakinala et al., 2008a). The similar degradation degree in the control and in the presence of H_2O_2 at 60°C after 120 and 150 min sonication times may be attributed to the increased level of $OH^\bullet$ scavenging by the PAHs and by H_2O_2 itself. During the sonolysis of aqueous solutions, $OH^\bullet$ and $H^\bullet$ are generated by the thermolysis of water in the solution medium and can scavenge $OH^\bullet$ produced. As the concentration of H_2O_2 in the solution is increased, it's $OH^\bullet$ scavenging effect increases causing decrease in degradation of PAHs. It was reported that at very high H_2O_2 concentrations detrimental effects are observed, since the recombination reaction of $OH^\bullet$ is more predominant and H_2O_2 acts as a scavenger for $OH^\bullet$ (Chakinala et al., 2008a). The scavenging of free $OH^\bullet$ becomes the dominant process at high H_2O_2 concentrations in the system, thereby lowering the ability of $OH^\bullet$ to degrade PAHs. A similar trend has been reported in the sonolytic destruction of 5,5–dimethyl–1–pyrroline–N–oxide and oxalic acid using H_2O_2 (Rae et al., 2005). The removal yields of all seventeen PAHs were above 95.00%. In other words, the PAHs containing one, two, three, four and five benzene rings were removed with efficiencies varying between 95.00 and 99.08% after 150 min sonication time at a H_2O_2 concentration of 2000 mg/l (Table 5.26).



(a)



(b)

Figure 5.18 Effect of increasing H_2O_2 concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

Table 5.26 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments in H_2O_2=2000 mg/l after 60 min, 120 and 150 min sonication times at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**Inf. $^{(A)}$T=0 min PAHs (ng/ml) ± SD**	**Eff. $^{(B)}$T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
NAP	1899.69 ± 66.50	461.41 ± 16.20	30.28	73.82	99.08
ACL	52.37 ± 1.83	1.56 ± 0.06	54.44	78.77	98.26
ACT	70.68 ± 2.47	1.81 ± 0.06	53.70	77.70	96.48
FLN	58.24 ± 2.04	1.59 ± 0.06	54.19	78.42	97.59
PHE	139.21 ± 4.87	5.28 ± 0.20	51.24	74.14	97.79
ANT	7.53 ± 0.26	0.15 ± 0.005	59.43	81.66	95.00
CRB	14.36 ± 0.50	0.34 ± 0.01	58.11	81.19	98.70
FL	19.69 ± 0.70	0.43 ± 0.02	55.86	80.84	97.23
PY	15.75 ± 0.55	0.34 ± 0.01	56.04	81.10	97.40
BaA	0.55 ± 0.02	0.01 ± 0.0004	54.77	82.15	95.32
CHR	2.69 ± 0.09	0.05 ± 0.002	59.67	83.00	97.19
BbF	0.80 ± 0.03	0.02 ± 0.0007	56.76	82.13	95.68
BkF	0.80 ± 0.03	0.02 ± 0.0007	53.76	78.13	95.87
BaP	0.07 ± 0.003	0.001 ± 0.00004	56.79	83.18	98.66
IcdP	1.09 ± 0.04	0.02 ± 0.0007	57.74	82.11	98.78
DahA	4.60 ± 0.16	0.09 ± 0.003	56.57	84.87	97.95
BghiP	0.51 ± 0.02	0.01 ± 0.0004	56.77	80.15	97.85

(A) Inf.= influent, (B) Eff. = effluent.

H_2O_2 is an oxidizing agent. It was reported that this oxidant increases the extent of PAH removal through acustic cavitation (Chakinala et al., 2008a). During the sonolysis of H_2O, $OH^\bullet$ is produced and recombined into H_2O_2, if no organic compounds such as radical scavengers are present in the H_2O. The formed H_2O_2 and its sonolytic decomposition products would have an effect on the degradation of organic compounds like PAHs during sonication. The H_2O_2 may be mainly present not inside the cavitation bubbles but in the bulk solution due to the high H_2O solubility and low volatility (Benabdallah El-Hadj et al., 2007). In our study, no significant total PAHs yields were obtained by the addition of H_2O_2. The scavenging of free $OH^\bullet$ becomes the dominant process at high H_2O_2 concentrations in the system, thereby lowering the ability of $OH^\bullet$ to degrade PAHs (Chakinala et. al., 2008a). It is also possible that the presence of high H_2O_2 concentrations results in a lower intensity of cavitation, due to the fact that vaporous cavities will be generated in this case, as reported by Rae et al. (2005). This is not valid for our study since it was perfomed at high sonication intensity.

Since less hydrophobic PAHs are considerably non-volatile with low Henry's law constant and solubility (Lindsey & Tarr, 2000a), sono-degradation inside the cavitation bubble is expected to be insignificant. Therefore, hydroxyl radical-induced reactions are likely to be the main degradation mechanism of less hydrophobic ones as follows in Eqs. (5.8) and (5.9):

$$H_2O +))) \quad \rightarrow \quad H^\bullet + OH^\bullet \tag{5.8}$$

$$PAHs\ (less\ hydrophobic) + OH^\bullet \rightarrow metabolites + OH^\bullet \rightarrow end - products \tag{5.9}$$

It should be pointed out that $OH^\bullet$, formed via water sonolysis, can partly recombine yielding H_2O_2 which in turn reacts with H_2 to regenerate $OH^\bullet$ in Eqs. (5.10) and (5.11):

$$OH^\bullet + OH^\bullet \quad \rightarrow \quad H_2O_2 \tag{5.10}$$

$$H_2O_2 + H^\bullet \quad \rightarrow \quad H_2O + OH^\bullet \tag{5.11}$$

The formation of H_2O_2 during ultrasound irradiation was confirmed experimentally during sonication in the absence and presence of less and more hydrophobic PAHs. As the H_2O_2 concentration increased to 176 mg/l after 60 min sonication time the less hydrophobic PAHs removals increased to 96.00-98.00% while the removals of more hydrophobic PAHs remained aroud 60.24-62.32% after 120 min (Table 5.27). This process ends with decreasing of H_2O_2 to 5.00 mg/l As BbF, BkF, BaP and its degradation metabolites scavenge $OH^{\bullet}$ (Eqs. 5.10 and 5.11), the yield, defined as H_2O_2 formed in the presence of less hydrophobic PAHs over H_2O_2 formed in deionized water.

Table 5.27 Effect of H_2O_2 production on the removals of less (BbF, BkF, BaP) and more (IcdP, DahA, BghiP) hydrophobic PAHs after 60 and 120 min sonications times at 30°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

H_2O_2 Concentration (mg/l)			**Less Hydrophobic PAHs**			**More Hydrophobic PAHs**		
in deionized water	**After 60 min sonic.**	**After 120 min sonic.**	**BbF**	**BkF**	**BaP**	**IcdP**	**DahA**	**BghiP**
13.00	156.00	5.00						
Removal eff (%) after 30 min			34.21	32.44	38.10	19.40	21.12	20.28
Removal eff (%) after 120 min			95.35	96.76	97.65	76.33	75.35	77.32

The PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww were detemined with HPLC in H_2O_2=2000 mg/l after 120 min sonication time at 25°C (Table 5.28).

Table 5.28 The measurements of PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) performed in PCI ww with HPLC in H_2O_2=2000 mg/l concentration after 120 and 150 min sonication times at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs Intermediates	**PAH_0 (ng/ml)**	**120 min**			**150 min**
		PAH (ng/ml)	**PAHR (%)**	**PAHI (ng/ml)**	**PAHIR (%)**
1–Methylnaphthalene	1378.77	275.75	80.00	226.67	83.56
9–Hydroxyfluorene	1378.77	275.75	80.00	138.02	89.99
9,10–Phenanthrenequione	1378.77	275.75	80.00	19.85	98.56
Benzoic acid	1378.77	275.75	80.00	93.48	93.22
1,2,3–Thiadiazole–4–carboxylic acid	1378.77	275.75	80.00	21.51	98.44

PAH_0: Initial total PAHs concentration (ng/ml), PAH: Total PAHs concentration (ng/ml) after 120 min sonication time, PAHR: Total PAHs removal efficiency (%) after 120 min sonication time, PAHI: PAHs intermediates concentration (ng/ml) after 120 min sonication time, PAHIR: removal of PAHs intermediates (%) after 150 min sonication time.

As shown in Table 5.28, the initial total PAHs concentration of 1378.77 ng/ml decreased to 275.75 ng/ml in H_2O_2=2000 mg/l after 120 min sonication time at 25°C. From 1378.77 ng/ml initial PAHs 226.67 ng/ml 1–methylnaphthalene, 138.02 ng/ml 9–hydroxyfluorene, 19.85 ng/ml 9,10–phenanthrenequione, 93.48 ng/ml benzoic acid and 21.51 ng/ml, 1,2,3–thiadiazole–4–carboxylic acid were produced after 120 min sonication time at 25°C. It was found that the initial PAHs sono-degraded to the inter-metabolites as mentioned above (Table 5.28). After 120 min sonication time the remaining PAH concentration was found as 879.24 ng/ml. The initial PAHs concentration of 1378.77 ng/ml converted to 499.53 ng/ml PAHs inter-metabolites in question as aforementioned. The low removal efficiency of the total PAHs (79.65%) could be attributed to the studied low low temperature (25°C) although, H_2O_2=2000 mg/l increased the PAHs yields at 60°C. The PAHs intermediates namely, 1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid and 1,2,3–thiadiazole–4–carboxylic acid were sonodegraded with yields of 83.56%, 89.99%, 98.56%, 93.22% and 98.44%, respectively, in H_2O_2=2000 mg/l after 150 min sonication time at 25°C (Table 5.28).

The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww was illustrated in Figure 5.19 in H_2O_2=2000 mg/l after 120 min sonication time at 25°C.

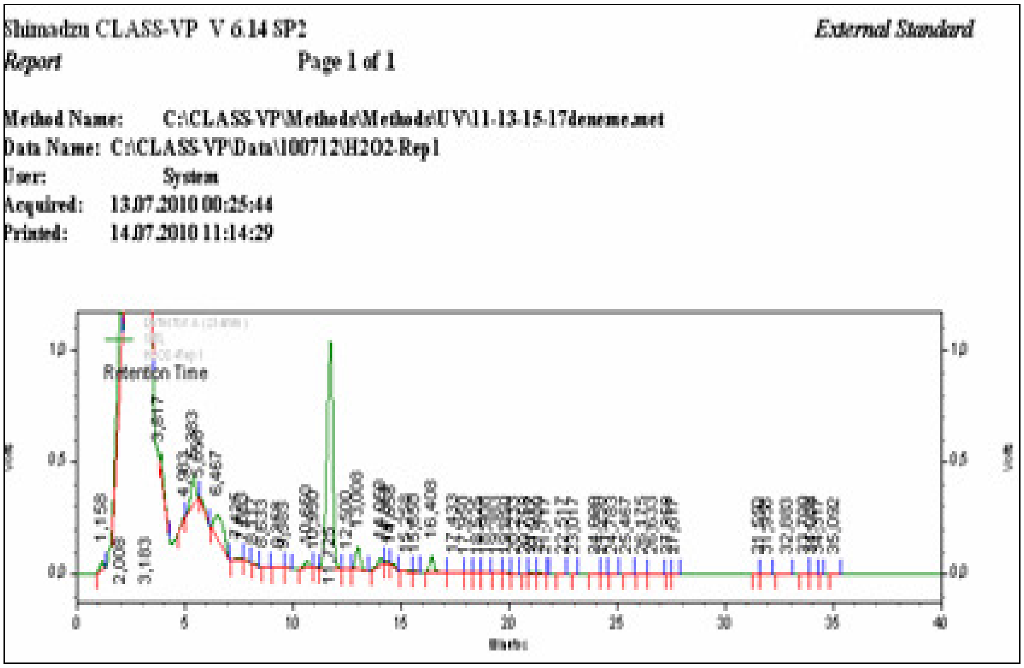


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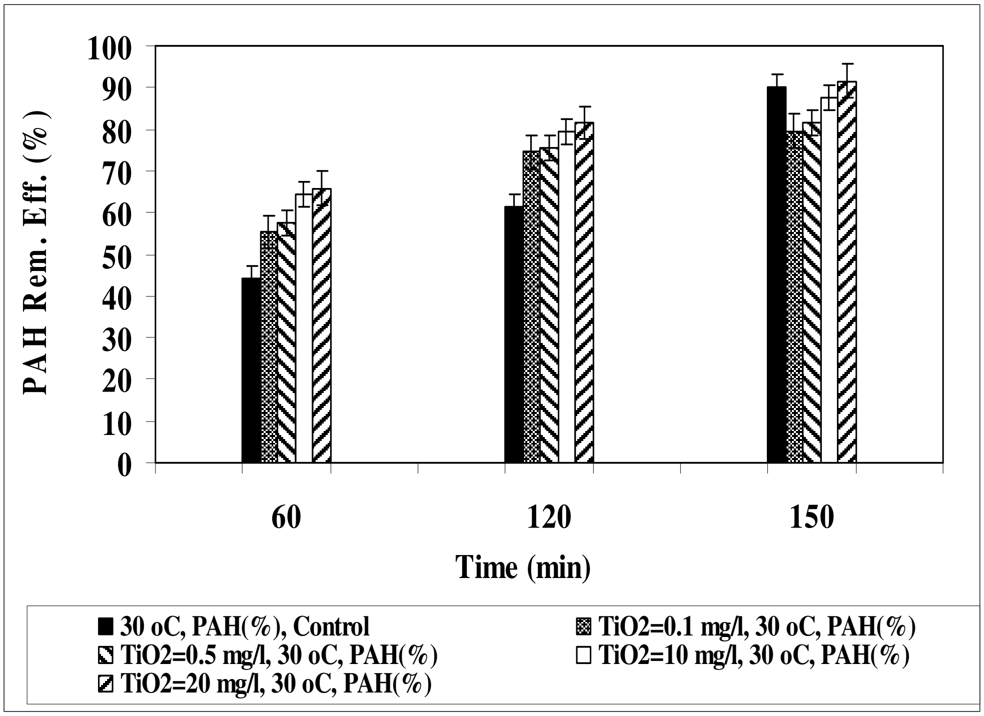
Figure 5.19 The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww in H_2O_2=2000 mg/l concentration after 120 min sonication time at 25°C (sonication power=640 W, sonication frequency=35 kHz).

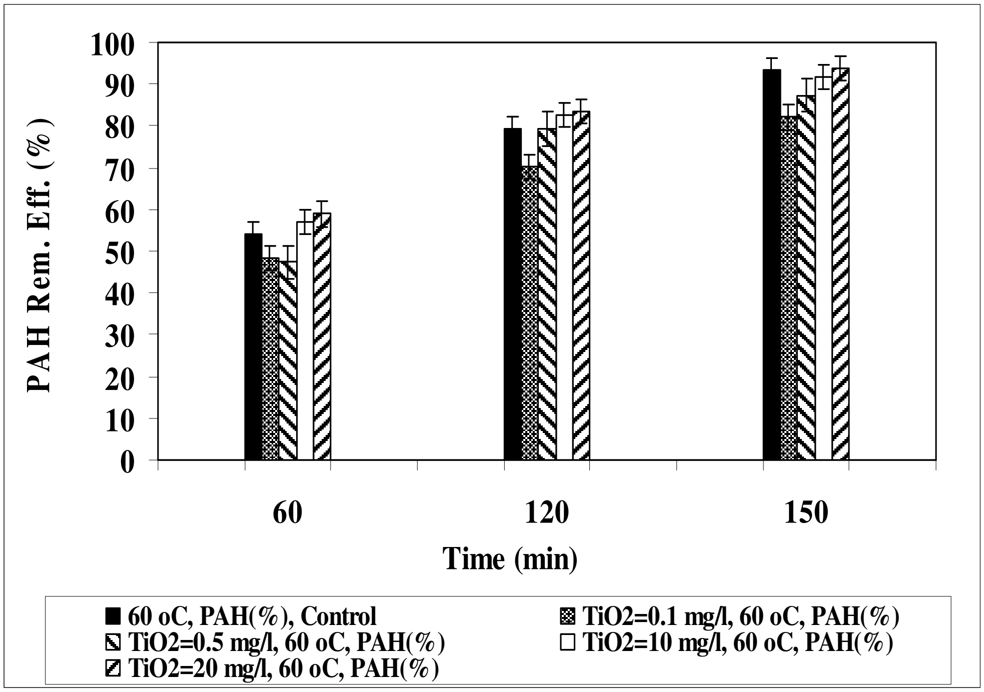
5.9.7 Effect of TiO_2 Concentrations on the PAHs Removal Efficiencies in PCI ww at Increasing Sonication Times and Temperatures

In order to optimize the addition of an amount of TiO_2 catalyst for the highest sonocatalytic destruction of PAHs 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2 was added to the PCI ww before the sonication experiments. In general, the results of this study showed that as the sonication time increased the total PAHs yields also increased at pH=7.0 and at 30°C. All the TiO_2 concentrations increased the total PAHs removals after 60 and 120 min sonication times, respectively, compared to the control reactor containing no TiO_2 (Figure 5.20a). The increase of TiO_2 concentrations from 0.10 mg/l up to 20.00 mg/l increased the total PAHs removal after 60 and 120 min sonication times at pH=7.0 and at 30°C. It was found that the total PAHs yields were the same as the control reactor free of TiO_2 and the reactor containing 20.00 mg/l TiO_2 after 150 min of sonication time at pH=7.0 and at 30 °C. The total PAHs removals were slightly lower in the reactors containing 0.10 and 0.50 mg/l TiO_2 concentrations after 150 min of sonication time, compared to the control (Figure 5.20a).

As the sonication time was increased from 60 min to 150 min the total PAHs removal increased in all reactors containing TiO_2 and in the control reactor free of TiO_2 at pH=7.0 and at a temperature of 60°C (Figure 5.20b). No significant increase in total PAHs yield was obtained by increasing the TiO_2 concentrations from 0.10 mg/l up to 20.00 mg/l at 60°C. The maximum total PAHs removal efficiency was 93.88% after 150 min sonication time in TiO_2=20.00 mg/l at pH=7.0 and at 60°C (Figure 5.20b). The increase of TiO_2 catalyst did not further decompose the PAHs in aqueous solution. Excessive TiO_2 particles sometimes result in mutual screens among TiO_2 particles, which not only protect the PAHs molecules, but also reduce the sonocatalytic activity of TiO_2 powder, at frequency and power of 32 kHz and 480 W after 150 min sonication time at 60°C as reported by Wen et al. (2003). In this study it was found that high temperature decreased the sonodegradation of total PAHs assisted by TiO_2, as reported by Wang, J. et al. (2006a). Both sonocatalytic and ultrasonic destructions in the presence of TiO_2 decreased gradually along with the increased temperatures (Liu et al., 2000).



(a)



(b)

Figure 5.20 Effect of increasing TiO_2 concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

In general, for most of the chemical reactions, the higher the temperature in the reaction system is, the quicker the reaction rate becomes and although, it is known that radical reactions do not depend very much on the systemic temperature. However, the acoustic cavitation which produces the holes on the surface of TiO_2 particles or $OH^{\bullet}$ in aqueous solution depends on the change of systemic temperature. It is well known that both sonocatalytic and ultrasonic degradation of organic pollutants are related to the acoustic cavitation. The acoustic cavitation can give rise to holes with strong oxidability on the surface of TiO_2 particles which either can directly decompose the organic pollutants adsorbed on the surface of TiO_2 particles or indirectly remove the organic pollutants in the aqueous solution through the $OH^{\bullet}$ resulting from hole oxidation of H_2O molecules. When the temperature in the aqueous solution becomes high, the vapor or gas bubbles escape rapidly from the reaction system and thus do not grow or collapse, which badly weakens the acoustic cavitation.

Sometimes high temperatures act against ultrasonic degradation. Similarly, high temperatures also act against sonocatalytic degradation because the holes on the surface or inside the TiO_2 particles result from the acoustic cavitation. In addition, the sonocatalytic degradation relates to the adsorbability of TiO_2 particles. In general, appropriate adsorbability is likely to encourage sonocatalytic removal. Suitable quantities of organic pollutants adsorbed on the surface of TiO_2 particles can be directly decomposed by the holes. However, high temperatures generally weaken the adsorbability of TiO_2 particles, permitting large numbers of organic pollutants to freely and rapidly move in the solution and thus avoid degradation.

As seen from Table 5.29 removal in all individual PAHs increased significantly as the sonication time increased from 60 to 150 min at 60^{o}C. The PAHs with four and five benzene rings namely BkF, BaP, IcdP, DahA and BghiP were removed with high efficiencies (> 92.00%) at 20.00 mg/l TiO_2 after 150 min sonication time at 60^{o}C, although these PAHs had less solubility in water, low vapor pressure, Henry's law constant, and high octanol-water coefficient (Table 5.30). This could be attributed to the hydrophobic PAHs which can be easily diffuse near cavitation bubbles and their destruction inside the collapsing bubble and thermal decomposition at its interfacial sheath at 60°C as reported by Davydov et al. (2001) and Dehghani et al. (2010).

Table 5.29 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments in TiO_2=20.00 mg/l concentration after 60 min, 120 and 150 min sonication times at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	Inf. [(A)] T=0 min PAHs (ng/ml) ± SD	Eff. [(B)] T=150 min PAHs (ng/ml) ± SD	T=60 min PAHs (%)	T=120 min PAHs (%)	T=150 min PAHs (%)
NAP	1871.45 ± 65.50	489.44 ± 17.13	31.88	75.16	96.99
ACL	52.30 ± 1.83	3.62 ± 0.13	56.52	80.07	94.30
ACT	70.56 ± 2.47	4.57 ± 0.16	55.78	79.01	95.47
FLN	58.16 ± 2.04	3.89 ± 0.14	52.28	78.72	92.08
PHE	138.78 ± 4.86	10.41 ± 0.36	53.30	75.50	92.75
ANT	7.52 ± 0.26	0.46 ± 0.02	58.53	82.91	94.88
CRB	14.35 ± 0.50	0.93 ± 0.03	58.21	82.45	95.74
FL	19.68 ± 0.70	1.24 ± 0.04	53.96	80.10	90.92
PY	15.74 ± 0.55	0.99 ± 0.03	59.14	82.36	91.47
BaA	0.55 ± 0.02	0.03 ± 0.001	58.87	78.39	94.99
CHR	2.69 ± 0.09	0.16 ± 0.006	58.77	80.25	94.32
BbF	0.80 ± 0.03	0.05 ± 0.002	53.86	83.38	95.80
BkF	0.80 ± 0.03	0.05 ± 0.002	60.86	84.38	92.92
BaP	0.07 ± 0.003	0.004 ± 0.0001	58.89	83.43	95.59
IcdP	1.09 ± 0.04	0.07 ± 0.003	55.84	81.36	96.00
DahA	4.60 ± 0.16	0.28 ± 0.01	50.67	81.11	93.28
BghiP	0.51 ± 0.02	0.03 ± 0.001	48.87	83.40	92.97

[(A)] Inf.= influent, [(B)] Eff. = effluent.

The results of this study showed that the PAHs removals were not dependent on the physicochemical properties of the PAHs mentioned above during sonication enhanced by 20.00 mg/l TiO_2 (R^2=0.45, P=4.67, p=0.001). High PAHs removals were also valid for the individual PAHs concentrations measured in a control containing no TiO_2 after 150 min of sonication time. It can be concluded that if PCI ww containing PAHs is sonicated for 150 min at 60°C, it could be removed efficiently without $TiO_{2.}$ As a result, the obtained removal for seventeen PAHs was nearly the same with 20.00 mg/l TiO_2 and without TiO_2 at 60°C after 150 min sonication time.

Table 5.30 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml).

PAHs	**CAS-No**	**MF**	**MW**	T_M	T_B	S_W (25°C)	V_P (25°C)	**H** (25°C)	**log** K_{OA} **(25°C)**	**log** K_{OW}	**IPC**
BkF	207-08-9	$C_{20}H_{12}$	252	217	480	8.00×10^{-4}	9.70×10^{-10}	5.84×10^{-7}	11.37	6.11	8.00×10^{-1}
BaP	50-32-8	$C_{20}H_{12}$	252	177	495	1.62×10^{-3}	5.49×10^{-9}	4.57×10^{-7}	11.56	6.13	7.50×10^{-2}
IcdP	193-39-5	$C_{22}H_{12}$	276	164	536	1.94×10^{-3}	1.25×10^{-10}	3.48×10^{-7}	12.43	6.70	10.93×10^{-2}
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	2.49×10^{-4}	1.00×10^{-10}	1.23×10^{-7}	12.59	6.75	45.78×10^{-2}
BghiP	191-24-2	$C_{22}H_{12}$	276	278	>500	2.67×10^{-4}	1.00×10^{-10}	3.31×10^{-7}	12.55	6.63	51.30×10^{-2}

benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g/mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg/l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 /mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng/ml)

The measurements of PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww were detemined with HPLC in TiO_2=20.00 mg/l concentration after 120 min sonication time at 25°C (Table 5.31).

Table 5.31 The measurements of PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) performed in PCI ww with HPLC in TiO_2=20.00 mg/l concentration after 120 and 150 min sonication times at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs Intermediates	**PAH_0 (ng/ml)**	**120 min**			**150 min**
		PAH (ng/ml)	**PAHR (%)**	**PAHI (ng/ml)**	**PAHIR (%)**
1–Methylnaphthalene	1378.77	220.60	84.00	206.77	85.00
9–Hydroxyfluorene	1378.77	220.60	84.00	170.89	87.61
9,10–Phenanthrenequione	1378.77	220.60	84.00	70.99	94.85
Benzoic acid	1378.77	220.60	84.00	140.89	89.78
1,2,3–Thiadiazole–4–c arboxylic acid	1378.77	220.60	84.00	72.78	94.72

PAH_0: Initial total PAHs concentration (ng/ml), PAH: Total PAHs concentration (ng/ml) after 120 min sonication time, PAHR: Total PAHs removal efficiency (%) after 120 min sonication time, PAHI: PAHs intermediates concentration (ng/ml) after 120 min sonication time, PAHIR: removal of PAHs intermediates (%) after 150 min sonication time.

As shown in Table 5.31, the initial total PAHs concentration of 1378.77 ng/ml decreased to 220.60 ng/ml in TiO_2=20.00 mg/l after 120 min sonication time at 25°C. From 1378.77 ng/ml initial PAHs 206.77 ng/ml 1–methylnaphthalene, 170.89 ng/ml 9–hydroxyfluorene, 70.99 ng/ml 9,10–phenanthrenequione, 140.89 ng/ml benzoic acid and 72.78 ng/ml, 1,2,3–thiadiazole–4–carboxylic acid were produced after 120 min sonication time at 25°C. It was found that the initial PAHs sono-degraded to the inter-metabolites as mentioned above (Table 5.31). After 120 min sonication time the remaining PAHs concentration was found as 666.45 ng/ml. The initial PAHs concentration of 1378.77 ng/ml converted to 712.32 ng/ml PAHs inter-metabolites in question as aforementioned. The low removal efficiency of the total PAHs (84.00%) could be attributed to the studied low low temperature (25°C) although, TiO_2=20.00 mg/l increased the PAHs yields at 60°C. The PAHs intermediates namely, 1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid were sonodegraded with yields of 85.00%, 87.61%, 94.85%, 89.78% and 94.72%, respectively, in TiO_2=20.00 mg/l after 150 min sonication time at 25°C (Table 5.31).

The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww were demonstrated in TiO_2=20.00 mg/l concentration after 120 min sonication time at 25°C (Figure 5.21).

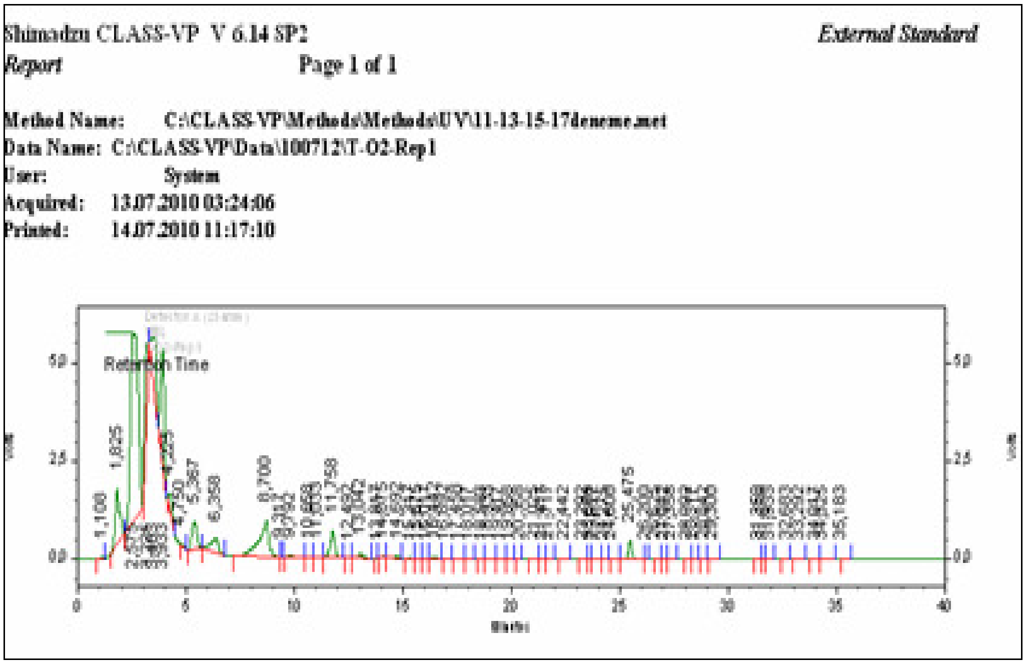


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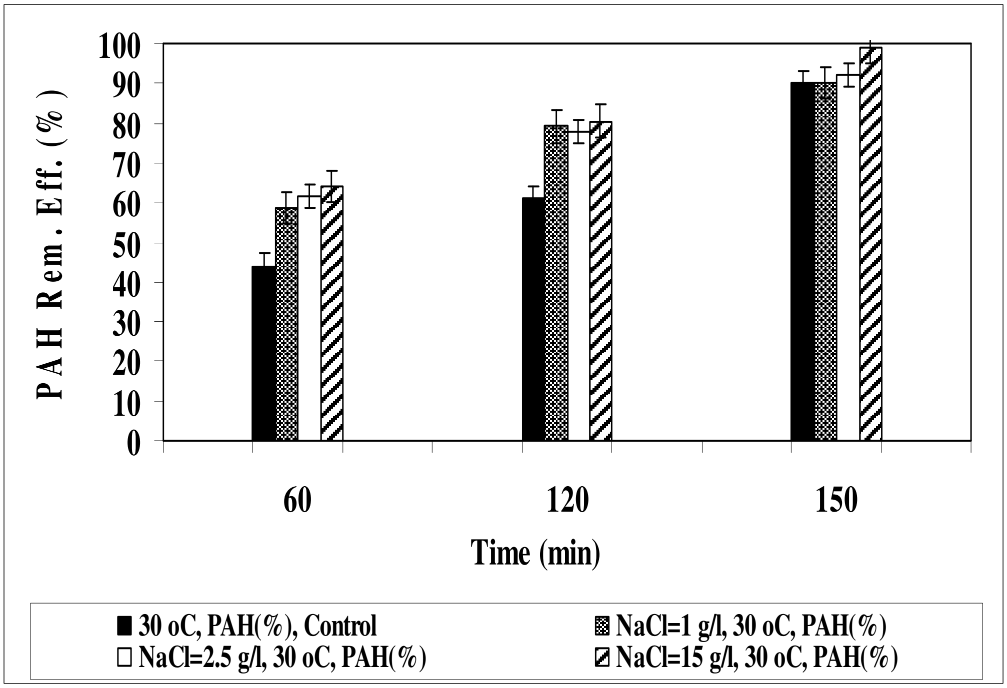
Figure 5.21 The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww in TiO_2=20.00 mg/l concentration after 120 min sonication time at 25°C (sonication power=640 W, sonication frequency=35 kHz).

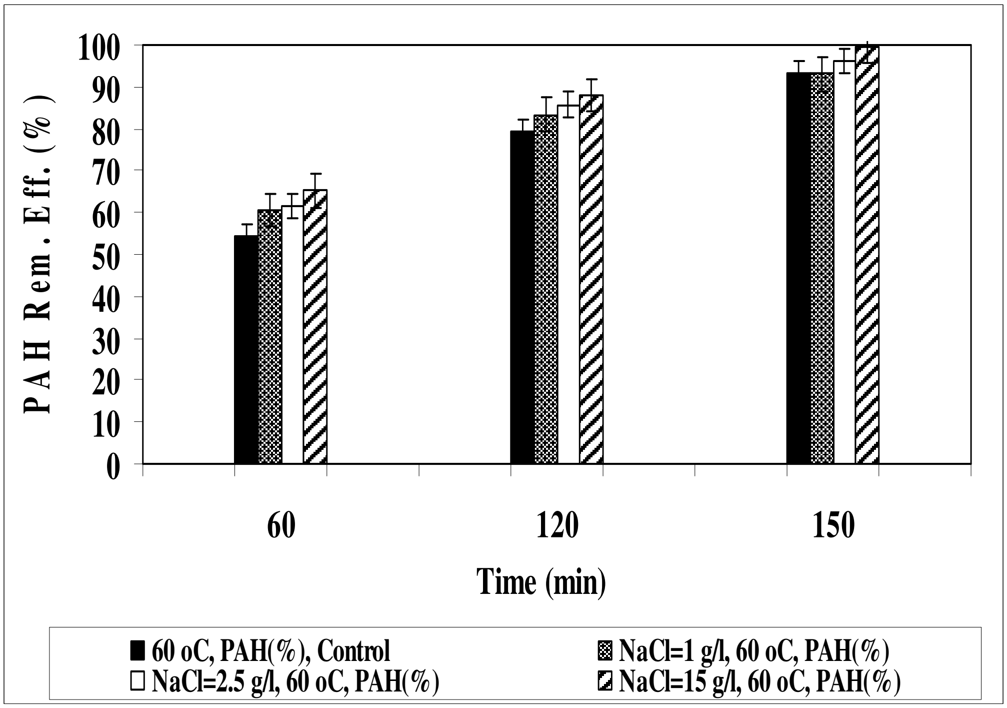
5.9.8 Effect of NaCl Concentrations on the PAHs Removal Efficiencies in PCI ww at Increasing Sonication Times and Temperatures

Increasing NaCl concentrations (1.00 g/l, 2.50 and 15.00 g/l) were added in PCI ww before sonication experiments. At 30^{o}C, 90.13%, 92.14% and 99.23% of total PAHs removals were observed in 1.00 g/l, 2.50 and 15.00 g/l NaCl after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.22a). The total PAHs yields were increased by 2.03% and 9.12% in 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication at pH=7.0 and at 30^{o}C, compared to the control (without NaCl while E=90.11% total PAHs at pH=7.0 and at 30^{o}C). A significant linear correlation between total PAHs yields and increasing NaCl concentration was not observed (R^2=0.38, F=0.31, p=0.01) (Figure 5.22a).

93.17%, 96.08% and 99.68% of total PAHs removals were obtained in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.22b). The contribution of NaCl to the PAHs removal was 2.78% in 15.00 g/l NaCl after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=96.90% total PAHs at pH=7.0 and at 60^{o}C). The maximum total PAHs removal efficiency was 99.68% after 150 min sonication time in NaCl=15.00 g/l at pH=7.0 and at 60^{o}C. A significant linear correlation between total PAHs yields and increasing NaCl concentration was not observed (R^2=0.33, F=0.215, p=0.01) (Figure 5.22b).



(a)



(b)

Figure 5.22 Effect of increasing NaCl concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

The effects of NaCl addition were evaluated in PHE, PY, ANT, DahA and BghiP at pH=7.0 under 1.50, 2.50, 5.00, 12.00, 15.00 and 18.00 g/l NaCl additions (Figure 5.23). The removals in PHE, PY, ANT, DahA and BghiP increased from 72.16-78.46%, up to 98.24% as the NaCl administration was increased from 1.50 up to 12.00 g/l whereas 15.00 and 18.00 g/l NaCl did not significantly contribute to the PAHs yields at 60°C after 150 min sonication time (Figure 5.23).

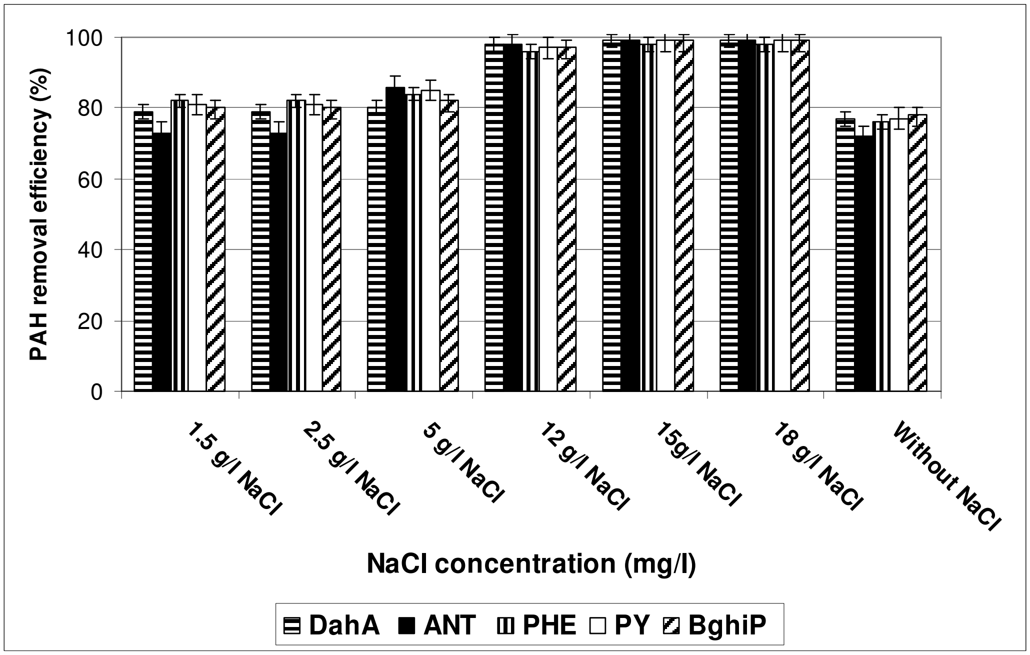


Figure 5.23 Effect of increasing NaCl on PAHs removal efficiencies at 60°C after 150 min sonication (sonication power=640 W, sonication frequency=35 kHz).

The contributions of the last two NaCl concentrations to the PAHs removals were only 2.80% and 3.20%, respectively. At NaCl concentrations > 12.00 g/l the partitioning of the PAHs molecules between interfacial and bulk region increases. Besides, addition of salt in the liquid medium reduces the DO concentration and hence, the scavenging of the radicals (Wang, J. et al., 2008). As a result, the probability of interaction between PAHs molecules and radicals decrease. The overall effect is reduction in the extent of degradation.

High NaCl concentrations (10.00-12.00 g/l) increase the ionic strength of the aqueous phase, driving the PAHs to the bulk–bubble interface through sonication (Sivasankar & Moholkar, 2008). This increases the partitioning of the PAHs species upon cavitation implosion in a sonicator resulting in increased surface tension of the PAHs. The higher NaCl concentrations (10.00-12.00 g/l) resulting in high removals can be explained by the fact that a higher amount of NaCl will create more salting out effect than the lower amount and thus increase the interfacial concentration of the PAHs. All of these factors help to collapse the bubbles more violently, causing high PAHs degradation. Since the Na^{+1} and Cl^{-1} concentrations in the sonicator were measured as 1.10 and 1.90 mg/l, respectively, after sonication, it can be concluded that a large part of 12.00 g/l NaCl reach an non-equilibrium adsorption level at the bubble/solution interface under the sonication conditions used. On the basis of this conclusion, it can be mentioned that the nonequilibrium surface excess values for solutes do not fully equilibrate with the bubble/solution interface during sonication. For the case of hydrophobic compounds, in the presence of excess NaCl, an acoustic bubble in a multibubble field has a finite lifetime, and that this lifetime increases with decreasing applied frequency. This resulting in a adsorption of excess salt to the bubble/solution interface during sonication as reported by Sunartio et al. (2007). Therefore, the NaCl remaining from the sonication did not cause serious pollution.

In our study, low contribution of NaCl > 12.00 g/l to the PAHs yields could be attributed to the synergistic and antagonistic effects of the by-products to the nature of hydrophobic PAHs, to the sonication time, temperature and their concentrations in PCI ww (Table 3.32). Previous studies have yielded similar results concerning the degradation of recalcitrant organics in the presence of NaCl through sonication (Wang, J. et al., 2008). They indicated that 0.50 mg/l NaCl increased the removal of refractory organics and promoted the sonication yields. As proved by Seymour & Gupta (1997) the hydrophobicity of the PAHs increases when NaCl is added to the aqueous PAHs solution. This causes the PAHs molecules to move towards the interface of the cavities created by sonication.

Table 5.32 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments in NaCl=15.00 g/l concentration after 60 min, 120 and 150 min sonication times at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**Inf. (A) T=0 min PAHs (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
NAP	1891.53 ± 66.20	440.69 ± 15.42	34.94	77.13	99.82
ACL	52.35 ± 1.83	0.72 ± 0.03	62.55	84.38	99.65
ACT	70.65 ± 2.50	0.71 ± 0.03	61.71	83.24	99.30
FLN	58.22 ± 2.04	0.68 ± 0.02	62.28	84.01	99.52
PHE	139.09 ± 4.87	3.19 ± 0.11	58.91	79.46	99.56
ANT	7.53 ± 0.26	0.03 ± 0.001	64.82	87.44	99.00
CRB	14.36 ± 0.50	0.11 ± 0.004	67.46	82.95	99.74
FL	19.68 ± 0.68	0.11 ± 0.004	64.18	86.57	99.45
PY	15.75 ± 0.55	0.09 ± 0.003	62.38	86.85	99.48
BaA	0.55 ± 0.02	0.002 ± 0.0001	65.21	87.96	99.06
CHR	2.69 ± 0.10	0.01 ± 0.0004	68.09	80.80	99.44
BbF	0.80 ± 0.03	0.003 ± 0.0001	65.20	87.94	98.33
BkF	0.80 ± 0.03	0.003 ± 0.0001	65.20	89.94	99.17
BaP	0.07 ± 0.003	0.0002 ± 0.00001	53.24	78.00	99.73
IcdP	1.09 ± 0.04	0.004 ± 0.0001	65.18	87.92	99.76
DahA	4.60 ± 0.16	0.02 ± 0.0007	64.99	88.66	99.59
BghiP	0.51 ± 0.02	0.002 ± 0.0001	59.21	87.97	99.57

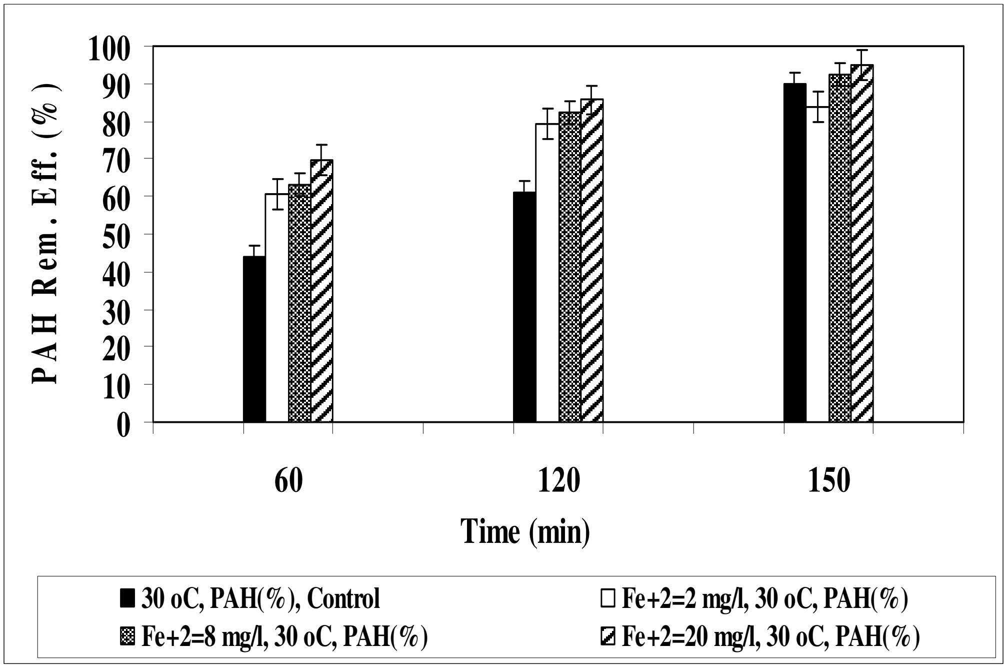
(A) Inf.= influent, (B) Eff. = effluent.

Depending on the nature of contaminants, addition of salt (NaCl) to the solution can decrease their solubility and consequently increase their hydrophobicity due to the salting-out effect. This is expected to enhance diffusion of solutes from the bulk solution to the bubble–liquid interface, thus leading to increased degradation rates. A possible explanation would be that adding salt to the reaction mixture results in reduced vapour pressure and increased surface tension, both of which tend to reduce the number of bubbles formed (Psillakis et al., 2004).

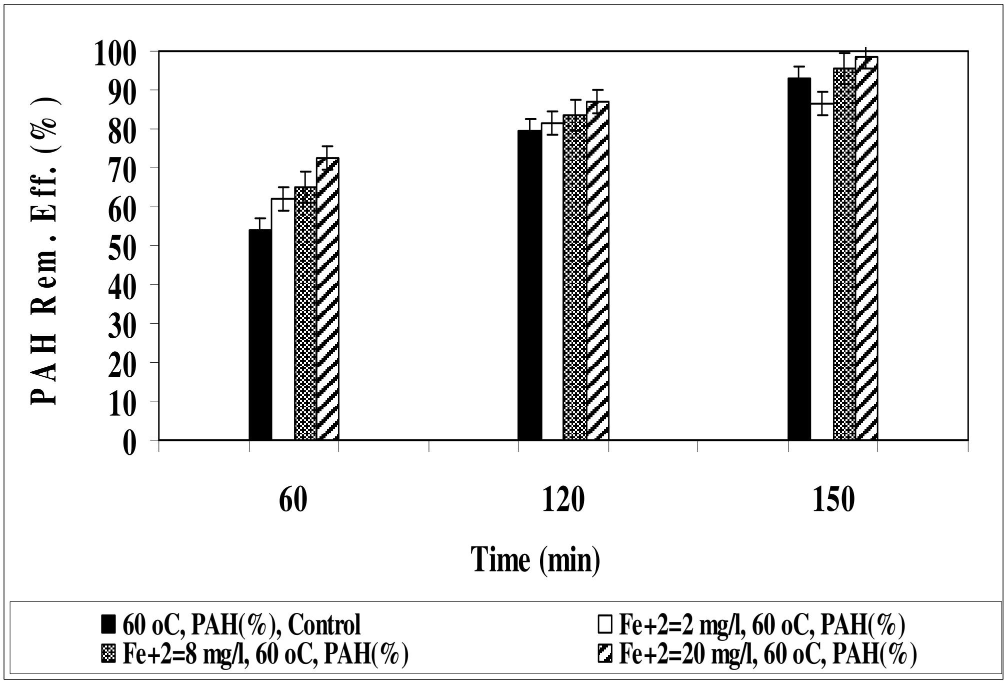
5.9.9 Effect of Fe^{+2} Concentrations on the Removal of PAHs in PCI ww at Increasing Sonication Times and Temperatures

2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2} ions (from $FeCl_2.4H_2O$) were added to the PCI ww before the sonication experiments. 83.27%, 92.62% and 95.12% total PAHs removals were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication at pH=7.0 and at 30^{o}C (Figure 5.24a). No significant increase in PAHs yields was obtained from 8.00 to 20.00 mg/l Fe^{+2} after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (without Fe^{+2} while E=90.11% for total PAHs at pH=7.0 and at 30^{o}C). A significant linear correlation between total PAHs yields and increasing sonication time was not observed (R^2=0.30, F=0.28, p=0.01) (Figure 5.24a).

86.28%, 95.27% and 98.56% total PAHs yields were observed in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.24b). No significant increase in total PAHs yields were obtained by increasing the Fe^{+2} concentrations compared to the control after 120 and 150 min sonication times at pH=7.0 and at 60^{o}C. Sonication alone provided 96.90% total PAHs yield after 150 min sonication time at pH=7.0 and at 60^{o}C The maximum total PAHs removal efficiency was 98.56% after 150 min sonication time in Fe^{+2}=20.00 mg/l at pH=7.0 and at 60^{o}C. A significant linear correlation between total PAHs yields and increasing Fe^{+2} concentrations was not observed (R^2=0.32, F=0.31, p=0.01) (Figure 5.24b).



(a)



(b)

Figure 5.24 Effect of increasing Fe^{+2} concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

The individual PAHs removal for seventeen PAHs are given in Table 5.33 in 20.00 mg/l Fe^{+2} after 150 min sonication at pH=7.0 and at 60°C. The removal efficiencies of all seventeen PAHs were above 90.00% after 150 min sonication time. The PAHs containing four (CHR, BaA), five (BkF, BaP) and six benzene (DahA, BghiP) rings were removed with high efficiencies at 60°C after 150 min of sonication time at pH=7.0 (Table 5.34).

Table 5.33 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments in Fe^{+2}=20.00 mg/l concentration after 60 min, 120 and 150 min sonication times at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**Inf. [(A)] T=0 min PAHs (ng/ml) ± SD**	**Eff. [(B)] T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
NAP	1884.52 ± 65.96	448.59 ± 15.70	38.99	76.87	98.94
ACL	52.34 ± 1.83	1.28 ± 0.05	69.57	83.63	97.99
ACT	70.61 ± 2.47	1.45 ± 0.05	68.64	82.51	95.93
FLN	58.20 ± 2.04	1.30 ± 0.05	69.27	83.27	97.21
PHE	138.98 ± 4.96	4.58 ± 0.16	65.55	78.79	97.44
ANT	7.52 ± 0.26	0.11 ± 0.004	71.08	86.65	94.22
CRB	14.36 ± 0.50	0.26 ± 0.009	70.68	86.16	98.50
FL	19.68 ± 0.70	0.33 ± 0.012	69.37	85.78	96.80
PY	15.75 ± 0.55	0.26 ± 0.009	71.59	86.06	96.99
BaA	0.55 ± 0.02	0.01 ± 0.0004	72.51	87.15	94.59
CHR	2.69 ± 0.09	0.04 ± 0.001	73.38	86.78	96.76
BbF	0.80 ± 0.03	0.01 ± 0.0004	70.49	84.14	90.37
BkF	0.80 ± 0.03	0.01 ± 0.0004	72.49	88.14	95.23
BaP	0.07 ± 0.003	0.001 ± 0.00004	75.54	89.19	98.45
IcdP	1.09 ± 0.04	0.02 ± 0.0007	72.47	87.12	98.59
DahA	4.60 ± 0.16	0.07 ± 0.003	72.26	86.86	97.63
BghiP	0.51 ± 0.02	0.01 ± 0.0004	70.51	82.16	97.52

[(A)] Inf.= influent, [(B)] Eff. = effluent.

Table 5.34 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml).

PAHs	**CAS-No**	**MF**	**MW**	T_M	T_B	S_W (25°C)	V_P (25°C)	**H** (25°C)	**log K_{OA} (25°C)**	**log K_{OW}**	**IPC**
BaA	56-55-3	$C_{18}H_{12}$	228	84	438	$9.40 x 10^{-3}$	$2.00 x 10^{-7}$	$1.20 x 10^{-5}$	10.28	5.76	$5.50 x 10^{-1}$
CHR	218-01-9	$C_{18}H_{12}$	228	258	448	$2.00 x 10^{-3}$	$6.23 x 10^{-9}$	$5.23 x 10^{-6}$	10.30	5.81	$2.68 x 10^{-1}$
BkF	207-08-9	$C_{20}H_{12}$	252	217	480	$8.00 x 10^{-4}$	$9.70 x 10^{-10}$	$5.84 x 10^{-7}$	11.37	6.11	$8.00 x 10^{-1}$
BaP	50-32-8	$C_{20}H_{12}$	252	177	495	$1.62 x 10^{-3}$	$5.49 x 10^{-9}$	$4.57 x 10^{-7}$	11.56	6.13	$7.50 x 10^{-2}$
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	$2.49 x 10^{-4}$	$1.00 x 10^{-10}$	$1.23 x 10^{-7}$	12.59	6.75	$45.78 x 10^{-2}$
BghiP	191-24-2	$C_{22}H_{12}$	276	278	> 500	$2.67 x 10^{-4}$	$1.00 x 10^{-10}$	$3.31 x 10^{-7}$	12.55	6.63	$51.30 x 10^{-2}$

benz[*a*]anthracene (BaA), chrysene (CHR), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g/mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg/l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 /mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng/ml)

These high removals in PAHs with high molecular weights could be attributed to effective sonication at 35 kHz with 20.00 mg/l Fe^{+2}. The findings of the study demonstrate that sonication enhanced with 20.00 mg/l Fe^{+2} can be used to improve the mass transport of poorly soluble PAHs in PCI ww and alleviate limiting steps of removal of hydrophobic refractory PAHs after 150 min sonication time at 60°C. Furthermore, the reaction of Fe^{+2} with H_2O_2 form $OH^{\bullet}$ ion. This phenomenon leading to the destruction of benzene rings of hydrophobic and hydrophilic PAHs. Some of the recent studies showed that there is a highly significant relationship between the average removal percentages and the hydrophobicity of PAHs, indicated as the octanol water partition coefficient is shown (Bremmer et al., 2008; Wu & Ondruschka, 2005). It becomes evident that a larger hydrophobicity resulted in smaller removal of the PAHs. However, in this study, the 4-ring, 5 and 6- ring PAHs, in contrast to the relationship mentioned above, exhibiting higher removals than expected from their log K_{ow} at 60°C after 150 min of sonication time. No significant correlation was observed between PAHs yields, water solubility, vapor pressure, C number in benzene rings, Henry's law constant through sonication assisted 20.00 mg/l Fe^{+2} at 60°C after 150 min of sonication time ($R^2=0.43$, $F=3.56$, $p=0.001$) (Table 5.34).

On the other hand, it was found that the coefficient of the correlation between the PAHs yields and the residual concentrations was strong and significant ($R^2=0.83$, $F=13.16$, $p < 0.001$) at 60°C after 150 min of sonication time (Figure 5.25). Similar PAHs removal in PAHs with low and high benzene rings could be attributed to the remaining PAHs percentages varying between 0.04% and 10.00% after 150 min of sonication time since the hydrophobic PAHs can easily diffuse near cavitation bubbles under pyrolytic destruction.

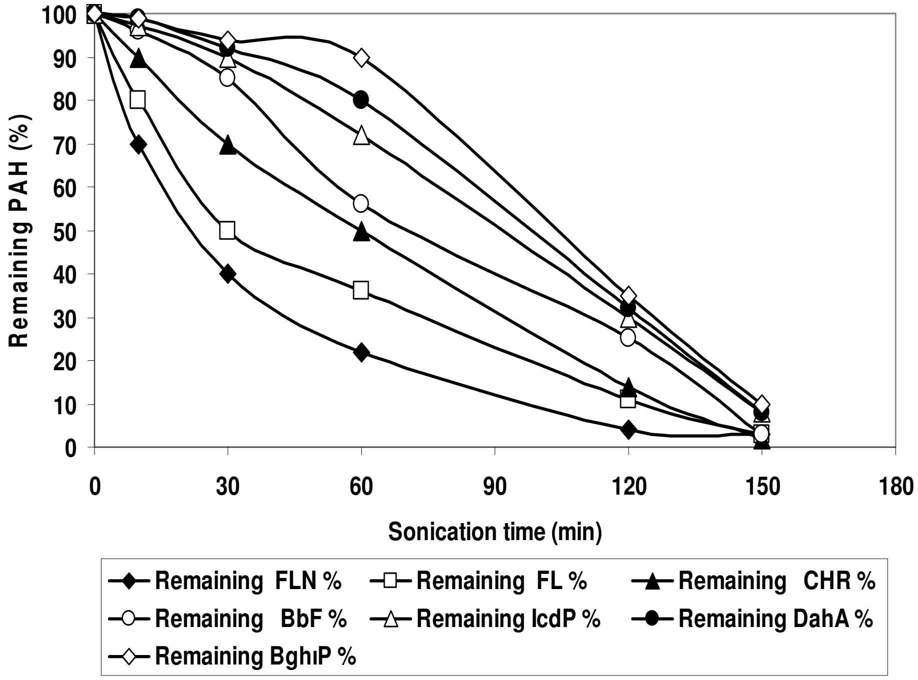
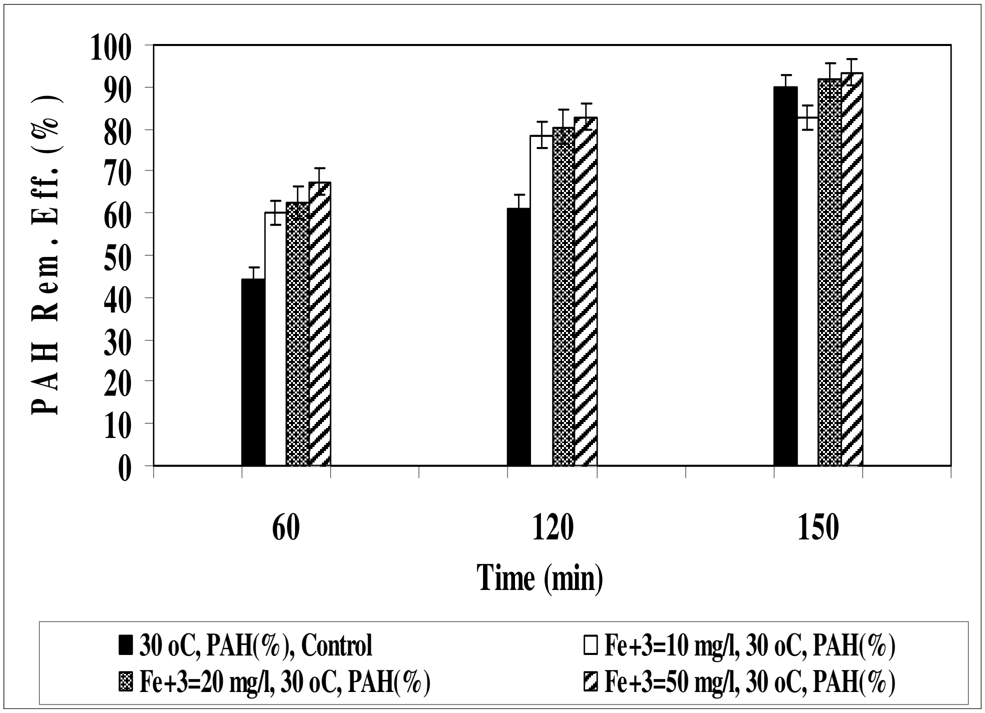


Figure 5.25 The remaining (untreated) PAHs percentages versus sonication time in pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

As reported by Lindsey & Tarr (2000b) a possible explanation of the postive effect of Fe^{+2} on the sonication of PAHs could be the reaction of Fe^{+2} with H_2O_2 to form $OH^\bullet$ at a 34 kHz and a power of 450 W after 125 min sonication at 60^oC. As this reaction proceeds, the concentration of Fe^{+2} declines, and consequently the rate of H_2O_2 consumption and $OH^\bullet$ formation decline. The loss of Fe^{+2} is eventually balanced by the formation of Fe^{+2} through reduction of Fe^{+3} by reaction with H_2O_2 or $O_2H^\bullet$, and a steady state Fe^{+2} concentration is reached. At this point (> 60 s), pseudo first order loss of H_2O_2 is observed. This explanation is also supported by evidence that the $OH^\bullet$ formation rate is significantly higher in the first 60 s. Psillakis et al. (2004) studied the sono-removal of 150 μg/l total initial concentration of PAHs mixture (NAP, ACT, PHE) in an aqueous solution. 92.20% of NAP, 96.25% of ACT and 89.80% of PHE removal efficiencies were found with Fe^{+2}=14.00 mg/l concentration in a sonicator with a power of 150 W, a frequency of 80 kHz, a sonication temperature of 20^oC, after 150 min irradiation. In our study the removal efficiencies for the aforementioned PAHs were found to be higher (E, NAP=99.00%, E, ACT=98.25% and E, PHE=98.11%) at 35^{o}C for the same sonication time. Beckett & Hua (2000, 2003) also found that the addition of 0.02-1.00 ng/l Fe^{+2} concentrations improved the 1,4–dioxane decomposition rate and mineralization efficiency at a 30 kHz and a power of 590 W after 115 min sonication time. During aqueous ultrasonic irradiation, $OH^{\bullet}$ formed during the thermolytic reactions of H_2O recombine to form H_2O_2 that tends to accumulate in the solution and does not usually play an important role in oxidizing organic species. However, the reaction between H_2O_2 and Fe^{+2} is known to produce $OH^{\bullet}$ and is commonly referred to as the Fenton process (Bremmer et al., 2008).

5.9.10 Effect of Fe^{+3} Concentrations on the Removal of PAHs in PCI ww at Increasing Sonication Times and Temperatures

Increasing Fe^{+3} concentrations (10.00 mg/l, 20.00 and 50.00 mg/l) were added to the PCI ww before sonication process. 82.92%, 91.72% and 93.58% total PAHs removals were measured in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.26a). An increase of 14.66-22.28% and 16.21-20.55% in total PAHs yields were measured for after 60 and 120 min sonication times, compared to the control (without Fe^{+3}) at pH=7.0 and at 30^{o}C. Although, a correlation between PAHs removal efficiencies and Fe^{+3} concentrations were obtained this relationship was not significant (R^2=0.76, F=2.56, p=0.01). control provided 90.11% total PAHs yield after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.26a).



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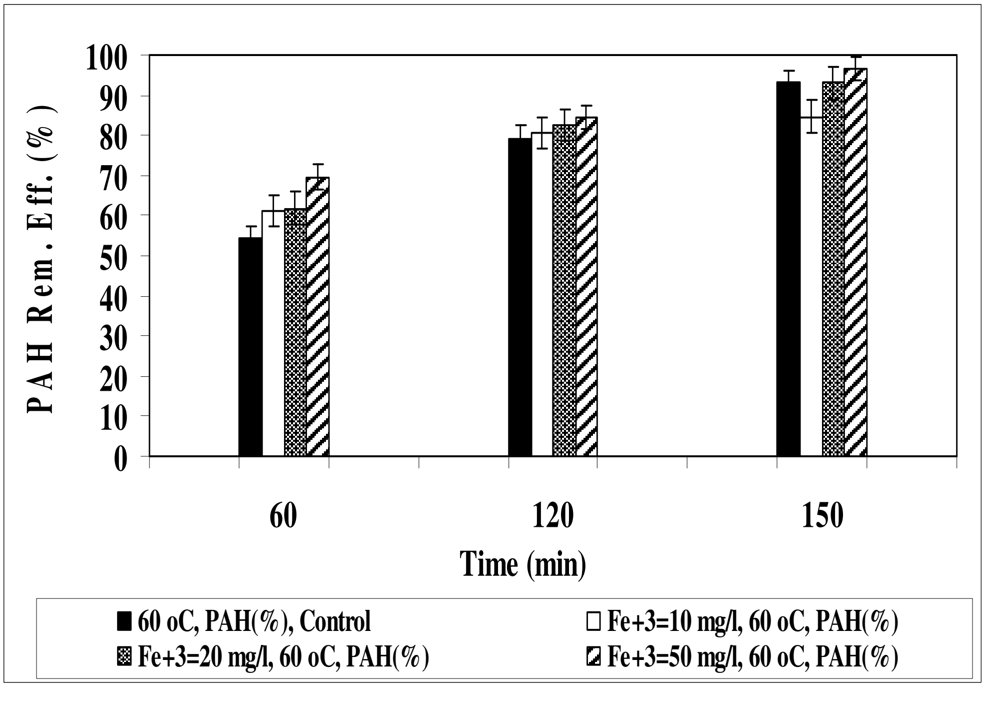


(b)

Figure 5.26 Effect of increasing Fe^{+3} concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

84.61%, 93.00% and 96.76% total PAHs yields were observed in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.26b). The contribution of increasing Fe^{+3} on the total PAHs removal was only 7.06-15.41% and 1.25-5.04% compared to the control after 60 and 120 min sonication times at pH=7.0 and at 60°C. The maximum total PAHs removal efficiency was 96.76% after 150 min sonication time in Fe^{+3}=50.00 mg/l at pH=7.0 and at 60°C. However this contribution of Fe^{+3} was no significant (R^2=0.66, F=9.86, p=0.01). Similarly, increasing the Fe^{+3} concentrations did not significantly affect the PAHs yields compared to the control after 120 and 150 min sonication times at pH=7.0 and at 60°C (R^2=0.52-0.56, F=8.34-9.91, p=0.01) (Figure 5.26b).

95.80% BbF, 90.29% BkF, 96.84% BaP, 97.13% IcdP, 95.18% DahA and 94.95% BghiP maximum removal yields were obtained for PAHs with four, five and six benzene rings after 150 min sonication time at 60°C in 50.00 mg/l Fe^{+3} (Table 5.35). The yields found in this study were not dependent to the physichochemical properties of the PAHs. Therefore, a significant correlation between the PAHs removals and the high octanol-air coefficient and the octanol-water coefficient of the heavily PAHs was not observed (R^2=0.39, F=3.91, p=0.01).

Table 5.35 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments in Fe^{+3}=50.00 mg/l concentration after 60 min, 120 and 150 min sonication times at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**Inf. (A) T=0 min PAHs (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
NAP	1896.53 ± 66.38	472.83 ± 16.55	47.18	75.05	97.84
ACL	52.37 ± 1.83	2.20 ± 0.08	66.74	80.85	95.91
ACT	70.67 ± 2.47	2.67 ± 0.09	65.83	79.76	91.71
FLN	58.23 ± 2.04	2.31 ± 0.08	66.44	80.50	94.32
PHE	139.17 ± 4.87	6.88 ± 0.24	62.83	76.12	94.80
ANT	7.53 ± 0.26	0.25 ± 0.009	69.18	83.81	94.40
CRB	14.36 ± 0.50	0.52 ± 0.02	68.78	83.33	96.94
FL	19.69 ± 0.70	0.68 ± 0.02	67.48	82.97	93.48
PY	15.75 ± 0.55	0.54 ± 0.02	68.70	83.24	93.88
BaA	0.55 ± 0.02	0.02 ± 0.0007	69.59	84.31	94.58
CHR	2.69 ± 0.09	0.09 ± 0.003	67.46	82.16	93.40
BbF	0.80 ± 0.03	0.03 ± 0.001	70.57	84.29	95.80
BkF	0.80 ± 0.03	0.03 ± 0.001	69.57	80.29	90.29
BaP	0.07 ± 0.003	0.002 ± 0.0001	72.62	87.34	96.84
IcdP	1.09 ± 0.04	0.04 ± 0.001	67.56	84.27	97.13
DahA	4.60 ± 0.16	0.15 ± 0.005	69.35	81.02	95.18
BghiP	0.51 ± 0.02	0.02 ± 0.0007	62.59	80.31	94.95

(A) Inf.= influent, (B) Eff. = effluent.

In the presence of Fe^{+3}, the sonolytic degradation of less hydrophobic PAHs was enhanced by the increase in $OH^{\bullet}$ induced from the decomposition of the recombined H_2O_2 (Yim et al., 2003). Under these conditions, it can be expected that $Fe–O_2H^{+2}$ as an intermediate produced from the reaction of Fe^{+3} with H_2O_2 and it may be partitioned as Fe^{+2} and $O_2H^{\bullet}$ by the ultrasonic irradiation in Eqs. (5.12) and (5.13) (Yim et al., 2003). The regenerated Fe^{+2} also catalyze the decomposition of H_2O_2 in Eq. (5.13). These results suggest that in the presence of Fe^{+3}, the sonolytic degradation of less hydrophobic PAHs was enhanced by the increase in $OH^{\bullet}$ (Yim et al., 2003) in Eq. (5.14).

$$Fe^{+3} + H_2O_2 \quad \rightarrow \quad Fe - O_2H^{+2} + H^{+} \tag{5.12}$$

$$Fe - O_2H^{+2} \quad \rightarrow \quad Fe^{+2} + O_2H^{\bullet} \tag{5.13}$$

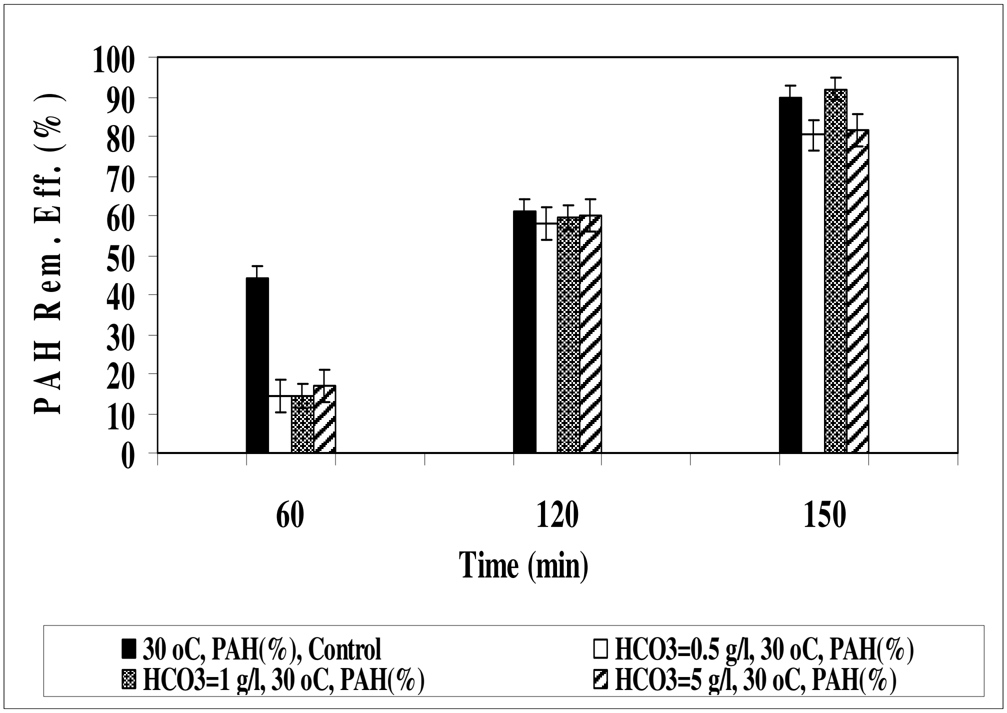
$$Fe^{+3} + O_2H^{\bullet} \quad \rightarrow \quad Fe^{+2} + O_2 + H^{+} \tag{5.14}$$

A large fraction of Fe^{+3} formed from the reaction Fe^{+2} with H_2O_2 would mainly exist in the form of $Fe^{+3}–O_2H$ or $Fe^{+3}–OH$ complexes. Fe^{+3} /ultrasound it can be expected that $Fe–O_2H$ as an intermediate produced from the reaction of Fe^{+3} with H_2O_2 may be partitioned as Fe^{+2} and $O_2H^{\bullet}$ by the ultrasonic irradiation. It was found that the Fe^{+3}/ultrasound system under O_2 is more effective for mineralization than the Fe^{+2}/ultrasound system and ultrasound only (Lindsey & Tarr, 2000b). For Fe^{+3}, the overall degradation of organic compounds by oxidation is slower, but the mineralization process is successfully achieved. The degradation of organic compounds by the attack of $OH^{\bullet}$ can be enhanced.

5.9.11 Effect of HCO_3^{-1} Concentrations on the Removal of PAHs in PCI ww at Increasing Sonication Times and Temperatures

Increasing HCO_3^{-1} (0.50 g/l, 1.00 and 5.00 g/l) concentrations were added to the PCI ww before sonication process. 80.43%, 92.14% and 81.66% total PAHs yields were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.27a). Total PAHs yields were sligthly increased in 1.00 g/l HCO_3^{-1} (2.00%) compared to the control (without HCO_3^{-1} while E=90.11% total PAHs) at pH=7.0 and at 30°C after 150 min sonication time. A significant linear correlation between total PAHs yields and increasing sonication time was not observed (R^2=0.32, F=0.30, p=0.01) (Figure 5.27a).

78.09%, 81.69% and 82.62% total PAHs removals were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.27b). Total PAHs yields did not change after 150 min sonication time compared to the control (E=96.90% total PAHs) at pH=7.0 and at 60°C. A significant linear correlation between total PAHs yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.34, F=0.40, p=0.01) (Figure 5.27b).



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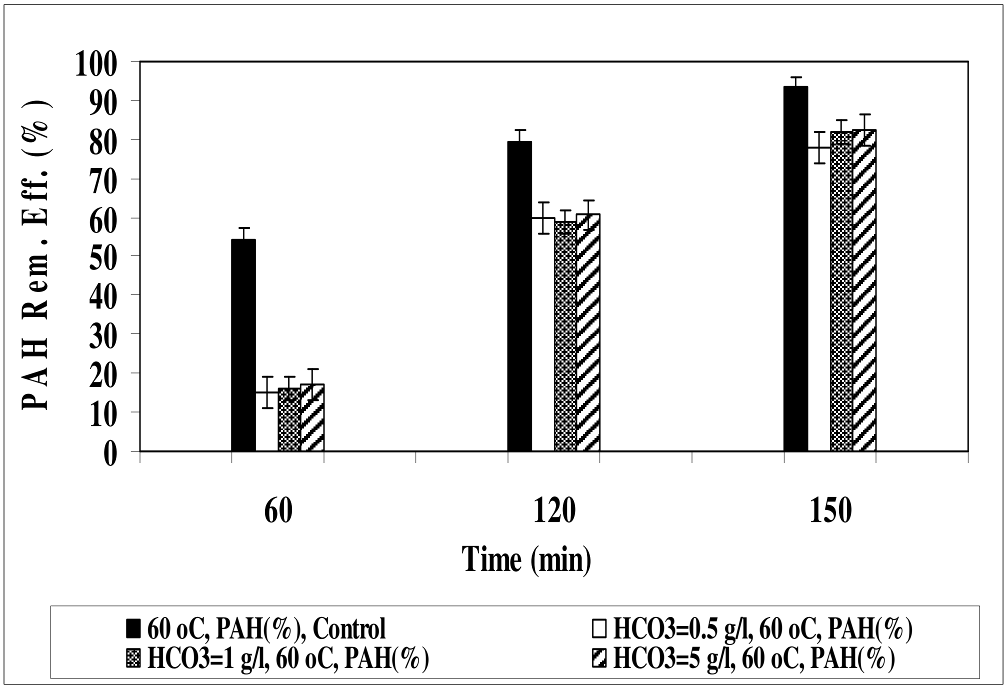


(b)

Figure 5.27 Effect of increasing HCO_3^{-1} concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

In order to identify the contribution of $OH^\bullet$ in the sonolytic degradation of PAHs, the role of $OH^\bullet$ was examined in the absence and presence of HCO_3^{-1}. Therefore, one refractory non-volatile, more hydrophobic PAHs namely DahA (4.57 ng/ml) was taken into consideration among the other seventeen PAHs present in PCI ww. Figure 5.28 presents the percent reduction of DahA during these experiments. As shown in this figure, the degradation curves can be mainly divided into three regions (initiation, acceleration and stabilization steps), but the most degradation of DahA was observed in two regions (initiation and acceleration steps). The degradation curves given in Figure 5.28 can be estimated with the sigmoidal model based on the best fits by trial and error using Eq. (5.15):

$$y = y_o + \frac{a}{\left[1 + \left(\frac{x}{x_0}\right)^b\right]} \tag{5.15}$$

where, y is the degradation percent of PAHs and y_o is the intercept, x_o is the time at the inflection point (the time dividing between the first two stages), and a and b are dependent variables. This sigmoidal model Eq. (5.15) was used to divide the curves in Figure 5.28 mainly into two stages, the initiation and the acceleration step as reported by Son et al. (2006). By fitting the data into Eq. (5.15), R^2 values (the conformity to the sigmoidal model) of each degradation curve in the runs with HCO_3^{-1} and without HCO_3^{-1} at 0 and 60 min sonication times were obtained, and found to be R_1^2=0.98 and R_2^2=0.97, respectively. The R^2 values obtained from Eq. (5.15) also provided the estimation of reaction time in each step, and this estimated reaction time in each step is shown.

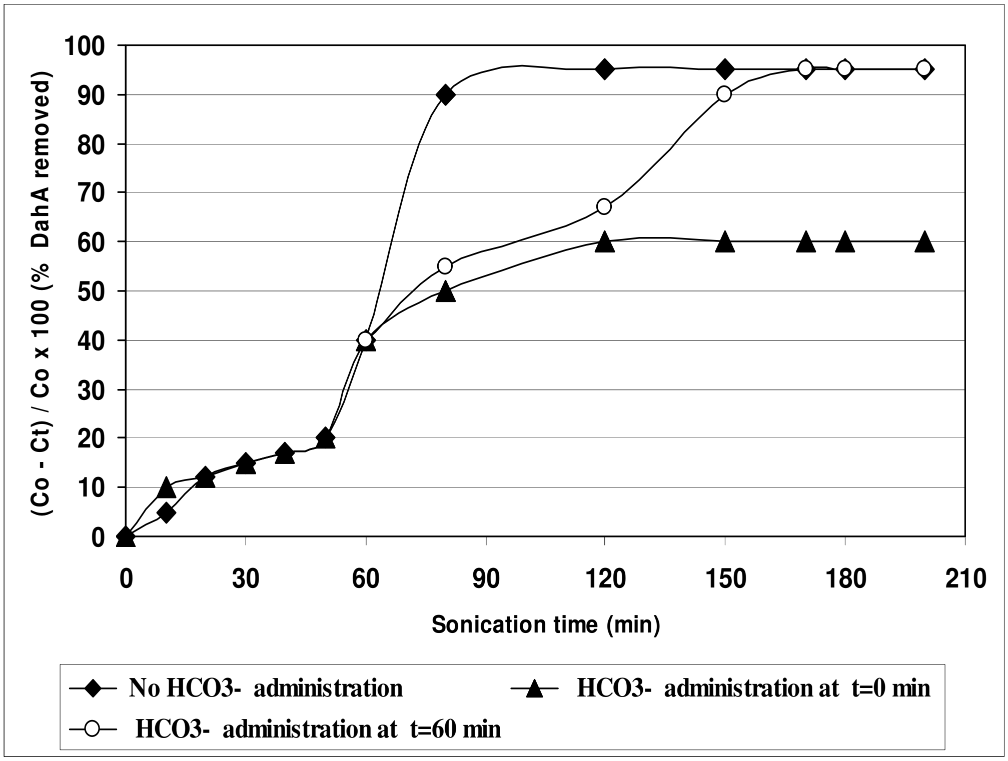


Figure 5.28 Percent reduction of DahA with HCO_3^{-1} trough sonication times (sonication power=640 W, sonication frequency=35 kHz).

As shown in Figure 5.28, the total percent degradation values of DahA during the initiation steps were not significantly different (ANOVA, F=13.98, p=0.001) between these two cases. However, significant differences (ANOVA, F=2.67, p=0.001) were observed between the percent degradation values at the acceleration steps. Similar statistical results were obtained between the trials with HCO_3^{-1} and without HCO_3^{-1} after 60 min sonication time (ANOVA, F=1.98, p=0.001 and F=2.80, p=0.001) at the initiation steps. HCO_3^{-1} is a well known $OH^{\bullet}$ scavenger as shown in Eq. (5.16):

$$HCO_3^{-} + OH^{\bullet} \quad \rightarrow \quad HCO_3^{\bullet} + OH^{-} \tag{5.16}$$

Since HCO_3^{-1} is an ion, it will scavenge free radicals predominantly in the bulk water phase. Water-soluble compounds that are non volatile will be signicantly affected by the HCO_3 concentration (Guo et al., 2008; Wang, J. et al., 2006b). Since DahA is non-volatile, a refractory compound, the HCO_3 can complete with DahA for available free radicals in the interfacial and bulk region and decrease the sonical destruction efficiency of the PAHs in question. Figure 5.28 also shows the contribution of HCO_3^{-1} in the role of $OH^\bullet$ scavenger during sonolysis. The effect of radical scavenging by HCO_3^{-1} mainly occurred during the acceleration step, and suggesting that the most $OH^\bullet$ in the sonication is generated at the acceleration step. From the results in Figure 5.28 during the sonication it can be induced that the reaction between $OH^\bullet$ and HCO_3^{-1} mainly occurs at the acceleration step rather than at the initial step. As aforementioned $OH^\bullet$ are mainly produced at the acceleration step, which react with HCO_3^{-1} to produce $OH^\bullet$ ion, resulting in the increase in pH of the solution. However, at the initiation step, the production of $OH^\bullet$ is insufficient for the reaction with HCO_3^{-1}, as shown in Eq. (5.16). Instead, the presence of 10.00 mg/l HCO_3^{-1} may act as a buffer in the solution, resulting in almost no change of pH.

The sonication of DahA at the initiation step may proceed by a thermal reaction, while the degradation of DahA is dominated by $OH^\bullet$ reaction at the acceleration step. As shown in Figure 5.28, thermal degradation and chemical oxidation contributed approximately 25.00% and 34.00% to the degradation of 1,4–dioxane according to the result of the sonication without HCO_3^{-1} as reported by Son et al. (2006).

The sonic degradation of DahA in the PCI ww was found to be varied between zero and pseudo first order with respect to PAHs concentration in the initiation and acceleration steps with HCO_3^{-1} and without HCO_3^{-1} at a frequency of 35 kHz and at 60°C in Eqs. (5.17) and (5.18):

$$-\frac{d[PAH]}{dt} = k[PAH]_t \qquad (5.17)$$

$$\frac{d\,[\,PAH\,]}{dt} = k \qquad (5.18)$$

Table 5.36 shows the results of rate constants of DahA removals, and also, R_1^2 and R_2^2 values fitted by zero and first order model estimation at the initiation and acceleration steps. As shown in this table the kinetic data obtained in the initiation step the DahA removal with and without HCO_3^{-1} follows the zero order kinetic rate models. However, in both acceleration steps DahA destruction followed the pseudo-first order rate model.

Table 5.36 Effect of HCO_3^{-1} on DahA removal kinetic at three different sonication steps (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

Conditions	**Runs (min)**	**Pseudo Zero Order**		**Pseudo First Order**	
		k_o (ng/lmin) (x 10^{-2})	**R^2**	**k_1 (1/min) (x 10^{-3})**	**R^2**
No HCO_3^{-1} administration	Overall	4.45	0.96	6.67	0.99
	İnitiation (< 100 min)	1.67	0.95	4.78	0.98
	Acceleration (< 110 min)	23.67	0.96	45.08	0.99
HCO_3^{-1} administration at t= 0 min	Overall	4.54	0.95	5.98	0.98
	İnitiation (< 90 min)	1.98	0.97	3.89	0.99
	Acceleration (< 120 min)	25.90	0.98	32.67	0.99
HCO_3^{-1} administration at t= 60 min	Overall (< 120 min)	4.01	0.96	3.78	0.99
	İnitiation (< 40 min)	2.01	0.97	4.34	0.99
	Acceleration (< 90 min)	13.89	0.97	10.78	0.99

Linear regression analysis was performed in order to determine the conformity to zero order or the pseudo-first order model in each step, based on Eq. (5.17) (Benabdallah El-Hadj et al., 2007). R_1^2 and R_2^2 stand for the linear regression coefficients for zero order and pseudo-first order reaction kinetic model in each step, respectively. However, the kinetic constants found for DahA removal in the presence of HCO_3^{-1} after 60 min sonication exhibited a zero order kinetic rate model for both initiation (R_1^2=0.97) and acceleration (R_2^2=0.91) steps. Under these conditions, a maximum DahA removal efficiency was achieved. Similar results was obtained in the study performed by Son et al. (2006) treating 1,4–dioxane.

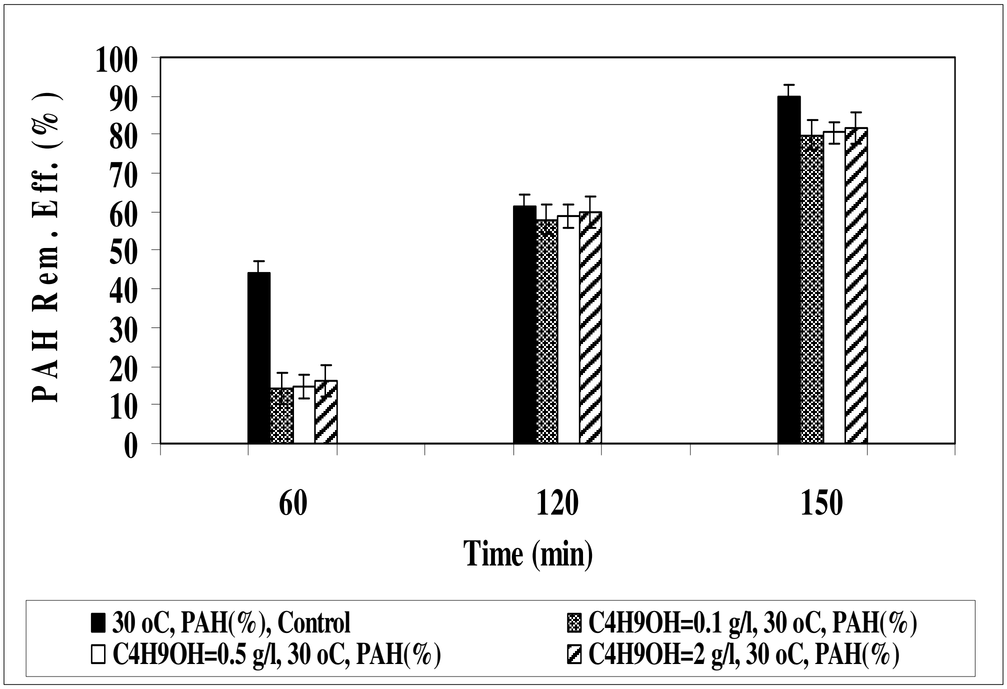
The results of this part of this study showed that the degradation trend of the DahA at the acceleration step was also not significantly different between two conditions with and without HCO_3^{-1} at the beginning of the sonication (0 min). However, the rapid decrease of DahA degradation was observed at the acceleration step in the presence of HCO_3^{-1} after 60 min of sonication time. The initiation step of the DahA degradation followed the zero order kinetic rate models, while the acceleration step followed the pseudo-first order. In the presence of HCO_3^{-1} as a radical scavenger, the degradations of DahA were suppressed, indicating that $OH^\bullet$ is an important factor in the sonication, especially at the acceleration step. Since DahA is hydrophobic, HCO_3^{-1} can compete with DahA for available free radicals in the interfacial and bulk region and decrease its decomposition efficiency. Similar results was also found by Shaw & Lee (2009): HCO_3^{-1} added in the concentration interval 10^{-3} to 185 mg/l acted as $OH^\bullet$ scavenger and the expected effect was found to be inhibition of degradation of some dyes and hydrocarbons in pulp and paper industry wastewater. They reported that water soluble compounds that are less volatile will be significantly influenced by the HCO_3^{-1} concentration. This contradicts with the results obtained by Minero et al. (2008). They found that the degradation rate of Acid Blue 40 was increased in the presence of CO_3 and HCO_3^{-1}, with a maximum around 610 mg/l total concentration at pH=9.0 and a saturation trend at pH=11.0. They mentioned that in the presence of HCO_3^{-1} not all the sonochemically formed $OH^\bullet$ can induce the substrate degradation since with an elevated OH at the air–water interface, radical–radical recombination to yield H_2O_2 and H_2O would be much more important than the reaction with the substrates. Furthermore, thus would also limit the diffusion of reactive radical species to the solution bulk in the sonicator with a frequency of 29 kHz and a power of 450 W.

5.9.12 Effect of Iso-butanol (C_4H_9OH) Concentrations on the Removal of PAHs in PCI ww at Increasing Sonication Times and Temperatures

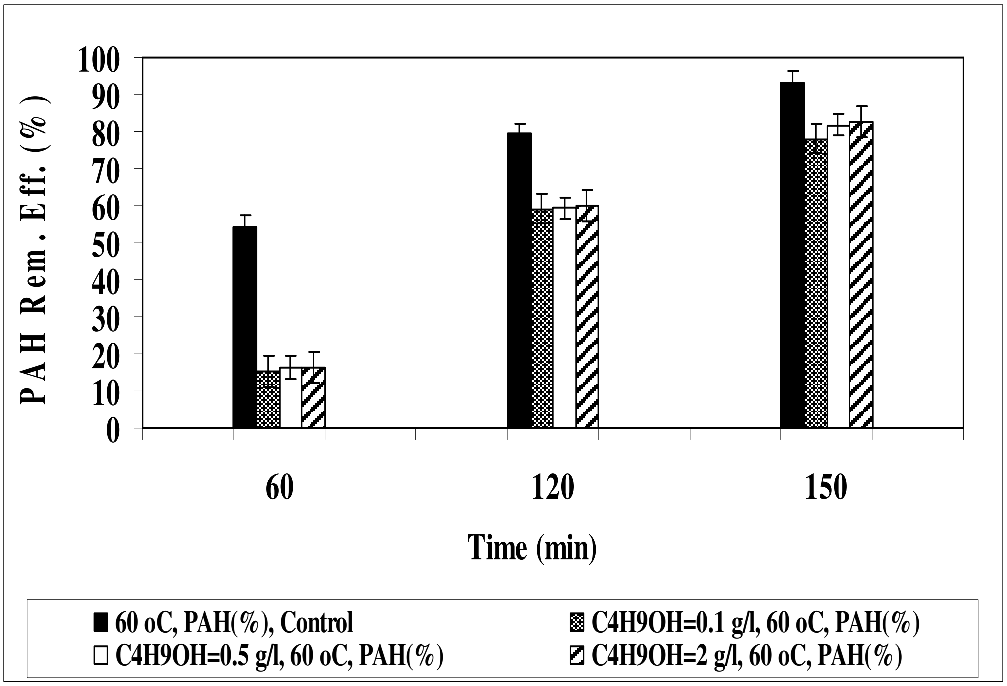
0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH concentrations were added to the PCI ww before sonication process. As the sonication time increased from 60 to 150 min sonication times the total PAHs removals increased from 14.41% to 60.14% and 92.14% in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, at pH=7.0 and at 30^{o}C (Figure 5.29a). Sonication alone provided 45.34%, 62.40% and 90.11% total PAHs yields after 60, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^{o}C. In this study, it was found that C_4H_9OH addition decreased the PAHs yields significantly for 60 and 120 min sonication times at pH=7.0 and at 30^{o}C. A significant linear correlation between total PAHs yields and increasing C_4H_9OH concentrations was not observed (R^2=0.32, F=0.43, p=0.01) (Figure 5.29a).

No significant contributions of C_4H_9OH to the total PAHs yields was observed at 60^{o}C (Figure 5.29b). Sonication alone provided 54.21%, 79.31% and 96.90% total PAHs removals after 60, 120 and 150 min sonication times, respectively, while the PAHs yields decreased to 15.24%, 60.56% and 82.62% for the sonication given above at 60^{o}C in the samples containing 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, at pH=7.0. The maximum total PAHs removal efficiency was 82.62% after 150 min sonication time in C_4H_9OH=2.00 g/l at pH=7.0 and at 60^{o}C. A significant linear correlation between total PAHs yields and increasing C_4H_9OH concentrations was not observed (R^2=0.34, F=0.38, p=0.01) (Figure 5.29b).

The effect of C_4H_9OH on the yields of less (BaA, CHR and BbF) and more hydrophobic PAHs (BkF, BaP, IcdP, DahA and BghiP) were investigated (Table 5.37). The individual PAH yields for more and less hydrophobic PAHs were observed in 2.00 g/l C_4H_9OH after 150 min sonication time at pH=7.0 and at 60^{o}C (Table 5.37).



(a)



(b)

Figure 5.29 Effect of increasing C_4H_9OH concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

Table 5.37 The individual PAHs yields for more and less hydrophobic PAHs measured in the influent and in the effluent of the sonication experiments after 60 min, 120 and 150 min sonication times in C_4H_9OH=2.00 g/l concentration at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**Inf. (A) T=0 min PAHs (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs(%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**
BaA	0.66 ± 0.02	0.10 ± 0.003	29.93	66.42	85.27
CHR	3.64 ± 0.12	0.52 ± 0.01	37.91	69.95	85.69
BbF	0.98 ± 0.03	0.14 ± 0.004	31.49	67.13	85.64
BkF	1.24 ± 0.04	0.14 ± 0.004	45.97	74.07	88.54
BaP	0.21 ± 0.007	0.01 ± 3E-04	70.39	85.84	93.82
IcdP	3.40 ± 0.11	0.21 ± 0.007	73.04	87.05	93.80
DahA	8.52 ± 0.29	1.02 ± 0.03	54.49	77.78	88.08
BghiP	0.91 ± 0.03	0.09 ± 0.003	52.69	77.33	89.91

The less hydrophobic PAHs (BaA, CHR and BbF) were removed with yields around 85.00%. Although, the more hydrophobic PAHs (BkF, BaP, IcdP, DahA and BghiP) have high number of benzen rings they were removed with yields (88.00-94.00%) as high as less hydrophobic PAHs and some times have high yieds (93.00%) than that the less hydrophobic ones. Thus, the more hydrophobic PAHs have low Henry's law constant (from $1.23x10^{-7}$ to $5.84x10^{-7}$ atm.m^3/mol at 25°C), low solubility (from $2.60x10^{-4}$ to $2.49x10^{-3}$ mg/l at 25°C) and high vapor pressure (from $5.49x10^{-9}$ to $9.70x10^{-10}$ mmHg at 25°C) are expected to remove with low yields (Table 5.38). The yields obtained for more hydrophobic PAHs did not exhibit a strong and significant correlation with the physicochemical properties of these PAHs (R^2=0.43, F=2.99, p=0.01). In this study, it was found that the yields in all individual PAHs decreased by iso-butanol addition since the removals in these PAHs are significantly higher in the samples containing no iso-butanol (Table 5.39).

Table 5.38 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml).

PAHs	**CAS-No**	**MF**	**M_W**	**T_M**	**T_B**	**S_W**	**V_P (25°C)**	**H (25°C)**	**log K_{OA} (25°C)**	**log K_{OW}**	**SORKC**	**IPC**
BaA	56-55-3	$C_{18}H_{12}$	228	84	438	9.40×10^{-3}	2.10×10^{-7}	1.20×10^{-5}	10.28	5.76	34.10	0.54
CHR	218-01-9	$C_{18}H_{12}$	228	258	448	2.00×10^{-3}	6.23×10^{-9}	5.23×10^{-6}	10.30	5.81	31.60	4.34
BbF	205-99-2	$C_{20}H_{12}$	252	168	-	1.50×10^{-3}	5.00×10^{-7}	6.57×10^{-7}	11.34	5.78	23.40	0.44
BkF	207-08-9	$C_{20}H_{12}$	252	217	480	8.00×10^{-4}	9.70×10^{-10}	5.84×10^{-7}	11.37	6.11	28.20	0.88
BaP	50-32-8	$C_{20}H_{12}$	252	177	495	1.62×10^{-3}	5.49×10^{-9}	4.57×10^{-7}	11.56	6.13	15.60	0.25
IcdP	193-39-5	$C_{22}H_{12}$	276	164	536	1.94×10^{-3}	1.25×10^{-10}	3.48×10^{-7}	12.43	6.70	12.50	4.06
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	2.49×10^{-4}	1.00×10^{-10}	1.23×10^{-7}	12.59	6.75	9.50	10.13
BghiP	191-24-2	$C_{22}H_{12}$	276	278	> 500	2.67×10^{-4}	1.00×10^{-10}	3.31×10^{-7}	12.55	6.63	7.60	1.08

benz[*a*]anthracene (BaA), chrysene (CHR), benz[*b*]fluoranthene (BbF), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF : Molecular formula, M_W: Molecular weight (g / mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg / L), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 / mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; SORKC: Second order reaction kinetic constant (ng / mL. s); IPC: Initial PAH concentration (mean, ng / mL).

Table 5.39 The effect of 2.00 g/l iso–butanol concentration on the removal of three less (BaA, CHR, BbF) and five more (BkF, BaP, IcdP, DahA, BghiP) hydrophobic PAHs removals measured in the influent and in the effluent of the sonication experiments after 60 min, 120 and 150 min sonication times at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**Inf. (A) T=0 min PAHs (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**PAHs Removal Efficiencies (%)**					
			T=60 min, 60°C		**T=120 min, 60°C**		**T=150 min, 60°C**	
			Control	**2.00 g/l Butanol**	**Control**	**2.00 g/l Butanol**	**Control**	**2.00 g/l Butanol**
BaA	0.66 ± 0.02	0.10 ± 0.003	46.47	29.93	67.32	66.42	92.24	85.27
CHR	3.64 ± 0.12	0.52 ± 0.01	46.36	37.91	77.16	69.95	95.35	85.69
BbF	0.98 ± 0.03	0.14 ± 0.004	46.46	31.49	67.31	67.13	86.21	85.64
BkF	1.24 ± 0.04	0.14 ± 0.004	46.46	45.97	79.30	74.07	93.17	88.54
BaP	0.21 ± 0.007	0.01 ± 3E-04	46.49	70.39	71.36	85.84	97.77	93.82
IcdP	3.40 ± 0.11	0.21 ± 0.007	46.44	73.04	67.28	87.05	97.98	93.80
DahA	8.52 ± 0.29	1.02 ± 0.03	46.26	54.49	67.02	77.78	96.60	88.08
BghiP	0.91 ± 0.03	0.09 ± 0.003	46.47	52.69	61.33	77.33	96.45	89.91

(A) Inf.= influent, (B) Eff. = effluent.

Iso-butanol is a known scavenger for the gaseous region and/or interfacial region of the collapsing bubble (Suslick et al., 1984), whereas inorganic salts, such as potassium iodide or bromide reside on the bulk liquid region or possibly at the interfacial region of the cavitation bubble (Wayment & Casadonte Jr., 2002). As the boiling point of iso-butanol (104^{o}C) is only slightly higher than that of water, the addition should not greatly affect the temperature inside the bubble, which is known to depend on vapor pressure (Quesada-Penata et al., 2009; Suslick, 1986). Aqueous sonication occurs in three important regions. The first region is the interior of the collapsing cavitation bubbles; the second region is the interfacial boundary between the gaseous and liquid phases, and the third is the solution bulk (Quesada-Penata et al., 2009). It is possible to obtain information about the sonochemical reaction zones by controlling the type of radical scavenger in which the free radicals are located or produced.

The volatile iso-butanol may scavenge the $OH^{\bullet}$ inside and at the interfacial region of the cavitation bubble and may be partly pyrolyzed inside the cavitation bubble with sufficient ultrasonic irradiation. The cavitation reactions should be influenced by the volatile products formed during the sonication of iso-butanol due to decrease of the temperature inside the collapsing cavitation bubble with long period of irradiation (Tauber et al., 1999a, 1999b). Addition of iso-butanol (740 mg/l) to the PAHs mixture (FL, BaP, BbF, BkF, BghiP and IcdP) leads to a partial inhibition of the PAHs degradation in agreement with Laughrey et al. (2001) and Psillakis et al. (2003).

5.9.13 Effect of $S_2O_8^{-2}$ Concentrations on the Removal of PAHs in PCI ww in the Presence of iso-Butanol (C_4H_9OH)

To verify the PAHs sonodegradation pathways, the effects of the radical scavenger, iso-butanol, on the removals of PAHs in a sonicator containing $S_2O_8^{-2}$ at pH=7.0 were examined. The addition of 200, 400 and 600 mg/l iso-Butanol to the sonicator containing $Na_2S_2O_8$ reduced the the PAHs yields from 98.00% to 47.00% (Figure 5.30). As the iso-butanol concentrations increased the PAHs yields decreased. Iso-butanol molecules pass in the cavitation bubbles, they are able to scavenge $OH^{\bullet}$ in the bubble and reduce significantly the degradation rate of the PAHs. Alcohols are commonly used to quench the $OH^{\bullet}$. The inhibition was explained by $OH^{\bullet}$ competitive reactions with PAHs and iso-butanol. In other words, the sono-degradation of PAHs was found to deccelerate by iso-butanol where the competition for $OH^{\bullet}$ increases as the quantity of iso-butanol relative to that of all individual more and less hydrophobic PAHs are increased. The inhibition in PAHs removals by adding iso-butanol indicates that the PAHs destruction pathway involves slightly $OH^{\bullet}$ in the bulk liquid and/or the interface region of the cavitation bubbles for more (DahA, BghiP, BaA, CHR and BbF) and less (BkF, BaP, IcdP) hydrophobic PAHs. Since the PAHs utilized here are less soluble in H_2O, and thus hydrophobic, their partitioning into the gas phase are possible and the solutes were pyrolyzed in the cavitation bubbles. Therefore, pyrolysis could be a major reaction pathway in a sonicator containing $Na_2S_2O_8$ through sonication of hydrophobic PAHs as reported by Quesada-Penate et al. (2009) and Grcic et al. (2010).

Figure 5.30 shows the effect of 2.00, 4.00, 6.00 and 10.00 mg/l $S_2O_8^{-2}$ as an oxidant on the degradation of seven PAHs, compared with sonication-only condition (without $S_2O_8^{-2}$). The degradation efficiency of seven PAHs in the sonication with 6.00 mg/l $S_2O_8^{-2}$ was enhanced by 36.00% after 150 min sonication time (Figure 5.30).

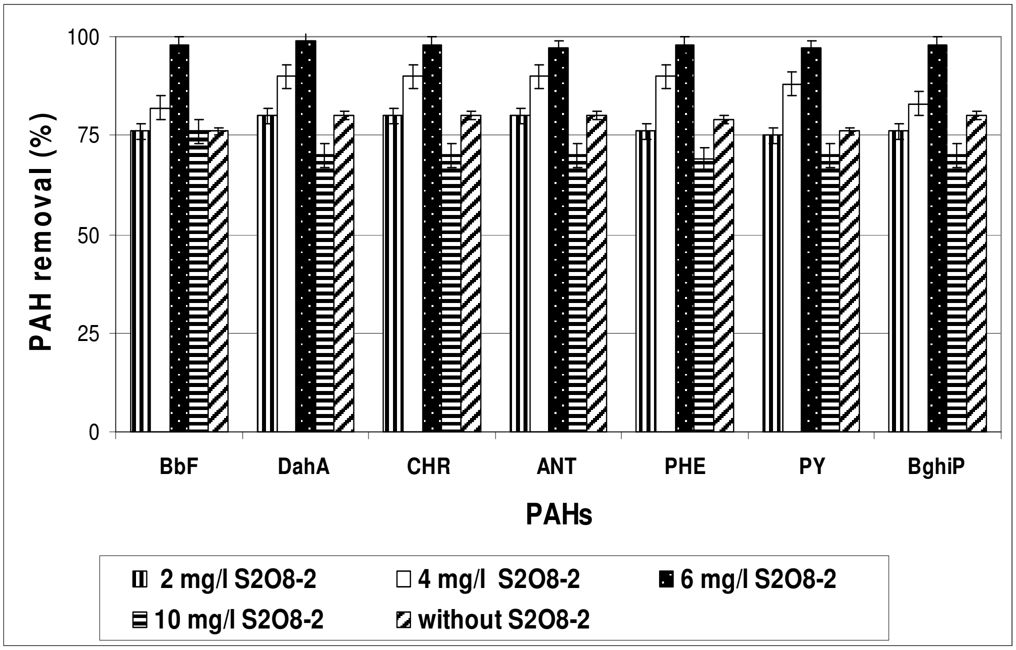


Figure 5.30 Effect of increasing $S_2O_8^{-2}$ on PAHs removal efficiencies at 60°C after 150 min sonication (sonication power=640 W, sonication frequency=35 kHz).

In other words, the maximum yields in all PAHs (E=97.00-99.00%) was found at 6.00 mg/l $S_2O_8^{-2}$. As the $S_2O_8^{-2}$ increased from 6.00 to 10.00 mg/l the PAHs removals decreased from 98.00-99.00% to 72.00% and 75.00%. The kinetics at the initiation step in the sonication with $S_2O_8^{-2}$ were found to be of the pseudo-first order rate model (k=0.008 1/day). We assumed that the $OH^{\bullet}$ is also produced by the reactions between sonication of PAHs and $S_2O_8^{-2}$, as shown in Eqs. (5.19), (5.20) and (5.21):

$$S_2O_8^{-2} + Sonication \rightarrow 2SO_4^{-\bullet} \tag{5.19}$$

$$S_2O_8^{-2} + H_2O + Sonication \rightarrow SO_4^{-1} + OH^{\bullet} \tag{5.20}$$

$$S_2O_8^{-2} + PAH \rightarrow 2SO_4^{-\bullet} + PAH^{\bullet} \tag{5.21}$$

As shown in Figure 5.30 the degradation percentage of seven PAHs in the absence of $S_2O_8^{-2}$ only was 78.12% after 150 min of sonication time. This indicates that BghiP can be directly degraded only with sonication as shown in Eq. (5.21) as reported by Fındık et al. (2006), Fındık & Gündüz (2007) and Son et al. (2006). The degradation efficiencies of PAHs were not statistically different between those with $S_2O_8^{-2}$ and those without $S_2O_8^{-2}$ (only sonication) ($R^2=0.87$, $F=6.37$, $p=0.001$). Persulfate ions trap the electrons generated through sonication. Thus they prevent the recombination of $S_2O_8^{-2}$ with positive holes, resulting in the simultaneous generation of sulfate free radicals ($SO_4^{\bullet}$) (Eq. (5.22). Then the $SO_4^{\bullet}$ react with H_2O molecules to form $OH^{\bullet}$ (Eq. (5.23) (Son et al., 2006). The mechanism of thermal decomposition is believed to involve the $SO_4^{\bullet}$, which can abstract H_2 from H_2O to yield $OH^{\bullet}$ (Son et al., 2006) in Eqs. (5.22) and (5.23).

$$S_2O_8^{-2} \rightarrow 2SO_4^{-\bullet} \tag{5.22}$$

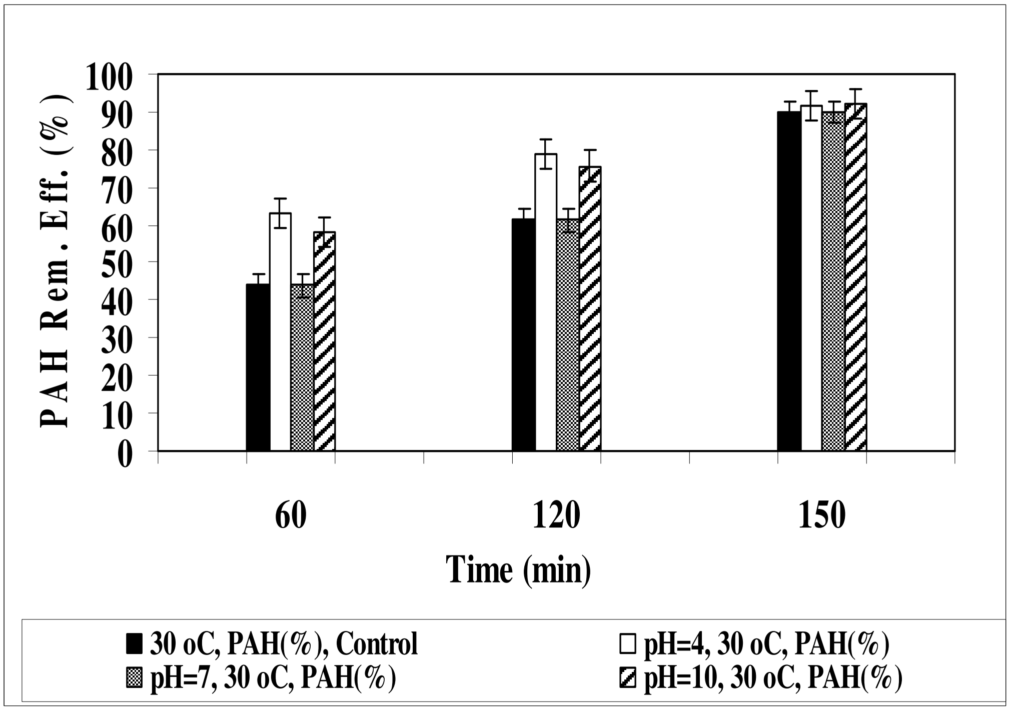
$$2SO_4^{-\bullet} + H_2O \rightarrow 2SO_4^{-\bullet} + OH^{\bullet} \tag{5.23}$$

The effects of temperature were evaluated in reactors with $S_2O_8^{-2}$ and without $S_2O_8^{-2}$ at an ambient 21°C, 30, and 60°C. The experimental results indicated that the all the PAHs removals were highest in the reactor containing 9.27 mg/l $S_2O_8^{-2}$ at 60°C, after 150 min sonication. It can be concluded that the PAHs yields in a sonicator with $S_2O_8^{-2}$ were higher than those in a sonicator without $S_2O_8^{-2}$ (Figure 5.30). Grcic et al. (2010) stated that the first order kinetics constants of the sonochemical decomposition of persulfate both increased with temperature.

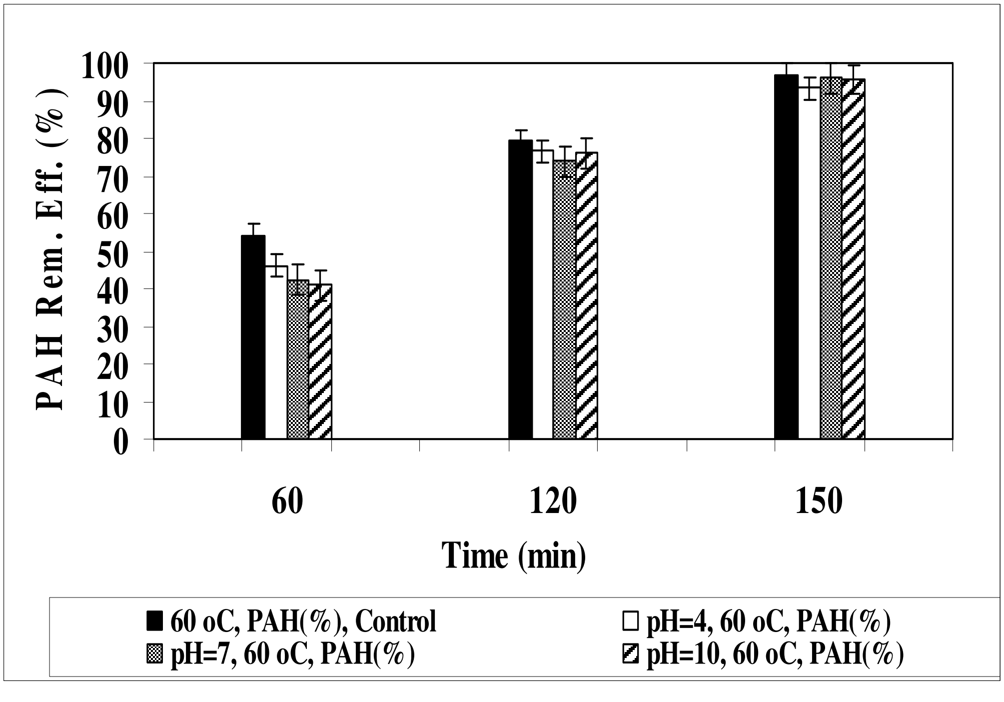
5.9.14 Effect of pH on the Removal of PAHs in PCI ww at Increasing Sonication Times and Temperatures

The pH was adjusted to 4.0–7.0 and 10.0 in the PCI ww before sonication process. 91.59%, 90.05% and 92.25% total PAHs removals were found at pH=4.0, pH=7.0 and pH=10.0, respectively, at 30°C after 150 min sonication time. Sonication alone provided 90.11% total PAHs removal at 30°C after 150 min sonication time at pH=6.98 (Figure 5.31a). At short sonication times (60 min and 120 min) the maximum PAHs yields were higher at pH=4.0 and pH=10.0 at 30°C. 63.11%-58.29% and 78.98%-75.70% total PAHs removals was obtained after 60 and 120 min sonication times at pH=4.0 and pH=10.0 at 30°C. A significant linear correlation between total PAHs yields and increasing sonication time was not observed (R^2=0.31, F=0.33, p=0.01) (Figure 5.31a).

93.37%, 96.09% and 95.66% total PAHs removals were observed at pH=4.0, pH=7.0 and pH=10.0, respectively, at 60°C after 150 min sonication time (Figure 5.31b). Total PAHs yields did not change after 150 min sonication time, compared to the control (at pH=6.98 while E=96.90% total PAHs) at 60°C (Figure 5.31b). The increasing of pH from 4.0 to 10.0 did not significantly affect the total PAHs removals for 60 and 120 min sonication times at 60°C. The maximum total PAHs yield was 96.09% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between total PAHs yields and increasing sonication time was not observed (R^2=0.81, F=11.20, p=0.01).



(a)



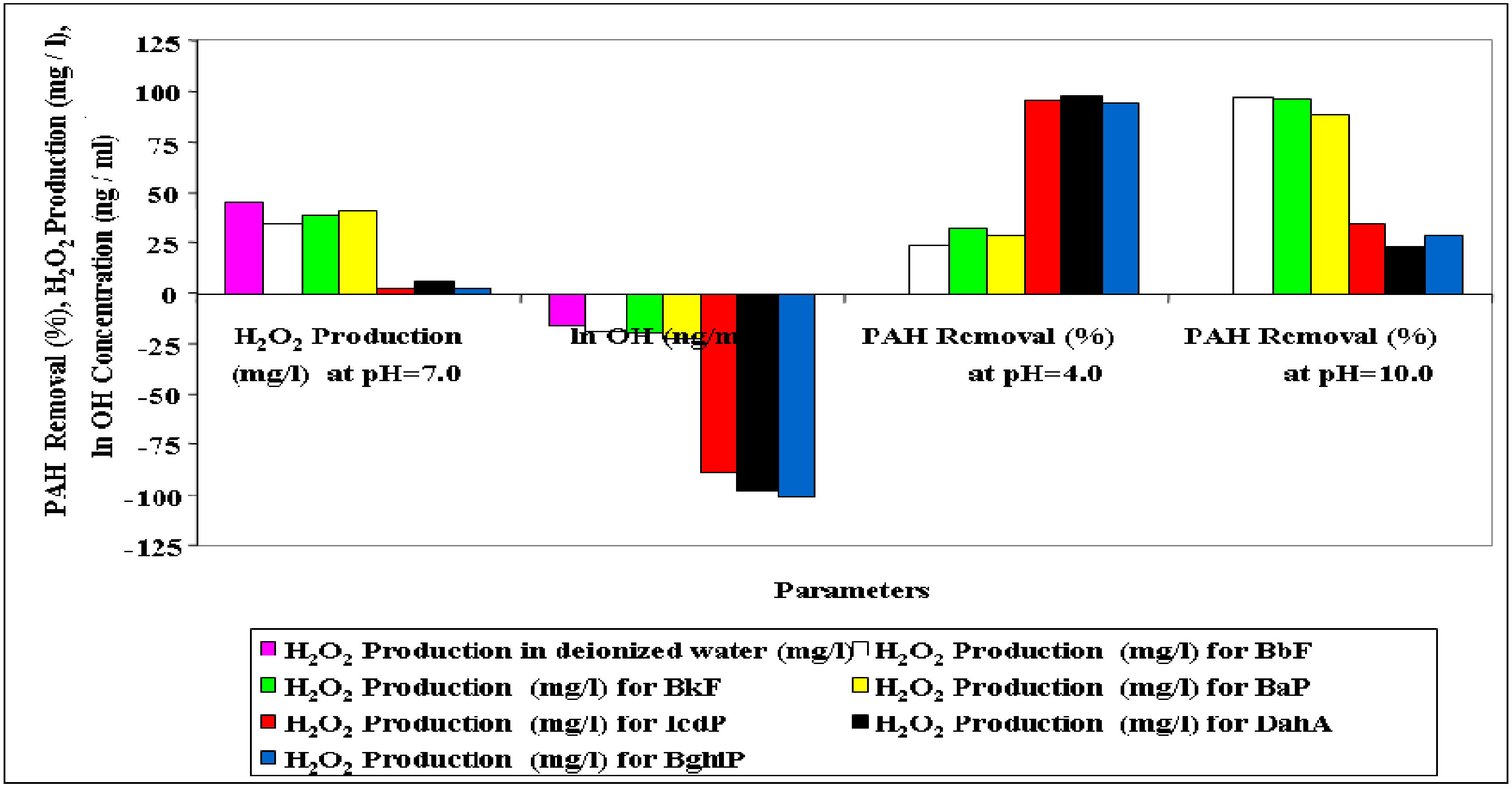
(b)

Figure 5.31 Effect of increasing pH values on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz).

In order to determine the effect of pH on the sonodestruction of PAHs, the pH of the PCI ww was adjusted to acidic (pH=4.0-5.0), neutral (pH=7.0) and alkaline (pH=10.0-11.0) conditions. Figure 5.32 shows the H_2O_2 production, $OH^\bullet$ ion concentrations and PAHs yields at acidic, neutral and alkaline pH values. The ln $OH^\bullet$ ion concentrations decreased in more hydrophobic PAHs (IcdP, DahA, BghiP) (ln -8, ln -23) while they increased in less hydrophobic PAHs (BbF, BkF, BaP) (ln -75, ln -100) at pH=7.0. The H_2O_2 concentration was high (35.00-48.00 mg/l) through sonication of less hydrophobic PAHs while is low (2.00-10.00 mg/l) through sonodegradation of more hydrophobic PAHs. The high H_2O_2 production through sonication of less hydrophobic PAHs verified the presence of high $OH^\bullet$ ion concentrations as illustrated in Figure 5.32.

The removal efficiency of more hydrophobic PAHs exhibited a tendency to increase from 8.45%-10.11% up to 81.21% when the acidity of the wastewater was increased (pH=4.0) while the yield of less hydrophobic PAHs reached a maximum (75.36-81.15%) in alkaline conditions (Figure 5.32). At lower pK_a (acid dissociation constant or acid-ionization constant) values (under acidic conditions), the more hydrophobic PAHs are principally found in their molecular form. As the molecular state of PAHs are more hydrophobic than the ionic one, the more hydrophobic PAHs are expected to accumulate in the vicinity of the cavitation bubbles under acidic conditions. These PAHs are sonodegraded via pyrolytic reaction that occurs in the hot cavitation bubbles and/or at the gas–liquid interface of the bubbles. According to work performed by Goskonda et al. (2002) the removal of some hydrophobic PAHs from an oil wastewater by toluene solvent would be significantly enhanced with a reduction of pH values. It was reported that the concenration of stronger hydrophobic PAHs increased at the gas–liquid interface of the bubbles with an increase of acidity of wastewater. Similarly, Chakinala et al. (2008b) reported that the sonochemical destruction of hydrophobic compounds like PAHs was enhanced by the addition of salicylic acid with acidic conditions. This showed that in acidic conditions, the radicals have a greater chance to attack hydrophobic PAHs rather than recombine and yield H_2O_2.

Figure 5.32 Effects of pH on the removals of PAHs, H_2O_2 production and $OH^{\bullet}$ ion concentrations (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml).



Under alkaline conditions at pH values greater than pK_a the less hydrophobic PAHs predominantly exist in their ionic form, react with $OH^\bullet$ at the gas–liquid interface of the bubbles and destruct via hydroxylation (Busetti et al., 2006) (Table 5.40). Since less hydrophobic PAHs (BbF, BkF, BaP) are considerably non-volatile with low Henry's law constant and solubility (Lindsey & Tarr, 2000), sonodegradation inside the cavitation bubble is expected to be insignificant and, therefore, $OH^\bullet$- induced reactions are likely to be the main degradation mechanism of less hydrophobic ones as Eqs. (5.8) and (5.9) [See Eqs. (5.8) and (5.9) in 5.9.6 H_2O_2 section]. It should be pointed out that $OH^\bullet$, formed via H_2O sonolysis, can partly recombine yielding H_2O_2 which in turn reacts with H_2 to regenerate $OH^\bullet$ in Eqs. (5.10) and (5.11) [See Eqs. (5.10) and (5.11) in 5.9.6 H_2O_2 section] (Table 5.40).

Table 5.40 Effect of H_2O_2 production on the removals of less (BbF, BkF, BaP) and more (IcdP, DahA, BghiP) hydrophobic PAHs after 60 and 120 min sonication times at 30°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

H_2O_2 Concentration (mg/l)			**Less Hydrophobic PAHs**			**More Hydrophobic PAHs**		
in deionized water	**After 60 min sonic.**	**After 120 min sonic.**	**BbF**	**BkF**	**BaP**	**IcdP**	**DahA**	**BghiP**
13.00	156.00	5.00						
Removal eff (%) after 30 min			34.21	32.44	38.10	19.40	21.12	20.28
Removal eff (%) after 120 min			95.35	96.76	97.65	76.33	75.35	77.32

The formation of H_2O_2 during ultrasound irradiation was confirmed experimentally during sonication in the absence and presence of less and more hydrophobic PAHs. As the 13.00 mg/l H_2O_2 increased to 156.00 mg/l after 60 min sonication time the less hydrophobic PAHs removals increased to 95.35-97.65% while the removals of more hydrophobic PAHs remained aroud 75.35-77.32% after 120 min sonication time (Table 5.40). This process ends with decreasing of H_2O_2 concentration to 5.00 mg/l after 120 min sonication time. As BbF, BkF, BaP and its degradation metabolites scavenge $OH^{\bullet}$ (Eqs. 5.10 and 5.11), the yield, defined as H_2O_2 formed in the presence of less hydrophobic PAHs over H_2O_2 formed in deionized water.

According to work performed by Goskonda et al. (2002) the removal of some hydrophobic PAHs from an oil ww by toluene solvent would be significantly enhanced with a reduction of pH values. These PAHs are sonodegraded via pyrolytic reaction that occurs in the hot cavitation bubbles and/or at the gas–liquid interface of the bubbles. It was reported that the concenration of stronger hydrophobic PAHs increased at the gas–liquid interface of the bubbles with an increase of acidity of wastewater. Similarly, Chakinala et al. (2008a) reported that the sonochemical destruction of hydrophobic compounds like PAHs was enhanced by the addition of salicylic acid with $pH < 7.0$. This showed that in $pH < 7.0$, the radicals have a greater chance to attack hydrophobic PAHs rather than recombine and yield H_2O_2.

5.10 Sonication of OMI ww

Olive mill effluent (OME) arises from the production of olive oil in olive mills. It is produced seasonally by a large number of small olive mills scattered throughout the olive oil-producing countries. Mediterranean countries alone produce 97.00% of the total olive oil production, while European Union (EU) Countries produce 80.00–84.00% (Paraskeva & Diamadopoulos, 2006). The largest olive oil-producing countries are Spain, Italy, Greece and Turkey, followed by Tunisia, Portugal, Morocco and Algeria (Paraskeva & Diamadopoulos, 2006). The composition of OME is quite variable and is composed of many complex substances that are toxic and not easily degradable (e.g. polyphenols, tannins, polyalcohols, pectins and lipids, etc.). Typical OME composition by weight is: 83.00–94.00% H_2O, 4.00–16.00% organic compounds and 0.40–2.50% mineral salts. The mineral fraction typically contains 47.00% potassium salts and 7.00% sodium salts. The organic fraction contains 2.00–15.00% of phenolic compounds corresponding to a concentration of 3.00–10.00 g/l (Arvanitoyannis et al., 2007; Azbar et al., 2002; Capasso et al., 1992; Garcia et al., 1990; Tuncel & Nergiz, 1993; Zouari, 1998).

The COD is also high, ranging from 45.00 to 220 g/l, as is the BOD_5 that ranges from 35.00 to 100 g/l. The pH of OME is acidic around 4.0–5.0 and the concentration of TSS could go up to 50.00 g/l depending on the olive mill (Azbar et al., 2002; Davies et al., 2004). The traditional three-phase continuous centrifugation process generally yields an oily phase (20.00% [w/v]), a solid residue phase (30.00% [w/v]), and an aqueous phase (50.00% [w/v]), the latter originating from the water content of the fruit (Borja et al., 2006).

In this study, OMI ww contains large amounts of monomeric and polymeric phenols (> 3000 mg/l), color (> 99.00 m^{-1}), TAAs (> 2000 mg/l), TFAs (> 4000 mg/l), oil (> 500 mg/l) among other organic compounds, and has high COD (> 80000 mg/l) and high BOD_5 (> 60000 mg/l) with a BOD_5/COD ratio of 0.74. The characterization of OMI ww was shown in Table 5.41 for minimum, medium and maximum values. All measurements were carried out three times and the results given as the means of triplicate samplings with standard deviation (SD) values.

Table 5.41 Characterization values of OMI ww (n=3, mean values ± SD)

Parameters	**Values**		
	Minimum	**Medium**	**Maximum**
pH_0	4.00 ± 0.14	4.56 ± 0.160	4.90 ± 0.172
DO_0 (mg/l)	0.01 ± 0.0004	0.05 ± 0.002	0.09 ± 0.003
ORP (mV)	120 ± 4.20	126 ± 4.41	132 ± 4.62
TSS (mg/l)	53.60 ± 1.876	53.74 ± 1.881	53.88 ± 1.886
TVSS (mg/l)	34.80 ± 1.218	35.6 ± 1.246	36.42 ± 1.275
COD_t (mg/l)	98780 ± 3457	126632 ± 4432	140560 ± 4920
COD_d (mg/l)	85400 ± 2989	109444 ± 3831	123500 ± 4323
TOC (mg/l)	58510 ± 2048	66488 ± 2327	80450 ± 2816
BOD_5 (mg/l)	63800 ± 2233	81254 ± 2844	99130 ± 3470
BOD_5 / COD_d	0.58 ± 0.020	0.74 ± 0.026	0.90 ± 0.032
Total N (mg/l)	194 ± 6.79	248 ± 8.68	300 ± 10.50
NH_4-N (mg/l)	23.40 ± 0.819	30 ± 1.050	36.60 ± 1.281
NO_3-N (mg/l)	39 ± 1.365	50 ± 1.750	61 ± 2.135
NO_2-N (mg/l)	17.63 ± 0.617	22.6 ± 0.791	27.57 ± 0.965
Total P (mg/l)	492 ± 17.22	630 ± 22.05	768.60 ± 26.901
PO_4-P (mg/l)	350 ± 12.250	448 ± 15.680	546.20 ± 19.117
Total phenol (mg/l)	3320 ± 116.20	4090 ± 143.15	5150 ± 180.25
TFAs (mg/l)	4050 ± 141.75	5200 ± 182	6344 ± 222.04
TAAs (mg benzidine/l)	2340 ± 81.90	3000 ± 105	3660 ± 128.10
Color (m^{-1})	99.70 ± 3.490	99.80 ± 3.493	99.90 ± 3.497
Oil (mg/l)	564 ± 19.74	640 ± 22.40	775 ± 27.125

5.10.1 Effect of Increasing Sonication Time on the Removals of COD_{dis} and TOC in OMI ww at 25°C Ambient Conditions

OMI ww samples were sonodegraded in a sonicator at increasing sonication times (60 min, 120 and 150 min) in ambient conditions at pH=7.0 and at 25°C (Figure 5.33). 12.58%, 41.74% and 60.91% COD_{dis} removal efficiencies were observed at an initial COD_{dis} concentration of 109444 mg/l after 60 min, 120 and 150 min sonication times, respectively. The maximum COD_{dis} removal efficiency was 60.91% after 150 min sonication at pH=7.0 and at 25°C. A significant linear correlation between COD_{dis} yields and increasing sonication time was observed (R^2=0.83, F=16.38, p=0.01) (Figure 5.33).

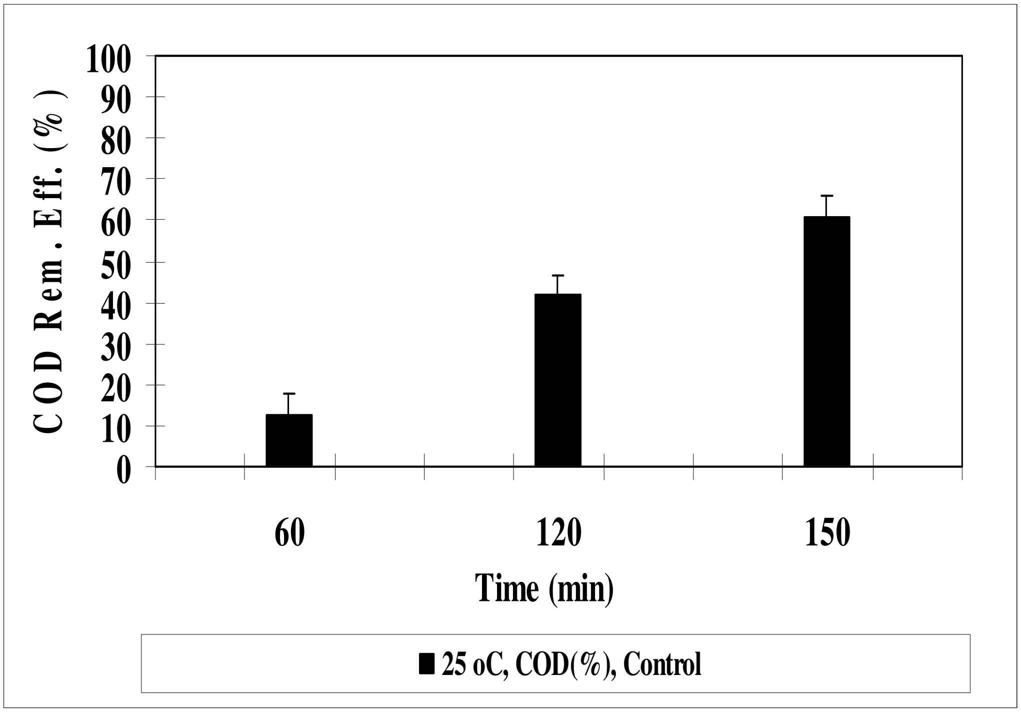


Figure 5.33 Effect of increasing sonication time on the COD_{dis} removal efficiencies in OMI ww at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

Organic compounds may be degraded either at the first two sites upon combined effects of pyrolytic decomposition and hydroxylation or in the solution bulk via oxidative degradation by $OH^{\bullet}$ and H_2O_2 throughout sonication of OMI ww (Boari et al., 1984). Preliminary studies showed that the organic pollutants in OMI ww were sonodegraded by hydroxylation reactions (Rozzi & Malpei, 1996). In this study, the effects of H_2O_2 production and the levels of $OH^{\bullet}$ concentrations were not determined in this step since the COD_{dis} removals are low for the sonication performed under ambient conditions (25^{o}C). It was found that low temperature under ambient conditions was not enhanced the COD_{dis} removals even it was studied at long sonication times as 150 min. This probably caused by the insufficient levels of $OH^{\bullet}$ formation. Hence, COD_{dis} are not the ability to attack to the low concentrations of $OH^{\bullet}$, thus leading to decreased sonodegradation rates of COD_{dis} as reported by Lafi et al. (2009). Furthermore, the high relative concentration of organic by-products generated in the system (without ultimate mineralization) is known to complete for the $OH^{\bullet}$ in solution, slowing the sonodecomposition rates of COD_{dis} (Khokhawala & Gogate, 2010).

12.47%, 40.80% and 59.28% TOC removal efficiencies were observed at an influent TOC concentration of 66488 mg/l after 60 min, 120 and 150 min sonication times, respectively, at 25^{o}C and at pH=7.0 (Table 5.34). The maximum TOC removal efficiency was 59.28% after 150 min sonication time at pH=7.0 and at 25^{o}C. A significant linear correlation between TOC yields and increasing sonication time was observed (R^2=0.83, F=16.17, p=0.01) (Figure 5.34).

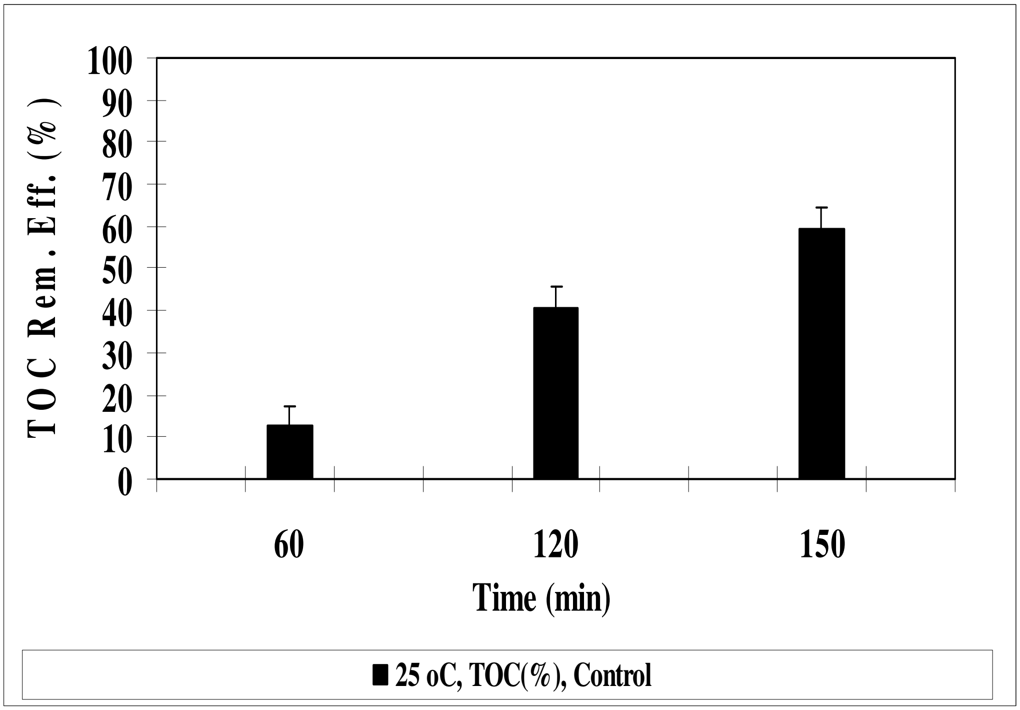


Figure 5.34 Effect of increasing sonication time on the TOC removal efficiencies in OMI ww at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial TOC concentration=66488 mg/l, n=3, mean values).

The treatment by sonication converts TOC to much smaller sonodegraded compounds. In such cases, it is obvious that higher sonication times are needed for complete mineralization of TOC in OMI ww since this wastewater contains high COD levels. Short sonication times (60 min) did not provide high degradation yields for refractory COD_{dis} and TOC since they were not exposed for a long enough time to ultrasonic irradiation. Therefore, a decrease in the percentage of remaining COD_{dis} and TOC were expected at longer sonication times due to sufficient radical reactions through cavitation. COD_{dis} and TOC were not completely removed under the ultrasonic action even with a long sonication time (150 min) in OMI ww. The reason of this could be explained by the fact that degradation products of COD (pyridine, straight-chain aliphatic compounds) sometimes are recalcitrant toward the sonochemical treatment. This is due to the fact that the intermediate products have very low probabilities of making contact with $OH^{\bullet}$, which react mainly at the interface of the bubble. Thus, the sonochemical action that gives rise to products bearing more hydroxyl (or carboxylic) groups is of low efficiency toward COD_{dis}

abatement. Canizares-Macias et al. (2004) investigated an ultrasound system assisted with Rancimat Method for the determination of the olive oil industry yields. 80.00% COD removal was found at 20 kHz frequency, and at a power of 400 W, after 60 min sonication time. In this study, 60.91% COD_{dis} removal was observed at 25^{o}C after 150 min sonication time. This COD_{dis} yield is lower than the yield obtained by Canizares-Macias et al. (2004) at 25^{o}C.

In a study performed by Atanassova et al. (2005b) it was found a COD yield of 45.00% after 240 min of sonication time at a power of 150 W and a frequency of 80 kHz at 25^{o}C. This COD_{dis} yield is lower than the yield obtained in this study at 25^{o}C as mentioned above. Azzam et al. (2004) tested to the maximum adsorption capacity for activated carbon in OMI ww for less than 4 h at 25^{o}C. The maximum removal of COD is 85.00%. The COD_{dis} yield found in this study is higher than the yield observed by the present study at 25^{o}C as mentioned above. In an Up-flow Anaerobic Sludge Blanket (UASB) reactor, 80.00–85.00% COD removals was obtained at a HRT=5 days with an influent COD concentration of 40 g/l and organic loading rate (OLR)=8 g/COD l. day (Sabbah et al., 2004) in OMI ww. This yield is higher than the yield obtained by this study at 25^{o}C as mentioned above. Anaerobic Filter (AF) compared with Aerobic Fluidized Bed Fermentor (AFBF) for removal of OMI ww by *Aspergillus niger* (Hamdi & Ellouz, 1993). The AFBF removes 57.00% of the total COD while AF reduces the COD_{total} and COD_{dis} with yields 67.00% and 68.10%, respectively.

5.10.2 Effect of Increasing Sonication Time on the Removals of Color, Total Phenol, Total Aromatic Amines (TAAs) and Total Fatty Acids (TFAs) in OMI ww at 25°C Ambient Conditions

Table 5.42 summarizes the removals of color, total phenol, TAAs and TFAs removal efficiencies at increasing sonication times at 25°C ambient conditions.

Table 5.42 Effect of increasing sonication time on color, total phenol, TAAs and TFAs removals in OMI ww before and after sonication experiments at pH=6.98 and at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, initial total phenol concentration=4090 mg/l, initial TAAs concentration=3000 mg benzidine/l, initial TFAs concentration=5200 mg/l, n=3, mean values ±SD).

Parameters	**Initial Conc.**	**Removal Efficiencies (%)**		
		25°C		
		60. min	**120. min**	**150. min**
Color	99.80 ± 3.493 m^{-1}	36.37	47.90	49.70
Total phenol	4090 ± 143.15 mg/l	26.89	54.74	58.25
TAAs	3000 ± 105 mg/l	33.67	48.27	63.17
TFAs	5200 ± 182 mg/l	12.73	18.84	37.51

5.10.2.1 Effect of Increasing Sonication Time on the Color Removal Efficiencies in OMI ww at 25°C in Ambient Conditions

36.37%, 47.90% and 49.70% color removal efficiencies were observed at an influent color concentration of 99.80 m^{-1} after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25°C (Table 5.2). In this study, it was found that the color removal efficiencies in OMI ww increased from 36.37% up to 49.70% as the sonication time was increased from 60 to 150 min sonication time at pH=7.0 and at 25°C. The maximum color removal efficiency was 49.70% after 150 min sonication at pH=7.0 and at 25°C. A significant linear correlation between color yields and increasing sonication time was observed (R^2=0.83, F=17.34, p=0.01) (Table 5.2).

Low color (46.00%) and phenol removals in OMI effluents showed that low sonication temperature (25°C) is not able to achieve the complete removal of the colorful organics (e.g., lignin, organic acids, etc.) and the phenolic compounds (e.g., tannins, antocyanins, catechins, etc.) (Adhoum & Monser, 2004). This might be due to the generation of high concentration of intermediate compounds that cannot be further oxidized by $OH^{\bullet}$ and consequently are accumulated in the system (Adhoum & Monser, 2004). In this study, 49.70% color removal was found at 25°C after 150 min sonication time. The color removal is higher than the yield obtained by Adhoum & Monser (2004) 46.00% at 25°C as mentioned above. Adhoum & Monser (2004) investigated the color removal in OMI ww by electrocoagulation with aluminium electrodes at pH=4.0-6.0, at a current density of 75 mA/cm^2 and 25 min retention time. 95.00% color removal was found after 25 min retention time at 25°C. This color yield is higher than the yield obtained in the present study at 25°C.

5.10.2.2 Effect of Increasing Sonication Time on the Total Phenol Removal Efficiencies in OMI ww at Ambient Conditions

26.89%, 54.74% and 58.25% total phenol removal efficiencies were measured at an influent total phenol concentration of 4090 mg/l after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25°C (Table 5.2). It was found that the total phenol removal efficiencies in OMI ww increased from 26.89% up to 54.74% as the sonication time was increased from 60 to 120 min. The maximum total phenol removal efficiency was 58.25% after 150 min sonication time at pH=7.0 and at 25°C. The contribution of 150 min sonication time on the total phenol removals was not significant ($R^2=0.43$, F=3.78, p=0.01) (Table 5.2).

Pyrolytic destruction of phenol in the gas phase is negligible; the degradation occurs mainly in the bulk solution. A possible explanation for this is that a considerable increase in the concentration results in the formation of a complex H-bonding network between the phenolic compounds (Vassilakis et al., 2004). During sonication low decrease of total phenol concentrations in the effluent samples results in the formation of a complex H-bonding network between the phenolic compounds after 60 min. It is well known that molecules containing COOH or CHO groups exist as dimmers in solution due to the formation of H-bonds between two neighboring molecules. This results in a more robust and stable configuration, thus leading to reduced degradation (Currell et al., 1963). In addition to this, the formation of such a network may impede their diffusion towards the bubble interface and this would also lead to reduced degradation of phenols (Atanassova et al., 2005a).

Canizares-Macias et al. (2004) investigated an Ultrasound-assisted with Rancimat method for the determination of the phenol yields in OMI effluents. 56.00% phenol removal was found at 20 kHz frequency, and at a power of 400 W, after 60 min sonication time at 25°C. In this study, 58.25% total phenol removal was measured at 25°C after 150 min sonication. This study exhibited similar phenol yields with the present study at 25°C. In a study performed by Atanassova et al. (2005a) it was found 6.00% - 14.00% sonodegradation yields for total phenolic compounds after 240 min of sonication time at power 75 and 150 W, respectively. These yields are significantly lower than the present study at 25°C.

Hydrophilic and less volatile compounds such as phenol and polyphenols e.g., 2-phenyl-phenol (vapor pressure; 3.10×10^{-7} mm Hg at 25°C, soluble in diethyl ether, acetone, ethanol, isopropanol, ethylene glycol, glycolethers, polyglycols and alkali hydroxide solutions. Insoluble in cold and hot water) and 3-phenyl-phenol (vapor pressure; 3.20×10^{-7} mm Hg at 25°C, easily soluble in diethyl ether, soluble in alkalies and most organic solvents, very soluble in alcohol, chloroform and pyrimidine, slightly soluble in petroleum ether, insoluble in cold and hot water) mainly degrade by reacting with $OH^{\bullet}$ at the gas–liquid interface and/or in the bulk liquid and possibly to a much lesser extent by thermal decomposition at the gas–liquid interface (Petrier et al., 1997).

Table 5.43 shows the measured phenol intermediates (2-phenyl-phenol and 3-phenyl-phenol) in OMI ww with HPLC after 60 min, 120 and 150 min sonication times at pH=7.0 and at 25°C.

Table 5.43 The measurements of phenol intermediates (2-phenyl-phenol and 3-phenyl-phenol) in OMI ww with HPLC after 60 min, 120 and 150 min sonication times at pH=7.0 and at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial Total Phenol concentration=4090 mg/l, n=3, mean values).

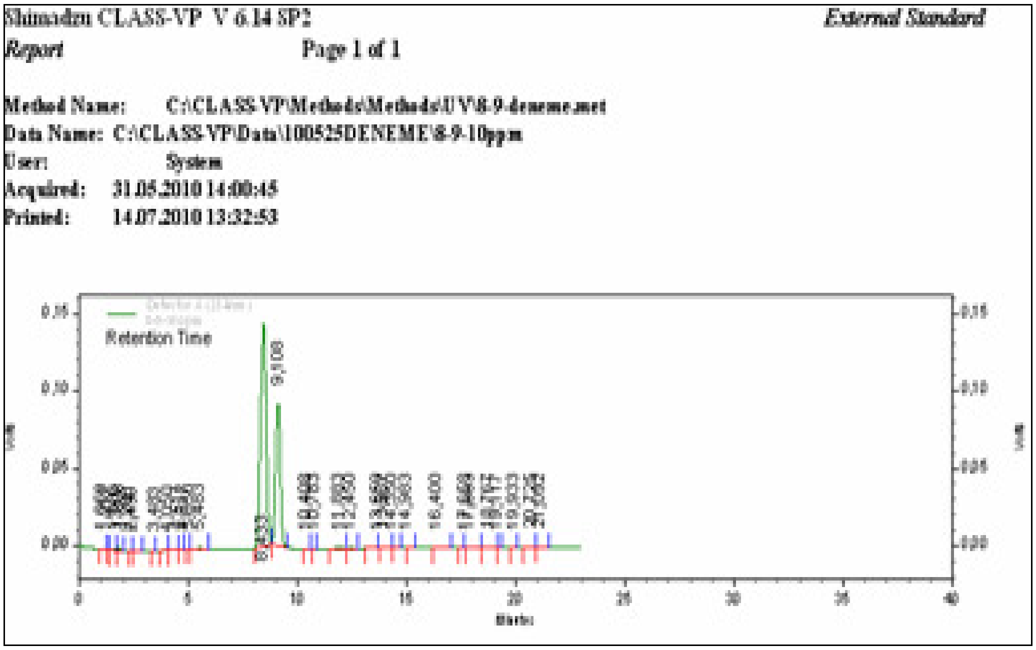
			2-phenyl-phenol		**3-phenyl-phenol**	
Time (min)	**PHE_0 (mg/l)**	**PHER (%)**	**2-PHE (mg/l)**	**2-PHER (%)**	**3-PHE (mg/l)**	**3-PHER (%)**
0	4090	0.00	0.00	0.00	0.00	0.00
60	2990	26.89	426.34	0.00	846.03	0.00
120	1851	54.74	70.74	83.41	101.29	88.03
150	1708	58.25	40.50	90.50	40.76	95.18

PHE_0: Initial total phenol concentration (mg/l), PHER: Total phenol removal efficiency (%), 2-PHE: 2-phenyl-phenol concentration after sonication (mg/l), 2-PHER: 2-phenyl-phenol removal efficiency (%), 3-PHE: 3-phenyl-phenol concentration after sonication (mg/l), 3-PHER: 3-phenyl-phenol removal efficiency (%).

As shown in Table 5.43 and mentioned in Table 5.42, 4090 mg/l initial phenol concentration in OMI ww decreased to 2990 mg/l, to 1851 mg/l and to 1708 mg/l after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25°C. It was found low phenol yields (58.25%) after 150 min sonication time. This could be attributed to the studied low temperature under ambient conditions. From 2990 mg/l total phenol 426.34 mg/l 2-phenyl-phenol and 846.03 mg/l 3-phenyl-phenol were produced after 60 min sonication time at pH=7.0 and at 25°C. 426.34 mg/l 2-phenyl-phenol reduced to 40.50 mg/l after 150 min sonication time at pH=7.0 and at 25°C. 846.03 mg/l 3-phenyl-phenol decreased to 40.76 mg/l after 150 min sonication time at pH=7.0 and at 25°C. The phenol metabolites (2-phenyl-phenol and 3-phenyl-phenol) were removed with yields 90.50% and 95.18%, respectively, after 150 min sonication time at pH=7.0 and at 25°C (Table 5.3). It was found that the total phenol breakdown to 1272.37 mg/l 2-phenyl-phenol and 3-phenyl-phenol. It can be assumed that the remaining total phenol (remaining phenol=4090-1272.37=2817.63 mg/l) could be mineralized, volatilized or cleaved to other phenol metabolites namely, tyrosol, hydroxytyrosol, oleurapein, caffeic acid, quercetin, ferulic acid, catechol, vanillic acid, o-quinone, *p*-coumaric acid, *p*-hydroxybenzaldehyde, etc., throughout sonication.

Some smaller more volatile phenolic by-products were vaporized in OMI ww after sonication experiments (Kallel et al., 2009a). In this reason, these smaller more volatile phenolic intermediates were rapidly removed in OMI ww after a long sonication time (150 min). Therefore, higher removal efficiencies of phenol intermediates (> 93.00%) were observed in OMI ww after 150 min sonication time at 25°C, compared to the total phenol yields (58.25%) in OMI ww after 150 min sonication time at pH=7.0 and at 25°C (Table 5.43).

The HPLC chromatograms of phenol by-products (2-phenyl-phenol and 3-phenyl-phenol) in OMI ww were demonstrated after 60 min, 120 and 150 min sonication times at pH=7.0 and at 25°C in Figures 5.35, 5.36 and 5.37, respectively.


Shimadzu CLASS-VP V 6.14 SP2 *External Standard*
Report Page 1 of 1

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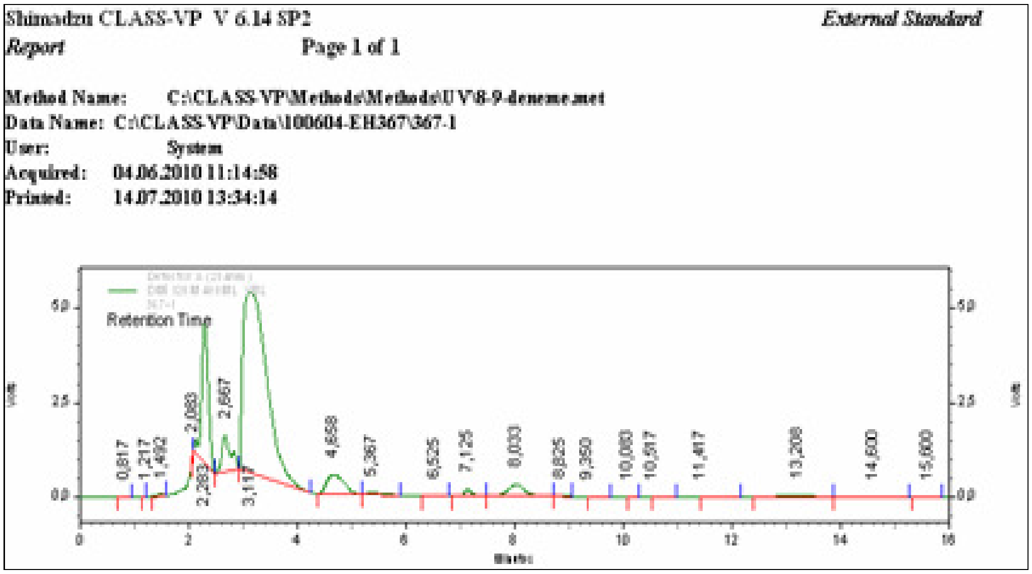
Acquired: 31.05.2010 14:00:45
Printed: 14.07.2010 13:32:53

Figure 5.35 The HPLC chromatogram of phenol by-products (2-phenly-phenol and 3-phenyl-phenol) in OMI ww at Shimadzu CLASS-VP V 6.14 SP2 with Phenomenex Hyperclone 125 mm x 4.60 mm x 5µm HPLC column using UV Method after 60 min sonication time at pH=7.0 and at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).



Shimadzu CLASS-VP V 6.14 SP2 *External Standard*
Report **Page 1 of 1**

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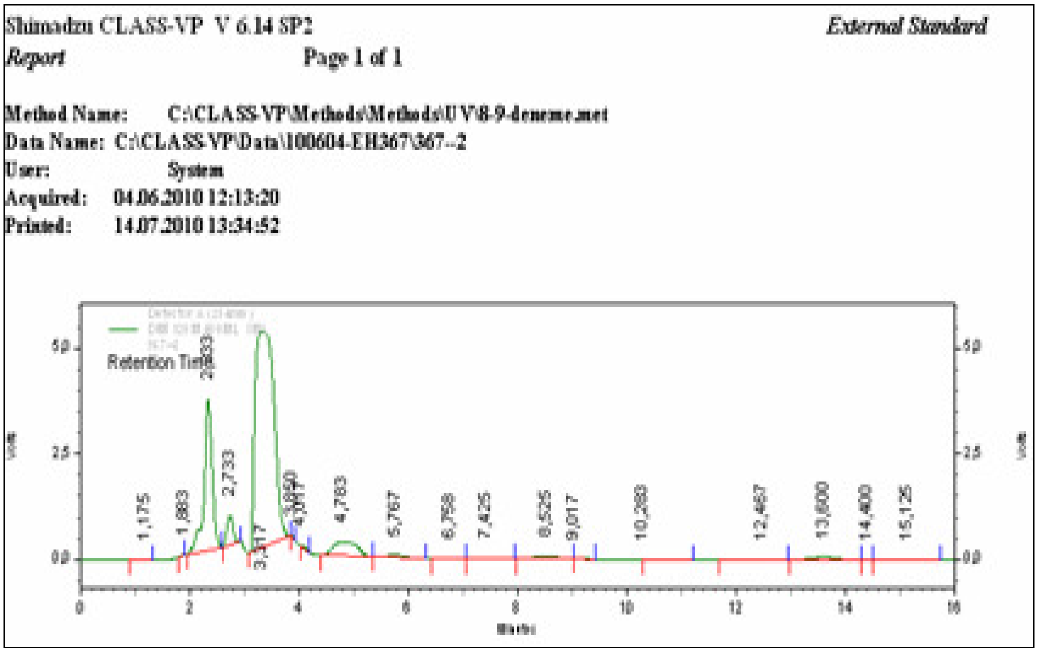
Figure 5.36 The HPLC chromatogram of phenol by-products (2-phenly-phenol and 3-phenyl-phenol) in OMI ww at Shimadzu CLASS-VP V 6.14 SP2 with Phenomenex Hyperclone 125 mm x 4.60 mm x 5µm HPLC column using UV Method after 120 min sonication time at pH=7.0 and at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).



Shimadzu CLASS-VP V 6.14 SP2 *External Standard*
Report **Page 1 of 1**

Method Name: C:\CLASS-VP\Methods\Methods\UV\8-9-deneme.met
Data Name: C:\CLASS-VP\Data\100604-EH367\367--2
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Figure 5.37 The HPLC chromatogram of phenol by-products (2-phenly-phenol and 3-phenyl-phenol) in OMI ww at Shimadzu CLASS-VP V 6.14 SP2 with Phenomenex Hyperclone 125 mm x 4.60 mm x 5µm HPLC column using UV Method after 150 min sonication time at pH=7.0 and at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

In a study performed by Kallel et al. (2009a) it was found that the polyphenol organics composed of alcohol [4-hydroxyphenylethanol (*tyroso*l), 4-hydroxybenzoic acid, 4-hydroxy-3-methoxyphenethylacohol (*homovanillyl alcohol*), 4-hydroxy-3-methoxybenzoic acid (*vanillic acid*), 3,4-Dihydroxyphenyl alcohol (*hydroxytyrosol*), 3,4-dihydroxybenzoic acid (*protocatechuic acid*), 3,4-dihydroxyphenylglycol and 3,4-dihydroxycinnamic acid (*caffeic acid*)]. The removal yields of these polyphenolic compounds were 30.00%, 40.00%, 50.00%, 35.00%, respectively, throught sonication of OMI ww at 25^{o}C. In this study, 90.50-95.18% phenol by-products (2-phenyl-phenol and 3-phenyl-phenol) removals were found at 25^{o}C after 150 min sonication time. In the present study the phenol by-products yields are higher than the yields obtained by Kallel et al. (2009a) at 25^{o}C.

Vassilakis et al. (2004) 30.00% *p*-coumaric acid (a polyphenolic compound) removal efficiency was found at a 80 kHz frequency with sonication. In this study, 90.50-95.18% phenol by-products (2-phenyl-phenol and 3-phenyl-phenol) removals was observed at 25^{o}C after 150 min sonication time. In the present study, the phenol by-products yields are higher than the yield obtained by Vassilakis et al. (2004) at 25^{o}C as mentioned above. In a study performed by Andreozzi et al. (1998) showed that total phenols are reduced to about 43.00% in 3 h by ozonation while the total COD removal remains unvaried in OMI ww. In the present study, the total phenol removal obtained by sonication is higher than the yield obtained by Andreozzi et al. (1998) at 25^{o}C as mentioned above. In this study 88.00% *p*-coumaric acid and 85.00% *p*-hydroxybenzaldehyde removal were obtained at 80 kHz frequency, and applied sonication powers varying between 75 and 150 W at 25^{o}C. The phenol by-products removal found in this study are higher than the yield observed by Andreozzi et al. (1998) at 25^{o}C. Adhoum & Monser (2004) found 88.00% polyphenol removal by electrocoagulation at 25 min retention time and at 25^{o}C. The phenol by-product yields found by sonication are higher than the data obtained by electrocoagulation at 25^{o}C.

It was reported that the dihydroxy phenols are further converted to organic mineral acids and finally to CO_2 and H_2O under sonication (Berlan et al., 1994)

17.00% total phenol and 56.00% dihydroxy phenols removals were obtained after 60 min sonication at 30 kHz frequency and 500 W powers. These results were significantly lower then the yields obtained in the present study. The study performed by Khoufi et al. (2006) showed that fenton reaction followed by an anaerobic biotreatment provided 80.00% orthobiphenols removals. These data were lower than the yields obtained for 2-phenyl-phenol and 3-phenyl-phenol having the same carbon rings.

5.10.2.3 Effect of Increasing Sonication Time on the TAAs Removal Efficiencies in OMI ww at 25^{o}C Ambient Conditions

33.67%, 48.27% and 63.17% TAAs removal efficiencies were observed at an influent TAAs concentration of 3000 mg benzidine/l after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25^{o}C (Table 5.42). The TAAs removal efficiencies in OMI ww increased from 33.67% up to 63.17% as the sonication time was increased from 60 to 150 min. The maximum TAAs removal efficiency was 63.17% after 150 min sonication time at pH=7.0 and at 25^{o}C. A significant linear correlation between TAAs yields and increasing sonication time was observed (R^2=0.79, F=15.32, p=0.01) (Table 5.42).

Low TAAs yields at low temperature could be attributed to the modifications of some sonodegraded aliphatic chains to generate condensed aromatic structures containing large proportions of hydroxyl, methoxyl, carboxyl and carbonyl groups (Oussi et al., 1997). The recent studies, showed that the destruction of TAAs from OMI ww are difficult since OMI ww contained some methoxyl groups of aromatic ethers, *N*-substituted aromatic carbons and amide moieties (Lafi et al., 2009)

Figure 5.38 shows the theoretical sono-degradation of aromatic amine (AA) namely “4-hydroxybenzoic acid” containing Cl^{-1}, CH_2, CH_3 and COOH groups with five aromatic benzene rings: In the first metabolic pathway the benzene rings in AAs cleaved with hydroxylation reaction with sonication of OMI ww. In the second metabolic pathway the destruction of carboxyl structure in 4-hydroxybenzoic acid occurred and the ethyl groups with N bound cleaved from the AAs in question via *N*-deethylation.

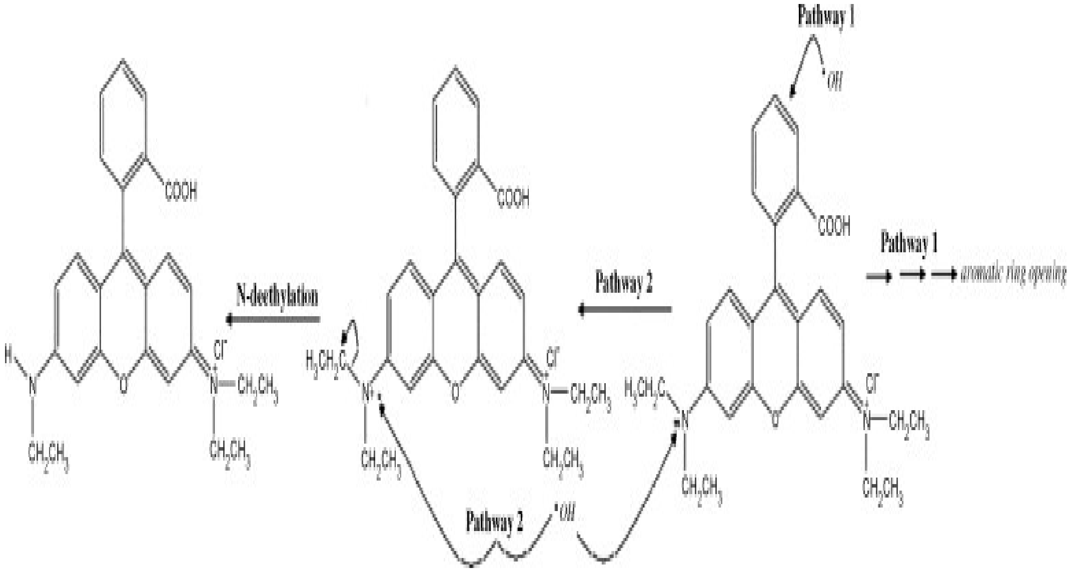


Figure 5.38 The sonodegradation mechanism of OMI ww with OH$^\bullet$ via two competitive processes: *N*-Deethylation and destruction of the Aromatic rings.

As can be seen in Table 5.44 the absorption spectra given in absorption band at wavelengths of λ=0.850 nm, λ=0.680 nm and λ=0.440 nm decreased with increasing sonication times and the minimum absorption wavelength shifts was obtained at 150 min sonication at pH=7.0. As a result, 4-hydroxybenzoic acid sonodegraded to benzene and carboxyl groups. Therefore, destruction of carboxyl structure takes place in the AA in question under sonication. The sonodegradation scheme of 4-hydroxybenzoic acid" AA showed spectral changes of *N*-deethylation under sonolysis (Figure 5.38).

Table 5.44 The absorbances measured throughout TAAs removals in OMI ww at different wavelengths (λ=0.850 nm, λ=0.680 nm and λ=0.440 nm) after 60 min, 120 and 150 min sonication times at pH=7.0 and at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

Time (min)	**Values**					
	λ=0.850 nm		**λ=0.680 nm**		**λ=0.440 nm**	
	Abs (nm)	**Rem (%)**	**Abs (nm)**	**Rem (%)**	**Abs (nm)**	**Rem (%)**
0	0.913	0.00	0.782	0.00	0.683	0.00
60	0.826	27.08	0.730	30.10	0.640	33.67
120	0.701	38.24	0.678	42.22	0.615	48.27
150	0.673	57.66	0.612	60.30	0.593	63.17

The absorption decreased with the concomitant high wavelength shift of band to the shorter wavelengths (from 0.683 nm to 0.640 nm, to 0.615 nm and to 0.593 nm). 33.67%, 48.27% and 63.17% absorbance removals for TAAs in OMI ww were observed as the wavelengths decreased from 0.683 nm to 0.640 nm and 0.615 nm, respectively, at pH=7.0 and at 25°C (Table 5.44). These results indicate that in the sonication of AAs the cleavage of aromatic chromophore ring structure takes place, but decomposition of aromatic structure is predominant as can be seen in Figure 5.38. With increasing the sonication time the poly-aromatic rings are destroyed and the produced aromatic rings and intermetabolites display low absorption levels compared to the initial wavelengths (λ=0.850 nm, λ=0.680 nm and λ=0.400 nm) (Table 5.44).

Although, in this study it was studied at a temperature as low as 25°C, long sonication time as high as 150 min provided high TAAs removals. At longer sonication times it was reached quickly to the equilibrium and faster rate of TAAs removals was obtained. The high TAAs yields could be attributed to the higher mass transfer and higher surface area produced by the cavitation process (Entezari & Sharif Al-Hosseini, 2007).

Hydrolysis and pyrolysis are main degradation mechanisms for AAs with ultrasound. The attack of non-volatile compounds in the ‘‘bulk water” by $OH^{\bullet}$ destroy the chromophoric system through azo bond cleavage. $OH^{\bullet}$ attack leads to hydroxyl amines followed by subsequent oxidation forming aromatic nitroso and nitro compounds. The attack at the carbon atom adjacent to the azo bond, leading to production phenyl derivative radicals. Further degradation pathways are difficult to predict since the fate of the fragments depends on their physical and chemical properties. Further reactions may occur inside the cavity (pyrolysis), in the hypercritical water layer or in the ‘‘bulk’’ water as reported by Rehorek et al. (2004).

Tang & Isacsson (2005) found 30.00% TAAs (toluene, ethyl benzene, m-xylene, p-xylene, o-xylene, 3-ethyltoluene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,3,4-tetramethylbenzene) removals in OMI ww after 60 min sonication time at 25°C. In this study, 33.67% TAAs removal was observed at 25°C after 60 min sonication time. The TAAs removals in both studies exhibited similarities at 25°C. Dungan (2005) 27.00% TAAs (benzene, toluene, xylene, ethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene) yields obtained after 60 min sonication time at 25°C. These TAAs removals were found to be lower than the present study at 25°C after 60 min sonication time.

5.10.2.4 Effect of Increasing Sonication Time on the TFAs Removal Efficiencies in OMI ww at 25°C Ambient Conditions

12.73%, 18.84% and 37.51% TFAs removal efficiencies were obtained at an influent TFAs concentration of 5200 mg/l after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25°C (Figure 5.39; Table 5.42.). The TFAs removal efficiencies in OMI ww increased from 12.78% up to 37.51% as the sonication time was increased from 60 to 150 min. The maximum TFAs removal efficiency was 37.51% after 150 min sonication time at pH=7.0 and at 25°C. A significant linear correlation between TFAs yields and increasing sonication time was observed (R^2=0.75, F=18.76, p=0.01) (Figure 5.39; Table 5.42).

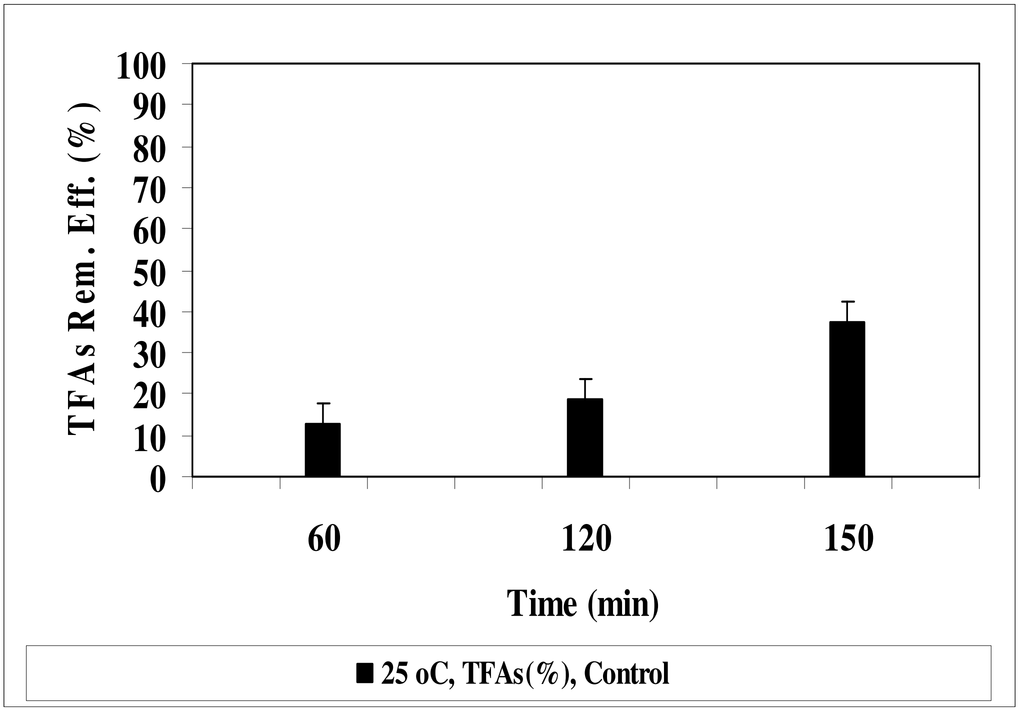


Figure 5.39 Effect of increasing sonication time on the TFAs removal efficiencies in OMI ww at pH=7.0 and at 25^{o}C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

In a study performed by Jimenez et al. (2007) 43.00%, 45.00% and 46.00% TFAs removals were found in OMI ww in 3 different sonicators with horn probe, cleaning bath and conventional thermal treatment, respectively at a power of 150 W at a frequency of 25 kHz for 20 min sonication time at temperatures varying between 28^{o}C and 30^{o}C. In the present study, low TFAs yields were obtained compared to the TFAs removals obtained by Jimenez et al. (2007).

5.10.3 Effect of Increasing Temperature on the Removals of COD_{dis} and TOC versus Sonication Times in OMI ww

5.10.3.1 Effect of Increasing Sonication Time on the Removals of COD_{dis} in the OMI ww

At the beginning of the studies the raw OMI ww samples were sonicated at 30°C and at 60°C, at increasing sonication times from 5 min up to 60 min to determine the lowest sonication times for the maximum COD_{dis} removal efficiencies at pH=7.0 (Table 5.45). The lowest sonication time was determined as 60 min for the maximum COD_{dis} removals at pH=7.0.

Table 5.45 Effect of increasing sonication times (5–10–15–20–25–30–35–40–45–50–55 and 60 min) on OMI ww at 30°C and at 60°C and at pH=7.0 (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values ±SD).

Time (min)	**30°C**		**60°C**	
	COD_{dis} (mg/l)	**Rem. Eff. (%)**	**COD_{dis} (mg/l)**	**Rem. Eff. (%)**
0	109444 ± 3831	0.00	109444 ± 3831	0.00
5	105857 ± 3705	3.28	105191 ± 3682	3.89
10	104128 ± 3645	4.86	104990 ± 3675	4.07
15	103490 ± 3622	5.44	104590 ± 3661	4.44
20	103061 ± 3607	5.19	104291 ± 3650	4.71
25	102851 ± 3600	6.02	103891 ± 3636	5.07
30	102168 ± 3576	6.65	102992 ± 3605	5.90
35	101394 ± 3549	7.36	101591 ± 3556	7.18
40	100665 ± 3523	8.02	100392 ± 3514	8.27
45	98756 ± 3457	9.77	98592 ± 3451	9.92
50	97582 ± 3415	10.84	94493 ± 3307	13.66
55	96208 ± 3367	12.09	92893 ± 3251	15.12
60	95479 ± 3342	12.76	89994 ± 3150	17.77

15.47%, 42.29% and 62.57% COD_{dis} removals were measured after 60 min, 120 and 150 min sonication times , respectively, at pH=7.0 and at 30°C (Figure 5.40). An increase of 2.89% and 1.66% in COD_{dis} yields was obtained compared to the control at pH=7.0 and at 25°C after 60 and 150 min sonication time, respectively, at 30°C. Sonication alone provided 41.74% and 60.91% COD_{dis} removals after 120 and 150 min sonication times at pH=7.0 and at 25°C. A significant linear correlation between COD_{dis} yields and sonication time was not observed (R^2=0.41, F=2.99, p=0.01) (Figure 5.40).

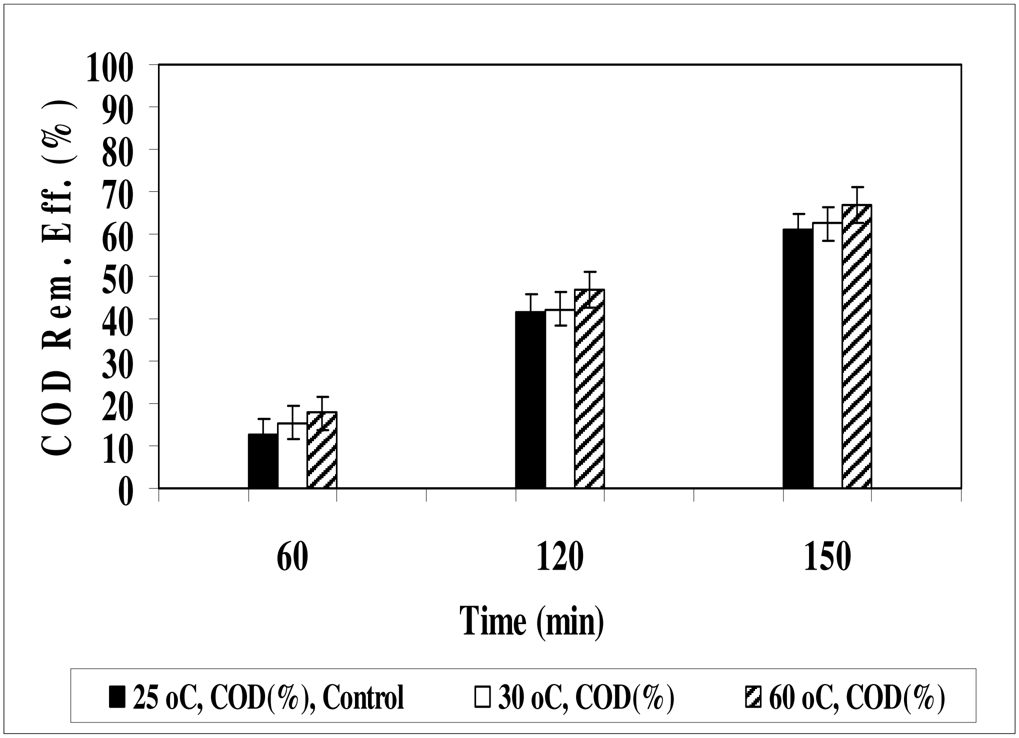


Figure 5.40 Effect of increasing temperature on the COD_{dis} removal efficiencies in OMI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

17.77%, 46.81% and 66.83% COD_{dis} removals were observed after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.40). 5.19%, 5.07% and 5.92% increases in COD_{dis} yields was obtained after 60 min, 120 and 150 min sonication times, respectively, at 60°C, compared to the control (E=60.91% COD_{dis} after 150 min sonication time at pH=7.0 and at 25°C). The maximum COD_{dis} removal efficiency was 66.83% after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between COD_{dis} yields and sonication time was not observed (R^2=0.47, F=3.67, p=0.01). A significant linear correlation between COD_{dis} yields and increasing Temperature was not found at all sonication times (Figure 5.40).

14.34%, 42.42% and 61.62% TOC removals were measured after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^{o}C (Figure 5.41). 1.87%, 1.62% and 2.34% increase in TOC yields was obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^{o}C, compared to the control (40.80% and 59.28% TOC removals after 120 and 150 min sonication times at pH=7.0 and at 25^{o}C) (R^2=0.36, F=2.78, p=0.01). A significant linear correlation between TOC yields and sonication time was not observed (R^2=0.40, F=2.99, p=0.01) (Figure 5.41).

17.83%, 45.27% and 65.92% TOC removals were obtained after 60 min, 120 and 150 min sonication, respectively, at pH=7.0 and at 60^{o}C (Figure 5.41). 5.36%, 4.47% and 6.64% increase in TOC yields was obtained after 60 min, 120 and 150 min sonication times, respectively, at 60^{o}C, compared to the control (E=59.28% TOC removals after 150 min sonication time at pH=7.0 and at 25^{o}C). The maximum TOC removal efficiency was 65.92% after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between TOC yields and sonication time was not observed (R^2=0.43, F=4.56, p=0.01) (Figure 5.41).

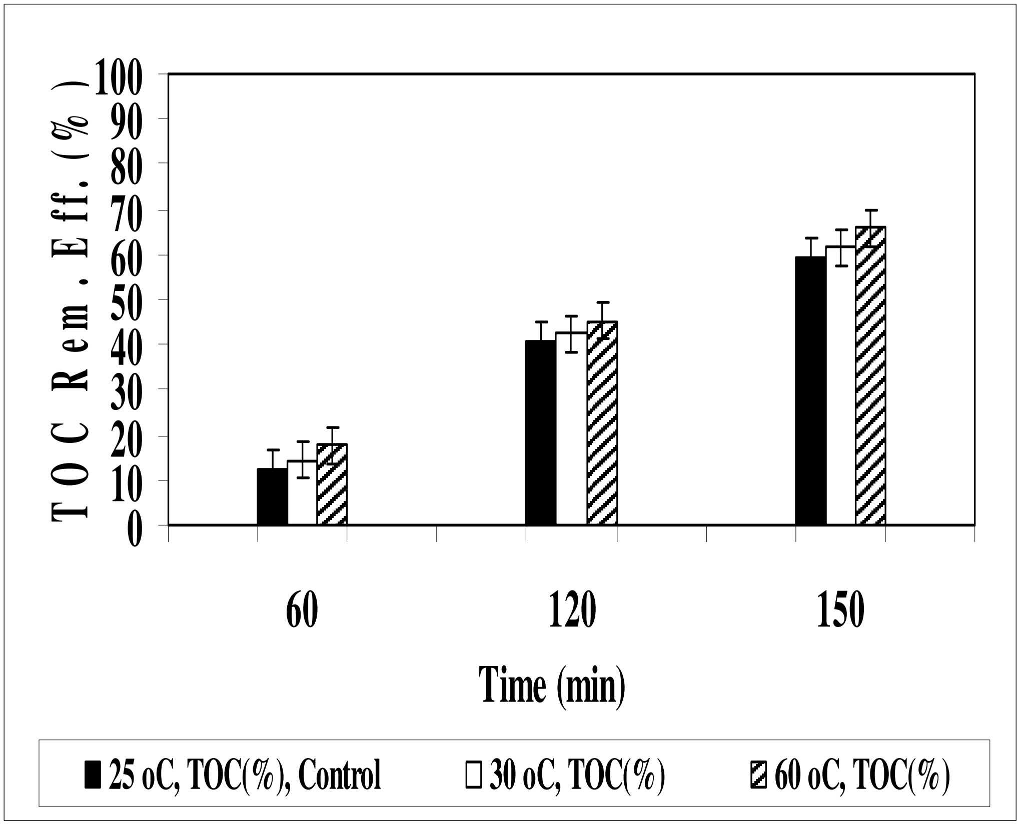


Figure 5.41 Effect of increasing temperature on the TOC removal efficiencies in OMI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TOC concentration=66488 mg/l, n=3, mean values).

It is generally believed that although, increased temperatures are likely to facilitate bubble formation due to an increase of the equilibrium vapor pressure, the sonochemical effect of such bubbles may be reduced. This is due to the fact that bubbles contain more vapor, which cushions the implosion growth as well as use enthalpy for condensation. The increase of aqueous temperature certainly increases the number of cavitation bubbles on sonolysis and thus the rate of production of radicals ($OH^{\bullet}$ and $OOH^{\bullet}$) results in a lowering of the cavitation threshold. Additionally, at low temperature (< 25°C), the vapor pressure of water is lower, and the solubility of gas is higher, hence the cavitation bubbles exhibit a more gaseous nature. As a result, the reaction rates do not decrease with increase in solution temperature between 30°C and 60°C. Therefore, reactions in the bulk are facilitated by increasing the temperature due to the higher mass transfer of different species at higher temperatures and this leads to an enhancement on the rate of reaction of radicals with pollutant (Inan et al., 2004).

5.10.3.2 Effect of Increasing Temperature on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times

38.68%, 52.61% and 74.45% color removals were found after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^{o}C (Figure 5.42). 2.31%, 4.71% and 24.75% increase in color yields was obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^{o}C, compared to the control (E=59.70% color after 150 min sonication time at pH=7.0 and at 25^{o}C). A significant linear correlation between color yields and temperature was not observed (R^2=0.37, F=3.28, p=0.01) (Figure 5.42).

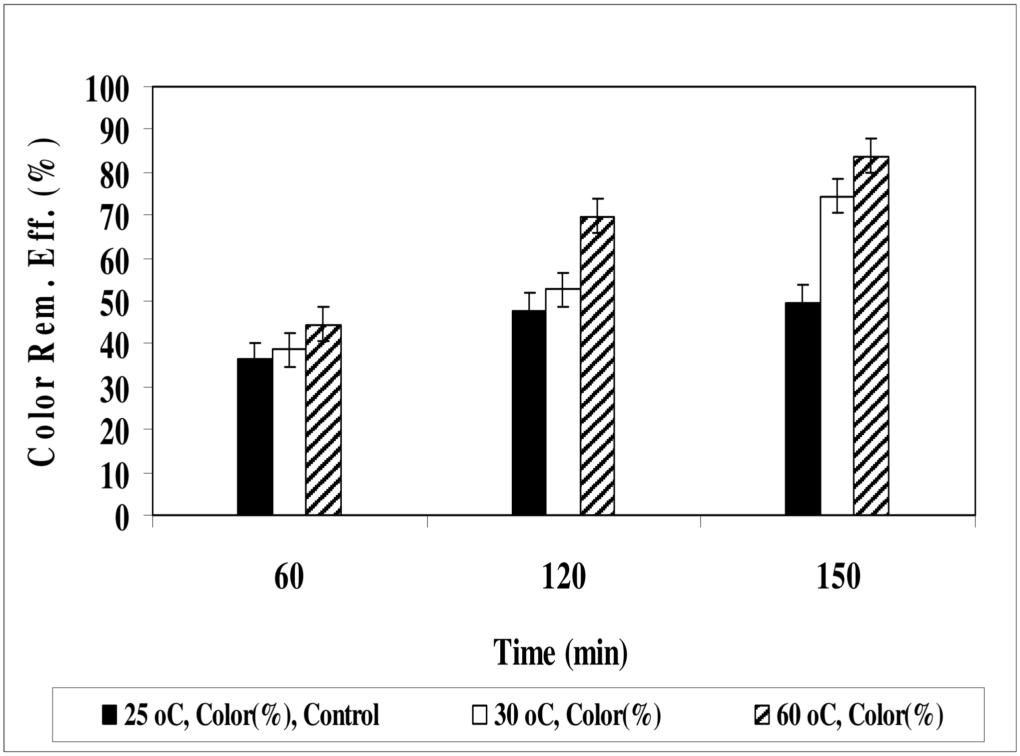


Figure 5.42 Effect of increasing temperature on the color removal efficiencies in OMI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

44.59%, 69.74% and 83.77% color yields were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.10). The contribution of temperature to the color yields in OMI ww were 8.22%, 21.84% and 34.07% after 60 min, 120 and 150 min sonication times, respectively, at 60°C, compared to the control (E=49.70% color at pH=7.0 and at 25°C). The maximum color removal efficiency was 83.77% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and temperature was not obtained in OMI ww (R^2=0.45, F=3.67, p=0.01) (Figure 5.42).

Oxidation and pyrolysis are main degradation mechanisms for decolorization with ultrasound. Reactions in the bulk are facilitated by increasing the temperature due to the higher mass transfer of different species at higher temperatures and this leads to an enhancement of the reaction rate of radicals ($H^\bullet$, $OH^\bullet$, $O_2H^\bullet$) with dye molecules (Ghodbane & Hamdaoui, 2009b). On the other hand, any increase in temperature will raise the vapor pressure of a medium and so lead to easier cavitation but less violent collapse (Behnajady et al., 2008). Under extreme alkaline conditions, $OH^\bullet$ scavenging effects become more significant (Vajnhandl et al., 2007). The enhancement of degradation rate at basic conditions may be caused by the change of hydrophobic property of dye (Ghodbane & Hamdaoui, 2009b). The hydrophilic property of the color originating from the ferric humates, humic materials, potassium chloroplatinate (K_2PtCl_6), MnO_2, Fe_2O_2 , etc., is mostly degraded outside the cavitation process by the $OH^\bullet$ produced by ultrasound.

The color of OMI ww varied from dark-red to brownish black depending on its age and the extraction procedure. While the monomeric phenols exhibit phytotoxic (Capasso et al., 1992) and antimicrobial activities (Hamdi & Ellouz, 1993), polymeric phenols have a lignin-like structure as their most recalcitrant fraction and are mainly responsible for the typical color of OMI ww (Hamdi & Ellouz, 1993; Perez et al., 1987). On the other hand, the high-molecular-weight phenolic compounds similar in structure to the lignin gives the characteristics recalcitrant brownish black color in OMI ww (Assas et al., 2002; D'Annibale et al., 2006).

Guzman-Duque et al. (2011) 53.00% color removal was measured at 80 kHz frequency after 180 min sonication time at 60°C in OMI ww. In this study 83.77% color removal was found at 60°C. In the present study, high color yields were observed compared to the color removals obtained by Guzman-Duque et al. (2011). In the study performed by Svitelska et al. (2004) 50.00% color yield was obtained at 20 kHz frequency, at pH > 10.0 and at 60°C. In this study, 83.77% color removal measured at 60°C after 150 min sonication time. In this study, the color yield is higher than the yield obtained by Svitelska et al. (2004) at 60°C as mentioned above.

5.10.3.3 Effect of Increasing Temperature on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times

28.26%, 56.00% and 59.40% total phenol removals were observed after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Figure 5.43). The contribution of temperature increase to the total phenol removals were found to be as 1.37%, 1.26% and 1.15% after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control (E=58.25% total phenol after 150 min sonication time at pH=7.0 and at 25°C). A significant linear correlation between total phenol yields and temperature was not obtained in OMI ww (R^2=0.42, F=3.99, p=0.01) (Figure 5.43).

30.20%, 57.94% and 61.24% total phenol yields were found after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.43). The contribution of temperature to the total phenol yields were only 3.31%, 3.20% and 2.99% after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control (E=58.25% total phenol after 150 min sonication time at pH=7.0 and at 25°C). The maximum total phenol removal efficiency was 61.24% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between total phenol yields and temperature was not observed (R^2=0.32, F=2.89, p=0.01) (Figure 5.43).

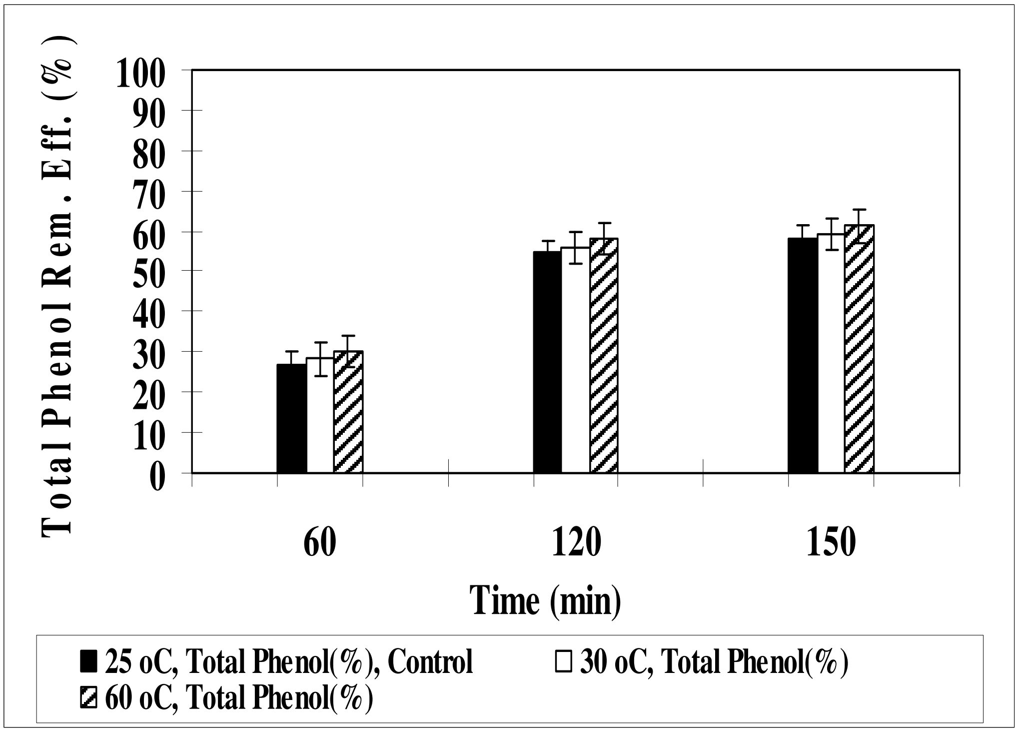


Figure 5.43 Effect of increasing temperature on the total phenol removal efficiencies in OMI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

The sonochemical degradation of actual OMI ww samples is likely to occur through complex reaction pathways involving the formation of numerous intermediates competing for the available sonication energy; moreover, several of these intermediates such as caffeic acid may be of phenolic nature. On the other hand, with caffeic acid as the starting molecule, fewer reactions and intermediates are likely to occur and this would explain the enhanced performance of sonochemical degradation (Adhoum & Monser, 2004).

The study performed by Kidak & Ince (2007) showed that 60.00% phenol removal could be achieved at acidic pH with sonication at frequency of 300 kHz after 90 min sonication time at 60^{o}C. In this study, 61.24% total phenol removal was observed at 60^{o}C after 150 min sonication. In the present study the total phenol removal is higher than the yield obtained by Kidak & Ince (2007). In a study performed by Entezari & Petrier (2004) 50.00%-60.00% phenol removal efficiency was measured at a frequency of 423 kHz, after 45 min sonication time at 60^{o}C. They reported that the OH$^\bullet$ produced by ultrasound can react with phenol resulting in a dephenolization process. In this study, 61.24% total phenol removal was observed at 60^{o}C after 150 min sonication. The total phenol removal is higher than the yield observed by Kidak & Ince (2007) as mentioned above.

Table 5.46 shows the measured phenol intermediates (2-phenyl-phenol and 3-phenyl-phenol) in OMI ww with HPLC at pH=7.0 after 60 min, 120 and 150 min sonication times at 30^{o}C and at 60^{o}C.

Table 5.46 The measurements of phenol intermediates (2-phenyl-phenol and 3-phenyl-phenol) in OMI ww with HPLC at pH=7.0 after 60 min, 120 and 150 min sonication times at 30^{o}C and at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Time (min)	**PHE$_0$ (mg/l)**	**30^{o}C**				
		PHER (%)	**2-phenyl-phenol**		**3-phenyl-phenol**	
			2-PHE (mg/l)	**2-PHER (%)**	**3-PHE$_0$ (mg/l)**	**3-PHER (%)**
0	4090	0.00	0.00	0.00	0.00	0.00
60	1763	56.89	496.99	0.00	898.03	0.00
120	1033	74.74	50.88	89.76	86.50	90.37
150	481	88.25	23.56	95.26	18.83	97.90
Time (min)	**PHE$_0$ (mg/l)**	**60^{o}C**				
		PHER (%)	**2-phenyl-phenol**		**3-phenyl-phenol**	
			2-PHE (mg/l)	**2-PHER (%)**	**3-PHE$_0$ (mg/l)**	**3-PHER (%)**
0	4090	0.00	0.00	0.00	0.00	0.00
60	1376	66.34	501.55	0.00	899.99	0.00
120	651	84.09	38.76	92.27	78.29	91.30
150	72	98.25	10.98	97.81	8.76	99.03

PHE$_0$: Initial total phenol concentration (mg/l), PHER: Total phenol removal efficiency (%), 2-PHE: 2-Phenyl-phenol concentration after sonication (mg/l), 2-PHER: 2-Phenyl-phenol removal efficiency (%), 3-PHE: 3-Phenyl-phenol concentration after sonication (mg/l), 3-PHER: 3-Phenyl-phenol removal efficiency (%).

As shown in Table 5.46 and mentioned in Table 5.42, from 4090 mg/l total phenol 501.55 mg/l 2-phenyl-phenol and 899.99 mg/l 3-phenyl-phenol were produced after 60 min sonication time at pH=7.0 and at 60^{o}C. 501.55 mg/l 2-phenyl-phenol was reduced to 10.98 mg/l after 150 min sonication time at pH=7.0 and at 60^{o}C. 899.99 mg/l 3-phenyl-phenol decreased to 8.76 mg/l after 150 min sonication time at pH=7.0 and at 60^{o}C. The phenol metabolites (2-phenyl-phenol and 3-phenyl-phenol) were removed with yields of 97.81% and 99.03%, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.46). It was found that 4090 mg/l total phenol sonodegraded to 1401.54 mg/l (2-phenyl-phenol and 3-phenyl-phenol). Since the total phenol yields are high (98.25%) after 150 min sonication time at pH=7.0 and at 60°C it can be assumed that the remaining total phenol (remaining phenol=4090-1401.54=2688.46 mg/l) mainly sono-degraded to the end products with high yields and minorly converted to other phenol metabolites which they are not measured in this study (tyrosol, hydroxytyrosol, oleurapein, caffeic acid, quercetin, ferulic acid, catechol, vanillic acid, o-quinone, *p*-coumaric acid, *p*-hydroxybenzaldehyde, etc.) through sonication.

Jahouach-Rabai et al. (2008) investigated the removal of OME using a sonicator at 20 kHz frequency, at a power of 750 W and at a temperature of 30°C. 61.00% removal efficiencies were obtained for some non-odorous organics (hexanal, hept-2-enal, 2(E)–decadienal, 4(E)-decadienal) and for some phenolic organics. Vassilakis et al. (2004) investigated to the sonochemical degradation of some phenolic by-products namely, *p*-coumaric acid and *p*-hydroxybenzaldehyde in OMI ww at a frequency of 80 kHz in a horn-type sonicator. 90.00% phenol removals were found at an initial phenolic compound concentration of 100 mg/l, at powers varying between 75 and 150 W and at sonication temperatures 25-70°C. 88.00% degradation yields were obtained for *p*-coumaric acid. The removals of the phenol metabolites mentioned above are lower than the yields of phenol metabolites (2-phenyl-phenol and 3-phenyl-phenol) found after 150 min sonication time at 60°C.

5.10.3.4 Effect of Increasing Temperature on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times

37.19%, 55.34% and 64.98% TAAs yields were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Figure 5.44). 3.52%, 7.07% and 1.81% increase in TAAs removals was obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control (E=63.17% TAAs after 150 min sonication time at pH=7.0 and at 25°C). A significant linear correlation between TAAs yields and temperature was not obtained in OMI ww (R^2=0.38, F=4.34, p=0.01) (Figure 5.44).

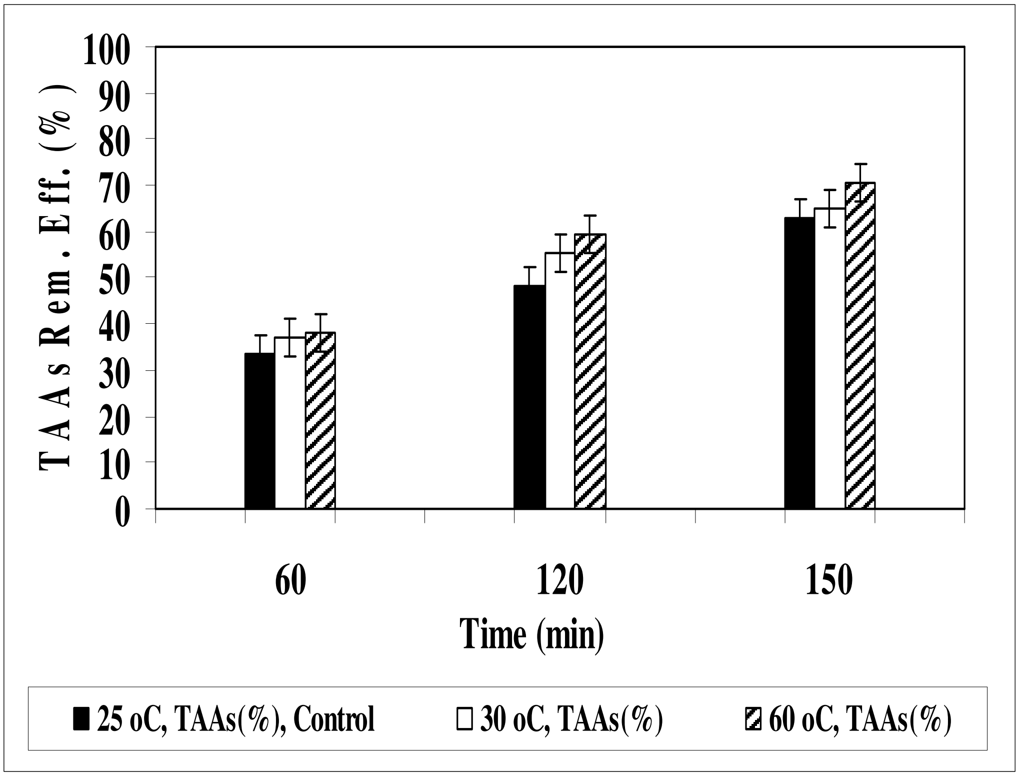


Figure 5.44 Effect of increasing temperature on the TAAs removal efficiencies in OMI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg/l, n=3, mean values).

38.14%, 59.39% and 70.52% TAAs removals were found after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.44). The contribution of temperature to the TAAs yields were 4.47%, 11.12% and 7.35% after

60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60^{o}C, compared to the removals obtained in control (E=63.17% TAAs after 150 min sonication time at pH=7.0 and at 25^{o}C). The maximum TAAs removal efficiency was 70.52% after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between TAAs yields and increasing sonication times was observed (R^2=0.73, F=15.87, p=0.01) while the correlation between temperature and TAA yields was not significant (R^2=0.43, F=2.87, p=0.01) (Figure 5.44).

In this study, the TAA content of OMI was measured based on Benzidine as mg/l. The identification of the TAAs was not performed. The recent literature showed that the sonochemical degradation of TAAs predominantly occurs via $OH^\bullet$ attack; although a thermal reaction occurring in the vicinity of the bubble cannot be completely discounted, its contribution should be small (Rehorek et al., 2004). Degradation proceeds through a series of aromatic and ring cleavage intermediates with $OH^\bullet$- mediated reactions being the prevailing mechanism occurred (Oussi et al., 1997).

Benzoic acid, terephthalic acid and isophthalic acid are the main TAAs by-products after the sonodegradation of hydroquinone. 53.00% benzoic acid, 47.00% terephthalic acid and 38.00% isophthalic acid removals were observed at 30 kHz, at 750 W at 75^{o}C (Entezari et al., 2003). In the present study, 70.52% TAAs removal was observed at 60^{o}C after 150 min sonication time.

5.10.3.5 Effect of Increasing Temperature on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times

15.62%, 22.37% and 45.66% TFAs yields were observed after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^{o}C (Figure 5.45). 2.89%, 3.53% and 8.15% increase in TFAs removals was observed after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^{o}C compared to the control (E=37.51% TFAs after 150 min sonication time at pH=7.0 and at 25^{o}C). A significant linear correlation between TFAs yields and increasing sonication times and increasing temperatures was not observed (R^2=0.37, F=3.09, p=0.01; R^2=0.41, F=3.07, p=0.01) (Figure 5.13).

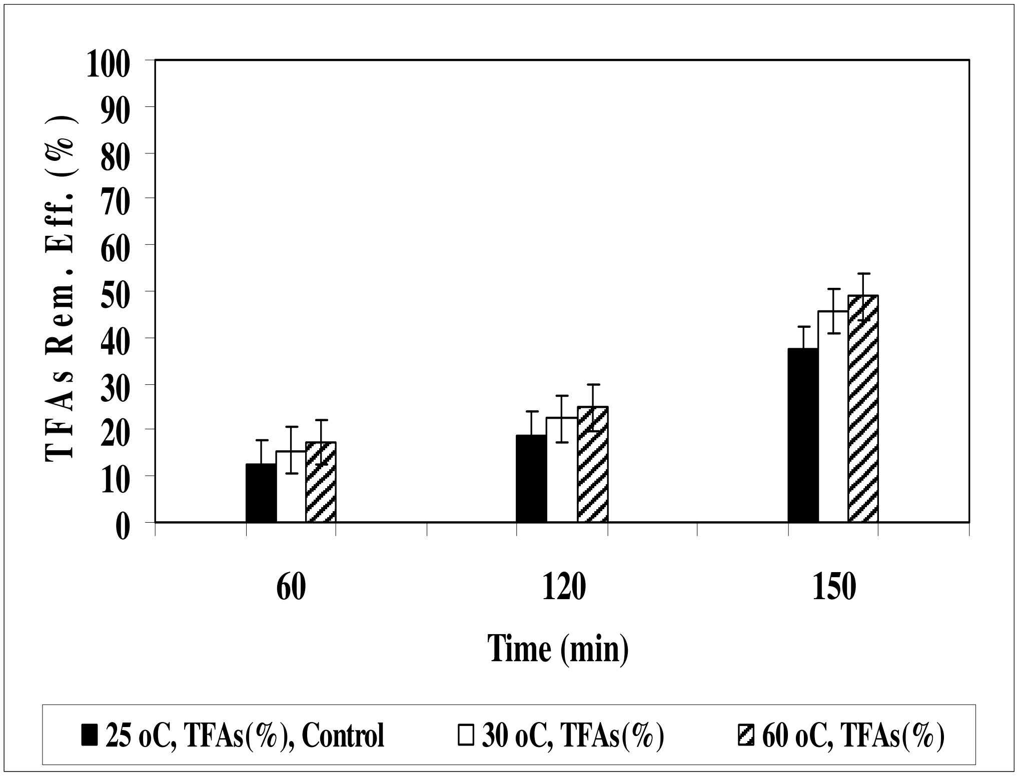


Figure 5.45 Effect of increasing temperature on the TFAs removal efficiencies in OMI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg/l, n=3, mean values).

17.33%, 24.77% and 48.84% TFAs removals were found after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.45). The contribution of temperature to the TFAs yields were 4.60%, 5.93% and 11.33% after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control (E=37.51% TFAs after 150 min sonication time at pH=7.0 and at 25°C). The maximum TFAs removal efficiency was 48.84% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TFAs yields and increasing temperature was not observed (R^2=0.33, F=2.37, p=0.01) (Figure 5.45).

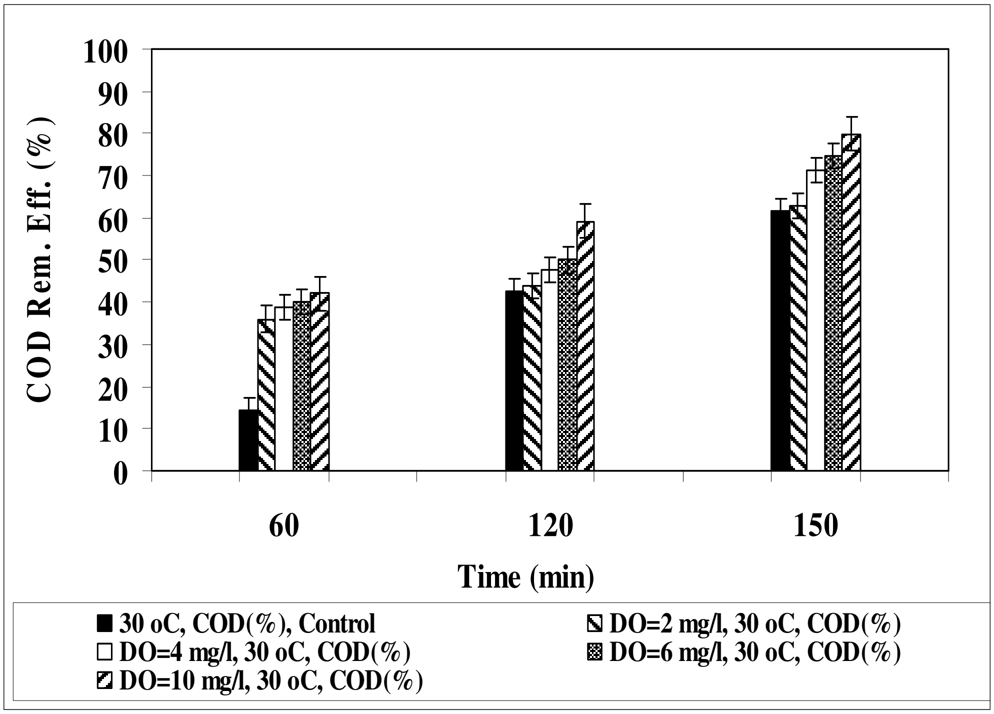
Chemat et al. (2004) found that the TFAs in an OMI ww composed of palmitic, stearic, oleic and linoleic acids. The removal yields of these TFAs were 61.00% in a sonicator at 20 kHz frequency, at a power of 150 W, after 20 min of sonication time at 50°C. In this study, 48.84% TFAs yields was observed at 60°C after 150 min sonication. This TFAs removal is higher than the yield found by in the present study.

Jahouach-Rabai et al. (2008) investigated the removal of olive mill effluents using a sonicator at 20 kHz frequency, at a power of 750 W, at a temperature of 30°C. In this study, it was found that many volatile compounds are responsible for the flavors originated from the degradation of triacylglycerols, polyunsaturated fatty acids or phospholipids in OMI. Other odor given compounds are derived from the autoxidation of fatty acids. In fact, a large number of volatiles can be formed during autoxidation of unsaturated acyl lipids. In a study performed by Hachicha, S. et al. (2009) it was found that the TFAs fraction of OMI sludge composed of oleic, palmitic and linoleic acids and degraded through sonication with yields varying between 50.40% and 52.00%. These removals are comparable similar with TFAs yields obtained in the present study.

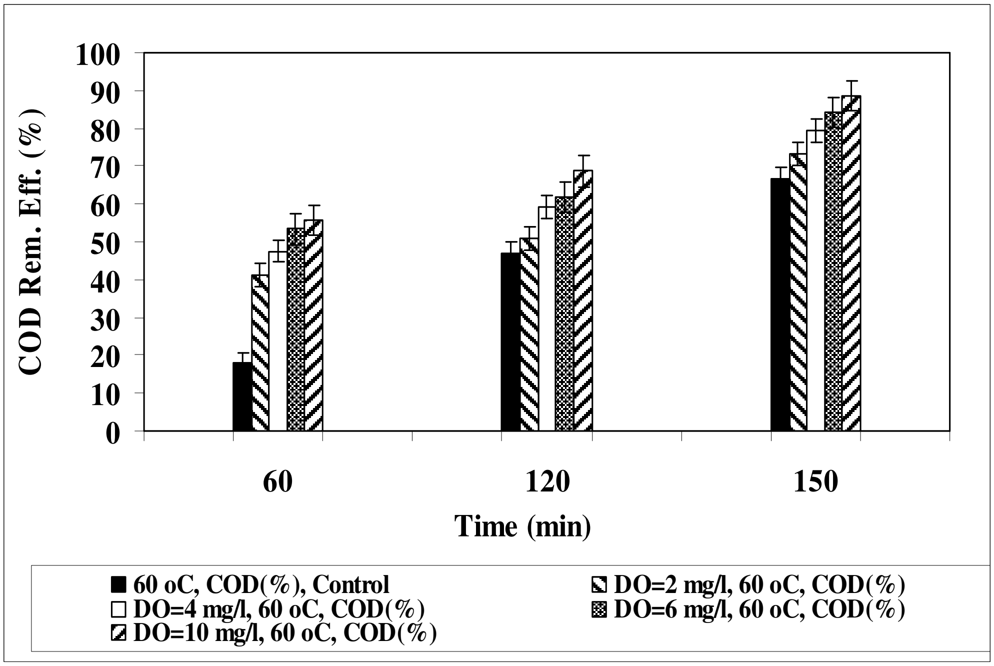
5.10.4 Effect of DO Concentrations on the Removals of COD_{dis} in OMI ww

OMI ww samples were oxygenated with increasing DO concentrations (2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l) with pure O_2 tubing before the sonication experiments. 62.71%, 71.22%, 74.83% and 79.86% COD_{dis} removals were obtained in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time, at pH=7.0 and at 30^{o}C (Figure 5.46a). Increasing sonication time and DO concentrations increased the COD_{dis} yields at 30^{o}C. 6.00-10.00 mg/l DO concentrations increased the COD_{dis} yields from 62.57% to 74.83% and to 79.86% after 150 min sonication time, respectively at pH=7.0 and at 30^{o}C, compared to the control (without DO at pH=7.0 and at 30^{o}C). Sonication alone provided 15.47%, 42.29% and 62.57% COD_{dis} yields after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^{o}C. A significant linear correlation between COD_{dis} yields and increasing DO concentrations was observed (R^2=0.94, F=17.37, p=0.01) (Figure 5.46a).

73.12%, 79.41%, 84.32% and 88.73% COD_{dis} yields were measured in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO after 150 min sonication times, respectively, at pH=7.0 and at 60^{o}C (Figure 5.46b). The COD_{dis} removals increased by 22.00-30.00% as the DO increased from 2.00 to 10.00 mg/l DO after 150 min sonication time at pH=7.0 and at 60^{o}C. Control reactor provided 17.77%, 46.81% and 66.83% COD_{dis} removals after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60^{o}C. 88.73% maximum COD_{dis} removals were obtained at a DO concentration of 10.00 mg/l after 150 min sonication time at pH=7.0 and at 60^{o}C as shown in Figure 5.46b. A significant linear correlation between COD_{dis} yields and increasing DO concentrations was observed (R^2=0.97, F=17.51, p=0.01).



(a)



(b)

Figure 5.46 Effect of increasing DO concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

It is clearly shown that the destruction of COD_{dis} increases significantly with an increase of O_2. This observation may be partially ascribed to the generation of $OH^{\bullet}$, resulted from dissociation of molecular O_2 in the bubble, which is likely to recombine to form H_2O_2 at the gas–liquid interface of the bubbles (Park et al., 2000) in Eqs. (5.24), (5.25) and (5.26):

$$O_2 \quad \rightarrow \quad 2O^{\bullet} \tag{5.24}$$

$$O^{\bullet} + H_2O \quad \rightarrow \quad 2HO^{\bullet} \tag{5.25}$$

$$2HO^{\bullet} \quad \rightarrow \quad H_2O_2 \tag{5.26}$$

O_2 present in the bubble (in gaseous form) and present in the medium (in dissolved or aqueous form as well as in the form of tiny bubbles suspended in the medium) can scavenge radicals inside the bubble as well as in the bulk medium in several ways. Dissociation of molecular O_2 in the bubble influences the formation of $OH^{\bullet}$ via Eqs. (5.27) and (5.28):

$$O_2 \quad \Leftrightarrow \quad 2O^{\bullet} \tag{5.27}$$

$$O^{\bullet} + H_2O \quad \Leftrightarrow \quad 2OH^{\bullet} \tag{5.28}$$

The O_2 in the bubble can also react with $H^{\bullet}$ formed out of H_2O dissociation to generate $OH^{\bullet}$ and $O_2H^{\bullet}$ via Eqs. (5.29), (5.30) and (5.31):

$$H_2O \quad \Leftrightarrow \quad H^{\bullet} + OH^{\bullet} \tag{5.29}$$

$$H^{\bullet} + O_2 \quad \Leftrightarrow \quad O^{\bullet} + OH^{\bullet} \tag{5.30}$$

$$H^{\bullet} + O_2 \quad \Leftrightarrow \quad O_2H^{\bullet} \tag{5.31}$$

Eqs. (5.30) and (5.31) can also occur in bulk liquid medium where DO can react with $H^\bullet$ released during transient bubble collapse. In addition to this, the DO in the medium can help revert the loss of oxidation potential due to recombination of $OH^\bullet$ released in the medium by generating $O_2H^\bullet$ species via Eqs. (5.32) and (5.33):

$$OH^\bullet + OH^\bullet \quad \Leftrightarrow \quad H_2O_2 \tag{5.32}$$

$$H_2O_2 + O_2 \quad \Leftrightarrow \quad 2O_2H^\bullet \tag{5.33}$$

Finally, the DO can also react with $OH^\bullet$ released in the medium to generate additional oxidizing species via Eq. (5.34):

$$OH^\bullet + O_2 \quad \Leftrightarrow \quad 2O_2H^\bullet + O^\bullet \tag{5.34}$$

The H_2O_2 measurement during acoustic cavitation, in absence and in the presence of OMI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the COD treatment by sonication in OMI ww decreases with increasing sonication time at 60°C (Table 5.47). In the absence of OMI ww (in deionized water) the H_2O_2 was accumulated and its concentration was measured as 185.00 mg/l while the H_2O_2 concentration increased to 98.00 and 145.00 mg/l after 30 and 120 min sonication times, whereas the H_2O_2 level was only 14.00 mg/l in OMI ww after 150 min sonication time in samples containing 10.00 mg/l DO (Table 5.7). The $OH^\bullet$ ion concentrations also increased from 10.00×10^{-62} to 43.00×10^{-7} mg/l after 150 min sonication time in OMI ww. This showed that hydroxylation is the main mechanism for the removal of COD_{dis}. In other words, $OH^\bullet$ is the major process for complete degradation of COD_{dis}. In this study, in OMI ww the most sonogenerated $OH^\bullet$ reacted with 87.00% maximum COD_{dis} removal and radical recombination to produce H_2O_2.

Table 5.47 Effect of DO=10.00 mg/l concentration on H_2O_2 and $OH^\bullet$ ion concentration in OMI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	185.00	0.00
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 30 min sonication	98.00	$10.00x10^{-62}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 120 min sonication	145.00	$2.00x10^{-52}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 150 min sonication	14.00	$43.00x10^{-7}$

In the study carried out Lafi et al. (2009) 28.90% COD_t removal efficiency was obtained with UV/O_3 process in OMI ww. Aerobic biodegradation followed by ozonation provided 80.00% COD removal in OMI ww at 50°C. In this study, 88.73% COD_{dis} yield was observed at 60°C after 150 min sonication time. In this study, the COD_{dis} removal is higher than the yield found by Lafi et al. (2009) at 50°C as mentioned above.

5.10.4.1 Effect of DO Concentrations on the Color Removal Efficiencies in OMI ww at Increasing Sonication Time and Temperature

80.16%, 84.07%, 86.27% and 87.47% color yields were observed in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO after 150 min sonication time, respectively, at pH=7.0 and at 30°C (Table 5.48). 2.00-10.00 mg/l DO concentrations increased the color yields from 42.59-68.84% to 54.81-78.06% after 60 and 120 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control (38.68%, 52.61% and 74.45% color removals after 60 min, 120 and 150 min sonication time, respectively, at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing DO concentrations was observed (R^2=0.91, F=19.12, p=0.01) (Table 5.48).

Table 5.48 Effect of increasing DO concentrations on the color removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times at pH=7.0 (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
DO=2.00 mg/l	42.59	54.81	80.16	70.84	75.85	86.87
DO=4.00 mg/l	52.00	77.66	84.07	73.75	79.86	89.58
DO=6.00 mg/l	62.42	78.96	86.27	74.75	79.96	91.38
DO=10.00 mg/l	68.84	83.07	87.47	80.86	84.17	93.79

86.87%, 89.58%, 91.38% and 93.79% color yields were found in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO after 150 min sonication time, respectively, at pH=7.0 and at 60°C (Table 5.48). 2.00-10.00 mg/l DO concentrations increased the color yields from 70.84-80.86% to 75.85-84.17% after 60 and 120 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control (44.59%, 69.74% and 83.77% color yield after 60 min, 120 and 150 min sonication times at pH=7.0 and at 60°C). The maximum color removal efficiency was 93.79% under DO=10.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing DO concentrations was observed (R^2=0.96, F=19.20, p=0.01) (Table 5.48).

Dissolved gas is an important factor that affects aqueous sonochemical processes and it acts as nucleation sites for cavitation (Nanzai et al., 2008). This may improve color removal in combination with ultrasonic irradiation. The efficiency of acoustic cavitation increased in the presence of DO since DO is strongly consumed inside the bubble when the bubble temperature at the bubble collapse is higher such as 60°C after 150 min sonication time. However, the presence of dissolved N_2 achieved less decolorization efficiency than that of DO. Thermal conductivities ($\gamma = C_p/C_v$) of the dissolved gases have been inversely correlated to the sonochemistry field. Though, the efficiency of acoustic cavitation under N_2 is almost equal to that under O_2 due to the little difference between their thermal conductivities, oxidants are strongly consumed inside a bubble by oxidizing N_2 when the bubble temperature at the bubble collapse is higher than about 7000°K. In addition, dissolved N_2 present in aqueous solution might scavenge the free radicals and inhibit $OH^{\bullet}$ oxidation of color (Mahamuni & Pandit, 2006).

5.10.4.2 Effect of DO Concentrations on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

77.20%, 80.04%, 82.92% and 88.02% total phenol removals were found in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time, at pH=7.0 and at 30°C (Table 5.49). 2.00-10.00 mg/l DO concentrations increased the total phenol yields from 28.26-56.00% to 43.46-43.98% and to 74.58-81.83% after 60 and 120 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control reactor (28.26%, 56.00% and 59.40% total phenol yields after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C). A significant linear correlation between total phenol yields and increasing DO concentrations was observed (R^2=0.92, F=18.11, p=0.01) (Table 5.49).

85.53%, 88.02%, 89.46% and 91.38% total phenol yields were found in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.49). 2.00-10.00 mg/l DO concentrations increased the total phenol yields from 30.20-57.94%, to 44.06-73.80% and to 79.25-84.66% and to 85.53-91.38% after 60, 120 min and 150 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control (30.20%, 57.94% and 61.24% total phenol yields after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C). The maximum total phenol removal efficiency was 91.38% at DO=10.00 mg/l after 150 min sonication time at 60°C. A significant linear correlation between total phenol yields and increasing DO concentrations was observed (R^2=0.90, F=19.68, p=0.01) (Table 5.49).

Table 5.49 Effect of increasing DO concentrations on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times at pH=7.0 (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
DO=2.00 mg/l	43.46	74.58	77.20	44.06	79.25	85.53
DO=4.00 mg/l	43.50	76.89	80.04	44.24	79.51	88.02
DO=6.00 mg/l	43.59	76.98	82.92	49.35	79.69	89.46
DO=10.00 mg/l	43.98	81.83	88.02	73.80	84.66	91.38

A number of studies have shown that ultrasonic treatment can result in successful sonodegradation of phenolic compounds (Entezari et al., 2003; Kotronarou et al., 1991; Okouchi et al., 1992; Pétrier & Francony, 1997; Serpone et al., 1992). In the presence of DO the total phenol were removed due to their interaction with $OH^\bullet$, produced during thermal base catalyzed decomposition of H_2O_2. This decomposition was more extended at higher temperatures such as 60°C.

Sonication at higher temperature caused higher total phenol removals as seen in Table 5.49. The highest efficiency of total phenol removal in the presence of ultrasound was found at high temperature. It was mentioned that the condensed tannins which are one of the phenolic constituents in OMI ww are polar compounds. Therefore, under sonication total phenol removal takes place in the solution bulk or at the bubble–liquid interface. This means that, during sonication, total phenol are removed by $OH^\bullet$ attack, produced from the H_2O_2 by low frequency ultrasound. The injection of H_2O_2 into the cavity and its cleavage into $OH^\bullet$ during the collapse of the cavitation bubble sono-degraded the phenol (Entezari et al., 2003) Usually high ambient temperatures (> 90°C) are not favorable for the majority of sonochemical reactions due to the decrease of dissolved gas and increase of vapor pressure (Suslick, 1989; Ince et al., 2001). Nevertheless, in our study the sonolytic reactions of H_2O_2 production from H_2O, was not affected negatively at a temperature as high as 60°C at low frequency (35 kHz).

O_2 present in the bubble (in gaseous form) and present in the medium (in dissolved or aqueous form as well as in the form of tiny bubbles suspended in the medium) can scavenge radicals inside the bubble as well as in the bulk medium in several ways. Dissociation of molecular O_2 in the bubble influences the formation of $OH^\bullet$ via Eqs. (5.35) and (5.36):

$$O_2 \quad \Leftrightarrow \quad 2O^\bullet \tag{5.35}$$

$$O^\bullet + H_2O \quad \Leftrightarrow \quad 2OH^\bullet \tag{5.36}$$

It should be noted that the second reaction could also occur in the bulk medium where $O^\bullet$ released in the medium with transient collapse of the bubble can react with water molecules to generate additional $OH^\bullet$. The O_2 in the bubble can also react with $H^\bullet$ formed out of water dissociation to generate $OH^\bullet$ and $O_2H^\bullet$ via Eqs. (5.37), (5.38) and (5.39):

$$H_2O \quad \Leftrightarrow \quad H^\bullet + OH^\bullet \tag{5.37}$$

$$H^\bullet + O_2 \quad \Leftrightarrow \quad O^\bullet + OH^\bullet \tag{5.38}$$

$$H^\bullet + O_2 \quad \Leftrightarrow \quad O_2H^\bullet \tag{5.39}$$

Table 5.50 shows the effect of 10.00 mg/l DO on H_2O_2 production, $OH^\bullet$ ion concentrations and phenol yields throughout phenol sonodegradation at 60°C. The $OH^\bullet$ ion concentrations increased from $4.00\text{x}10^{-56}$ to $10.00\text{x}10^{-6}$ mg/l after 150 min sonication time compared to the deionized water without OMI ww at pH=7.0. The H_2O_2 concentration in deionized water was high (156.00 mg/l) while it increased from 92.00 to 135.00 mg/l as the sonication time increased from 30 to 120 min in OMI ww. The high H_2O_2 production through sonication of OMI ww verified the presence of high $OH^\bullet$ ion concentrations and showed that the main removal mechanism of phenol was the hydroxylation. As the sonication time increased to 150 min the H_2O_2 production decreased to 11.00 mg/l by ending of sonication with a phenol yield of 93.00% at 10.00 mg/l DO concentration (Table 5.10).

Table 5.50 Effect of 10.00 mg/l DO concentration on H_2O_2 and $OH^\bullet$ ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	156.00	0.00
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 30 min sonication	92.00	$4.00x10^{-56}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 120 min sonication	135.00	$6.00x10^{-48}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 150 min sonication	11.00	$10.00x10^{-6}$

The degradation of phenol occurs in the bulk liquid medium due to hydroxylation reaction induced by $OH^\bullet$ generated from cavitation bubble. This is a consequence of low vapor pressure of phenol (due to which it does not evaporate into the cavitation bubble) and the hydrophilic nature of the phenol molecule. The interaction between radicals and phenol molecules becomes an important factor influencing the overall degradation. The scavenging phenomenon increases the sonodegradation of phenol. Moreover, the concentration of the radical scavenging species is another important factor affecting the degradation. The formation of $OH^\bullet$ and H_2 derived from sonolysis of H_2O in aqueous solution saturated with O_2 as an endpoint of inertial cavitation was examined.

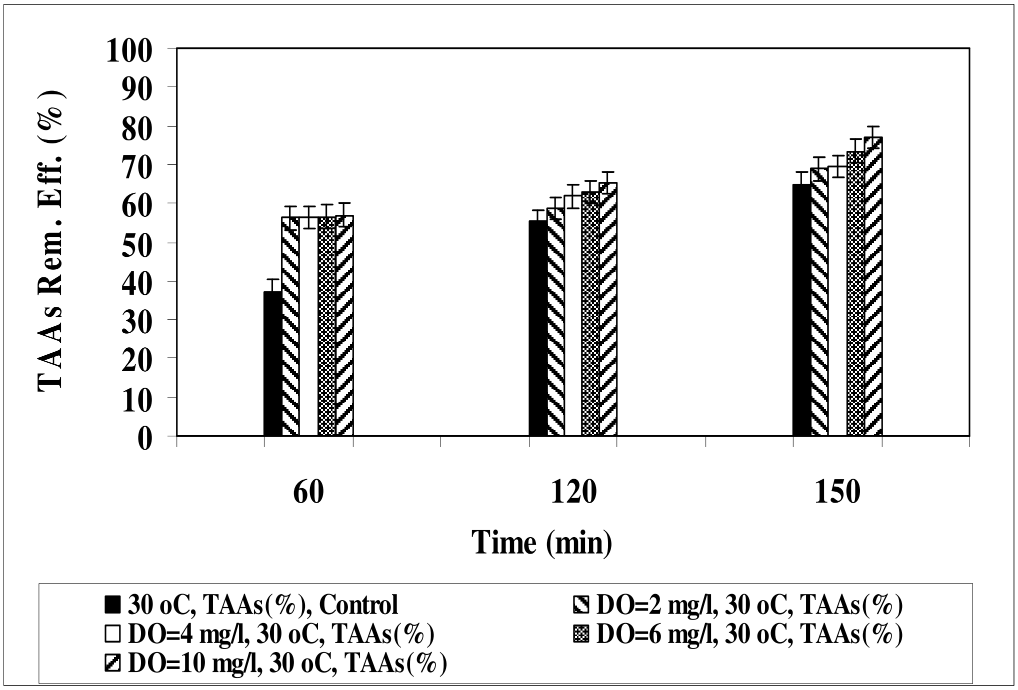
It should be pointed out that $OH^\bullet$, formed via H_2O sonolysis, can partly recombine yielding H_2O_2 which in turn reacts with H_2 to regenerate $OH^\bullet$ in Eqs. (5.40) and (5.41):

$$OH^\bullet + OH^\bullet \quad \Leftrightarrow \quad H_2O_2 \tag{5.40}$$

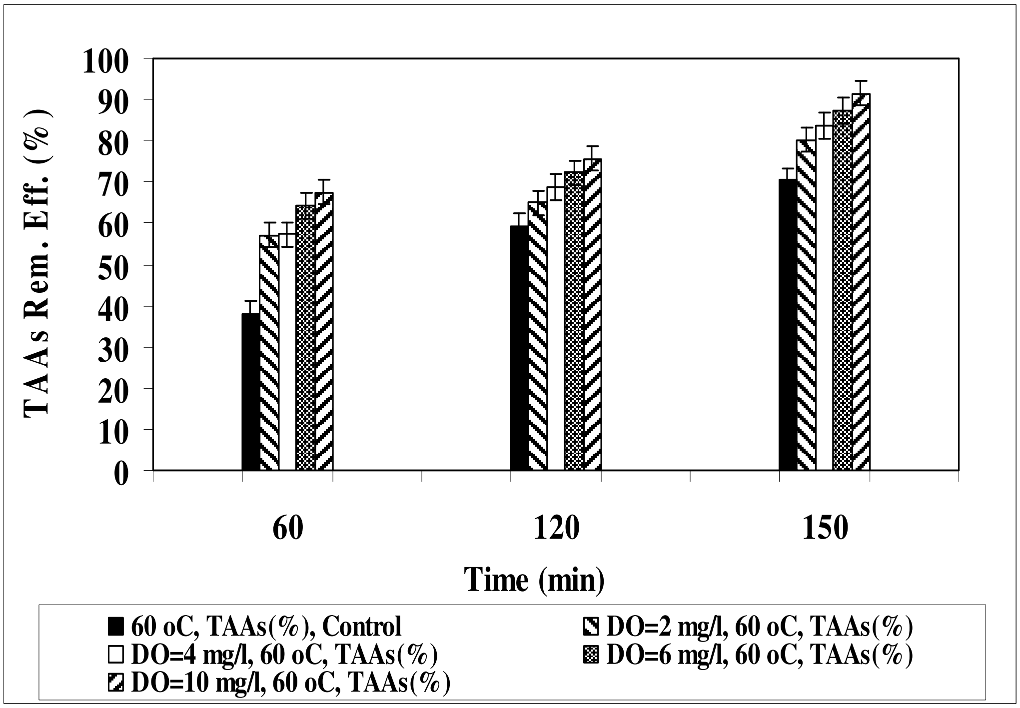
$$H_2O_2 + H^\bullet \quad \rightarrow \quad H_2O + OH^\bullet \tag{5.41}$$

5.10.4.3 Effect of DO Concentrations on the TAAs Removal Efficienciesin OMI ww at Increasing Sonication Times and Temperatures

68.91%, 69.45%, 73.37% and 77.00% TAAs removals were found in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.47a). 19.05-19.77% and 3.34-9.88% increase in TAAs removals were measured after 60 and 120 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control (37.19%, 55.34% and 64.98% TAAs yields after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing DO concentrations was not observed (R^2=0.30, F=2.08, p=0.01) (Figure 5.47a).



(a)



(b)

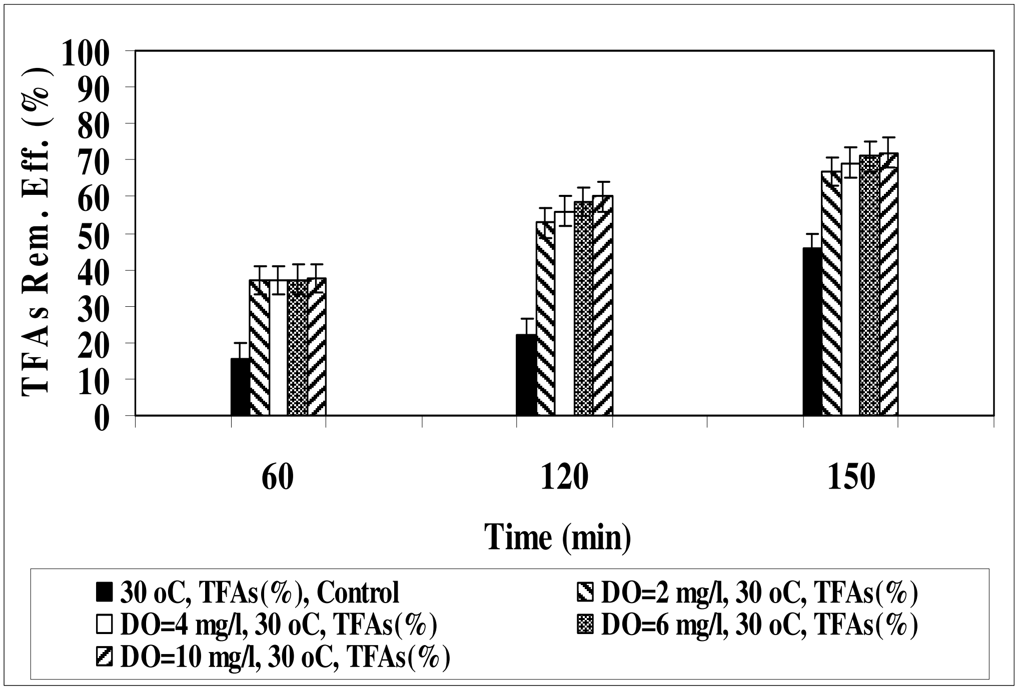
Figure 5.47 Effect of increasing DO concentrations on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

80.28%, 83.67%, 87.30% and 91.58% TAAs yields were measured in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 60^oC (Figure 5.47b). The contribution of increasing DO to the TAAs removals were 18.93-29.47% and 5.66-16.37% after 60 and 120 min sonication times, respectively, at pH=7.0 and at 60^oC, compared to the control (38.14%, 59.39% and 70.52% TAAs removals after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60^oC). The maximum TAAs removal efficiency was 91.58% in DO=10.00 mg/l after 150 min sonication time at pH=7.0 and at 60^oC. A significant linear correlation between TAAs yields and increasing DO concentrations was observed (R^2=0.82, F=16.71, p=0.01) (Figure 5.47b).

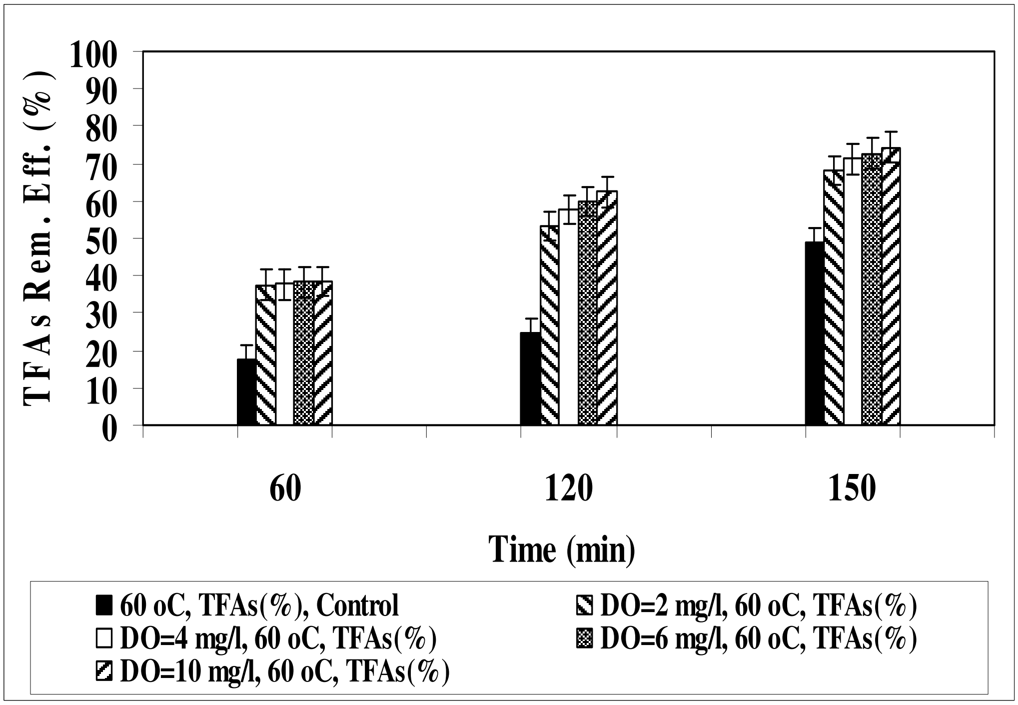
At longer sonication times and temperatures it was reached high TAAs removals. The high TAAs yields could be attributed to the higher mass transfer and higher surface area produced by the cavitation process (Entezari et al., 2007).

5.10.4.4 Effect of DO Concentrations on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

66.98%, 69.21%, 71.03% and 72.03% TFAs removals were obtained in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^oC (Figure 5.48a). 21.48-21.94% and 30.45-37.70% increase in TFAs yields were measured in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 60 and 120 min sonication times at pH=7.0 and at 30^oC, compared to the control (15.62%, 22.37% and 45.66% TFAs removals after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30^oC). A significant linear correlation between TFAs yields and increasing DO concentrations was observed (R^2=0.87, F=17.65, p=0.01) (Figure 5.48a).



(a)



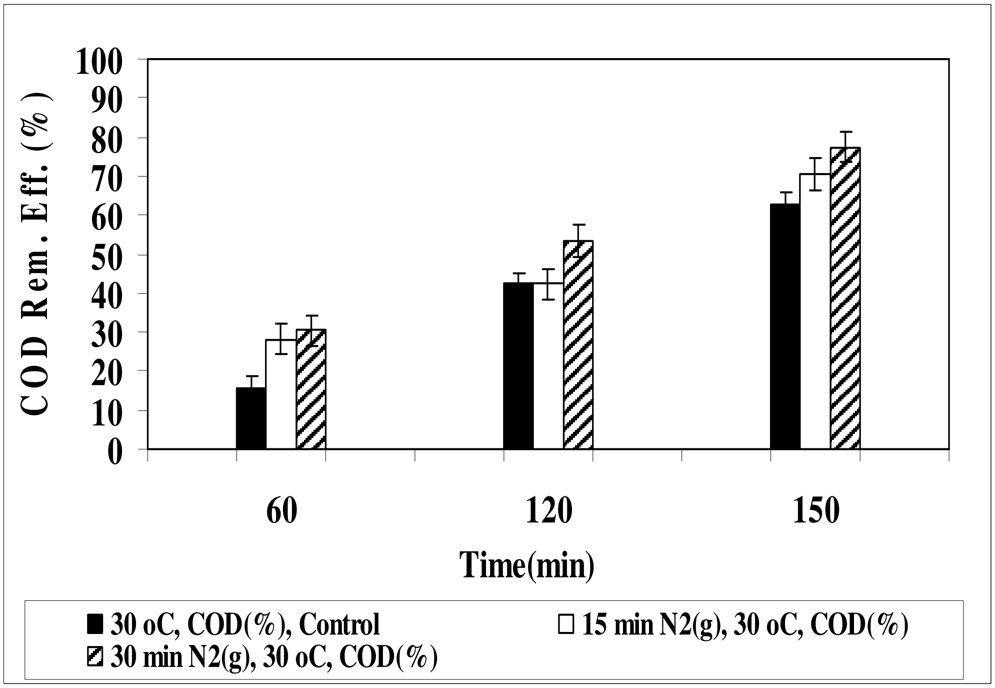
(b)

Figure 5.48 Effect of increasing DO concentrations on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

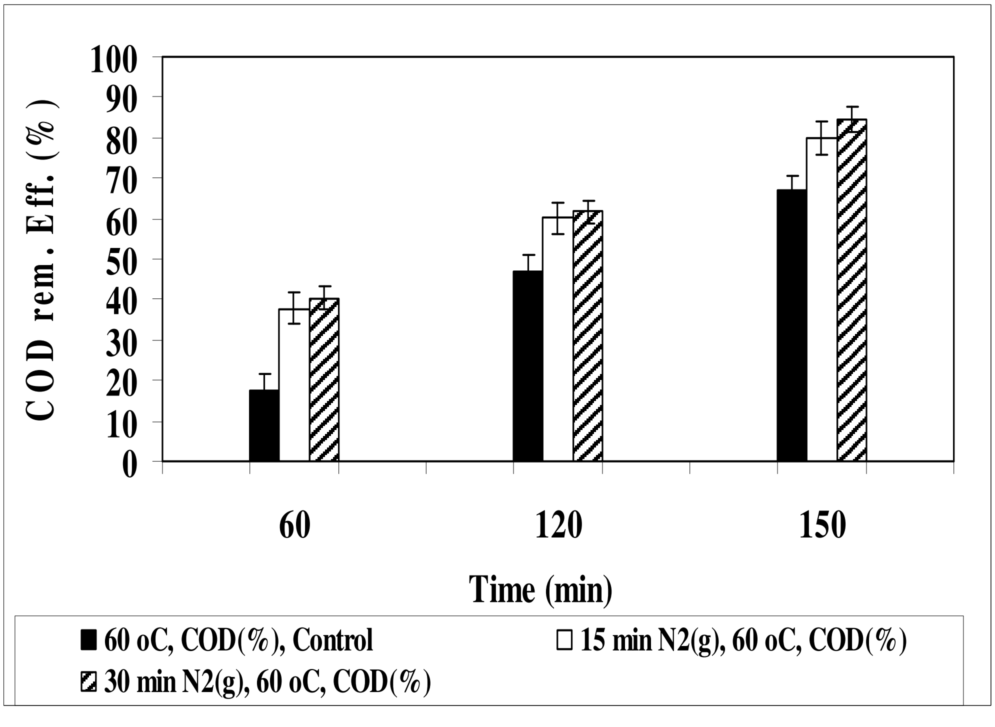
68.19%, 71.18%, 72.74% and 74.44% TFAs yields were found in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.48b). The contribution of increasing DO concentrations (from 2.00 to 10.00 mg/l) in TFAs removals were found as 22.01-22.76% and 28.46-37.64% after 60 and 120 min sonication times, respectively, at pH=7.0 and at 60°C compared to the control reactor (17.33%, 24.77% and 48.84% TFAs yields after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C). The maximum TFAs removal efficiency was 74.44% in DO=10.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TFAs yields and increasing DO concentrations was observed (R^2=0.89, F=17.96, p=0.01) (Figure 5.48b).

5.10.5 Effect of N_2(g) on the Removals of COD_{dis} in OMI ww

Pure N_2(g) was sparged in OMI ww before sonication experiments. 28.21%, 42.29% and 70.56% COD_{dis} removals were obtained after 60 min, 120 and 150 min sonication times, respectively, under 15 min N_2(g) (3.00 mg/l N_2) sparging at pH=7.0 and at 30°C (Figure 5.49a). 30.39%, 53.46% and 77.36% COD_{dis} removals were measured under 30 min N_2(g) (6.00 mg/l N_2) sparging after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C. 30 min N_2(g) (6.00 mg/l N_2) sparging increased the COD_{dis} yields from 42.29% to 53.46% after 120 min sonication time at 30°C, compared to the control [without N_2(g) sparging while E=62.57% COD_{dis} at pH=7.0 after 150 min sonication time at pH=7.0 and at 30°C]. A significant linear correlation between COD_{dis} yields and increasing N_2(g) sparging was not observed (R^2=0.42, F=16.34, p=0.01) (Figure 5.49a).



(a)



(b)

Figure 5.49 Effect of increasing N_2(g) sparging on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

37.81%, 60.09% and 79.89% COD_{dis} removals were obtained after 60 min, 120 and 150 min sonication times, respectively, under 15 min $N_2(g)$ (3.00 mg/l N_2) sparging at pH=7.0 and at 60^{o}C (Figure 5.49b). 40.44%, 61.62% and 84.51% COD_{dis} yields were obtained under 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60^{o}C. No significant differences in COD_{dis} yields was obtained under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging after 120 and 150 min sonication times at 60^{o}C. The contribution of the $N_2(g)$ sparging on the COD_{dis} removal efficiency varied between 13.28% and 14.81% under 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 120 min sonication time at 60^{o}C compared to the control (E=66.83% COD_{dis} after 150 min sonication time at pH=7.0 and at 60^{o}C). The maximum COD_{dis} removal efficiency was 84.51% under 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at 60^{o}C. A significant linear correlation between COD_{dis} yields and increasing $N_2(g)$ sparging was observed (R^2=0.85, F=18.62, p=0.01) (Figure 5.49b).

The predominant $N_2(g)$ species produced through sonication are no followed by N_2O, NO_2, HNO and HNO_2. $N_2(g)$ present in the air bubble scavenges $H^\bullet$, $OH^\bullet$ and $O^\bullet$ produced by the dissociation of entrapped water vapor through various reactions. Lindsey & Tarr (2000b) determined a few representative reactions are given in Eqs. (5.42), (5.43), (5.44), (5.45), (5.46) and (5.47):

$$N_2 + O^\bullet \Leftrightarrow N^\bullet + NO \qquad (5.42)$$

$$N_2 + OH^\bullet \Leftrightarrow N_2H + O^\bullet \qquad (5.43)$$

$$N_2 + OH^\bullet \Leftrightarrow N_2O + H^\bullet \qquad (5.44)$$

$$N_2 + OH^\bullet \Leftrightarrow NH + NO \qquad (5.45)$$

$$N_2 + H^\bullet \Leftrightarrow N_2H \qquad (5.46)$$

$$N_2 + H^\bullet \Leftrightarrow NH + N^\bullet \qquad (5.47)$$

The $N_2(g)$ species produced with the reactions given above also scavenge the radicals through various reactions. Some representative reactions are given in Eqs. (5.48), (5.49), (5.50), (5.51), (5.52), (5.53), (5.54) and (5.55) by Lindsey & Tarr (2000):

$$N + OH^\bullet \Leftrightarrow NO + H^\bullet \qquad (5.48)$$

$$N_2O + O^\bullet \Leftrightarrow 2NO \qquad (5.49)$$

$$NO + O^\bullet \Leftrightarrow NO_2 \qquad (5.50)$$

$$NH + OH^\bullet \Leftrightarrow NH_2 + O^\bullet \qquad (5.51)$$

$$NH_2 + O^\bullet \Leftrightarrow H^\bullet + HNO \qquad (5.52)$$

$$HNO + O^\bullet \Leftrightarrow NH + O_2 \qquad (5.53)$$

$$HNO + O^\bullet \Leftrightarrow NO + OH^\bullet \qquad (5.54)$$

$$HNO + OH^\bullet \Leftrightarrow NO + H_2O \qquad (5.55)$$

It needs to be specifically mentioned that Eqs. (5.42), (5.43), (5.44), (5.45), (5.46), (5.47), (5.48), (5.49), (5.50), (5.51), (5.52), (5.53), (5.54) and (5.55) also occur in the bulk liquid medium due to the reaction of dissolved N_2 with various radicals released into the bulk medium with collapse of cavitation bubble. However, the O_2 present in the bubble reacts concurrently with $N_2(g)$ species to regenerate $O^\bullet$ and $OH^\bullet$ through the following reactions given in Eqs. (5.56), (5.57), (5.58), (5.59) and (5.60) in the presence of DO:

$$N + O_2 \Leftrightarrow NO + O^{\bullet} \qquad (5.56)$$

$$NO + O_2 \Leftrightarrow NO_2 + O^{\bullet} \qquad (5.57)$$

$$NH + O_2 \Leftrightarrow HNO + O^{\bullet} \qquad (5.58)$$

$$NH + O_2 \Leftrightarrow NO + OH^{\bullet} \qquad (5.59)$$

$$N_2 + O_2 \Leftrightarrow N_2O + O^{\bullet} \qquad (5.60)$$

5.10.5.1 Effect of $N_2(g)$ on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

82.36% and 89.28% color removals were obtained under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.51). 37.47-38.88% and 25.05-30.56% increase in color removals were observed under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 60 and 120 min sonication times at pH=7.0 and at 30°C, compared to the control (E=74.45% color after 150 min sonication time at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing $N_2(g)$ sparging was observed (R^2=0.74, F=15.78, p=0.01) (Table 5.51).

85.87% and 91.88% color yields were measured under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.51). The contribution of $N_2(g)$ sparging to the color yield were 33.47-34.67% and 10.62-16.03% under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 60 and 120 min sonication times at pH=7.0 and at 60°C compared to the control (E=83.77% color yield after 150 min sonication time at pH=7.0 and at 60°C). The maximum color removal efficiency was 91.88% under 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at pH=7.0 and at

60°C. A significant linear correlation between color yields and increasing $N_2(g)$ sparging was observed ($R^2=0.83$, F=16.32, p=0.01) (Table 5.51).

Table 5.51 Effect of increasing DO concentrations on the color removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
15 min $N_2(g)$ (3.00 mg/l N_2)	76.15	77.66	82.36	78.06	80.36	85.87
30 min $N_2(g)$ (6.00 mg/l N_2)	77.56	83.17	89.28	79.26	85.77	91.88

The mechanism affecting the yield of color removals through sonication was explained as follows: $N_2(g)$ sparging changed the temperature within the cavitation site and the variations of chemical properties of the system resulting in high color removals at low temperature such as 30°C and 60°C (Minero et al., 2008). Gases with lower thermal conductivity (18.40 mW/mol.K) values such as $N_2(g)$ increased the temperature up to 90°C inside the cavitation bubble upon collapse because they allowed less heat to the surroundings such as 37°C. The ratio of specific heat plays a role in determining the maximum size of the cavitation bubble. The greater the ratio, the greater the radius of the bubble before collapse. Significant changes in the cavitation process, due to changes in the chemical properties of OMI ww occurred due to sparging with $N_2(g)$. The decolorization phenomenon in $N_2(g)$ sparged systems suggests that an O_2 dependent, $OH^\bullet$ pathway also exists. This pathway is most likely hydroxylation occurring in the gas-liquid phase (Dewulf et al., 2001). The color removal yields reached in this study was higher than that found by Svitelska et al. (2004) under similar operational and sonicational conditions. They observed 80.00% color removal efficiency for initial 75.30 m^{-1} color level at a power of 250 W and a frequency of 24 kHz under 25 min $N_2(g)$ (5.00 mg/l N_2) sparging at 60°C temperature after 150 min sonication time. In the present study, 91.88% color removal was observed under 30 min $N_2(g)$ (6.00 mg/l N_2) sparging at 60°C after 150 min sonication time. This color yield is higher than the yield obtained by Svitelska et al. (2004) at 60°C as mentioned above.

5.10.5.2 Effect of $N_2(g)$ on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

71.16% and 73.99% total phenol removals were found under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.52). 11.37-12.37% and 11.27-11.78% increase in total phenol yields were measured under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 60 and 120 min sonication times at pH=7.0 and at 30°C, compared to the control (E=59.40% total phenol yield after 150 min sonication time at pH=7.0 and at 30°C). A significant linear correlation between total phenol yields and increasing $N_2(g)$ sparging was not observed (R^2=0.42, F=3.78, p=0.01) (Table 5.52).

74.91% and 78.98% total phenol yields were measured under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.52). The contribution of increasing $N_2(g)$ sparging were 10.73-11.17% and 9.51-10.27% in total phenol removals under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 60 and 120 min sonication times at pH=7.0 and at 60°C, compared to the control (E=61.24% total phenol after 150 min sonication time at pH=7.0 and at 60°C). The maximum total phenol removal efficiency was 78.98% under 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between total phenol yields and increasing $N_2(g)$ sparging was not observed (R^2=0.36, F=2.71, p=0.01) (Table 5.52).

Table 5.52 Effect of increasing N_2(g) sparging on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial Total Phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
15 min N_2(g) (3.00 mg/l N_2)	39.63	67.27	71.16	40.93	67.45	74.91
30 min N_2(g) (6.00 mg/l N_2)	40.63	67.78	73.99	41.37	68.21	78.98

Berlan et al. (1994) observed that high dissolved N_2 concentrations present in the solution degassed the medium after an initial period of sonication resulting in a decrease in the amount $OH^\bullet$ generated. Kidak & Ince (2006) found higher phenol yields in the presence of air than that of N_2(g) at pH=7.0, at a frequency of 35 kHz after 150 min sonication at 60°C. Larger phenol yields in the presence of air despite its lower polytrophic gas ratio is due to the reactions of N_2 with molecular O_2 to yield HNO_3 and radical species such as $OH^\bullet$, $^\bullet NO_2$, and $^\bullet NO_3$ accelerate the oxidation process.

5.10.5.2.1 Effect of pH on the Removal of Phenol Removal Efficiencies in OMI ww in the Presence of 30 min N_2(g) (6.00 mg/l N_2) Sparging after 150 min Sonication at 60°C

In aqueous solutions of phenol the degree of ionization from molecular state to the phenolate ion increases as pH is raised, and at pH > pK_a (=10.0) phenolate ion is the major species, which due to repulsive forces are unable to approach the negatively charged cavity bubbles or even the bubble–liquid interface, where uncombined $OH^\bullet$ concentration is at a maximum. As pH is lowered and the fraction of molecular phenol increases, the probability of solutes approaching the interfacial area also increases, resulting in enhanced rates of phenol removal as reported by Mahamuni & Pandit (2006). In this study, phenol removals versus pH is demonstrated in Table 5.53 at there different pH at 60°C after 150 min sonication time. As shown in this Table the maximum phenol removal was obtained at a pH=4.0. The phenol yields in pH=7.0 and pH=10.0 followed this yield with phenol removals of 79.00%, 69.00% and 60.00%, respectively.

Table 5.53 Total phenol removal efficiencies at different pH values after 150 min sonication time at 60°C in the presence of 30 min $N_2(g)$ (6.00 mg/l N_2) sparging (sonication power=640 W, sonication frequency=35 kHz, initial Total Phenol concentration=4500 mg/l, n=3, mean values).

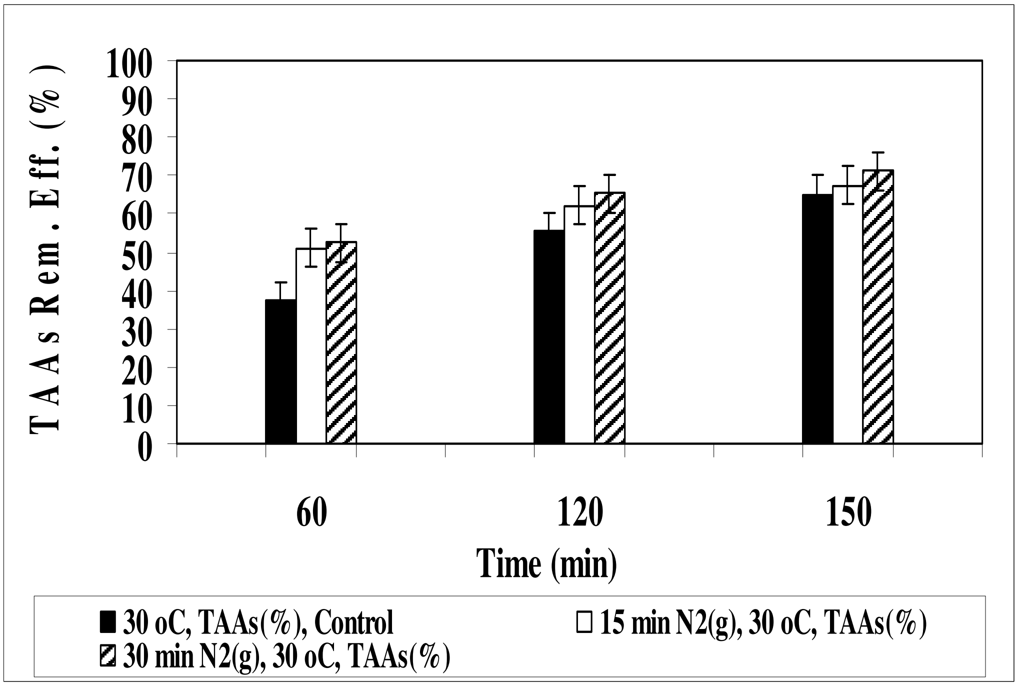
pH	Initial Phenol Conc. (mg/l)	Phenol Conc. (mg/l) after 150 min sonication	Phenol Rem. Eff. (%)
4.0	4500	945	79.00
7.0	4500	1395	69.00
10.0	4500	1800	60.00

During sonication low decrease of total phenol concentrations in the effluent samples results in the formation of a complex H-bonding network between the phenolic compounds at short sonication times (20-60 min). It is well known that molecules containing COOH or CHO groups exist as dimers in solution due to the formation of H-bonds between two neighboring molecules. This results in a more robust and stable configuration and leading to the reduced degradation. In addition to this, the formation of such a network may impede their diffusion towards the bubble interface and this would also lead to reduced degradation of phenols (Kallel et al., 2009a). In general, hydrophobic and volatile organics tend to partition into the bubbles and degrade mainly by direct thermal decomposition leading to the formation of combustion by-products.

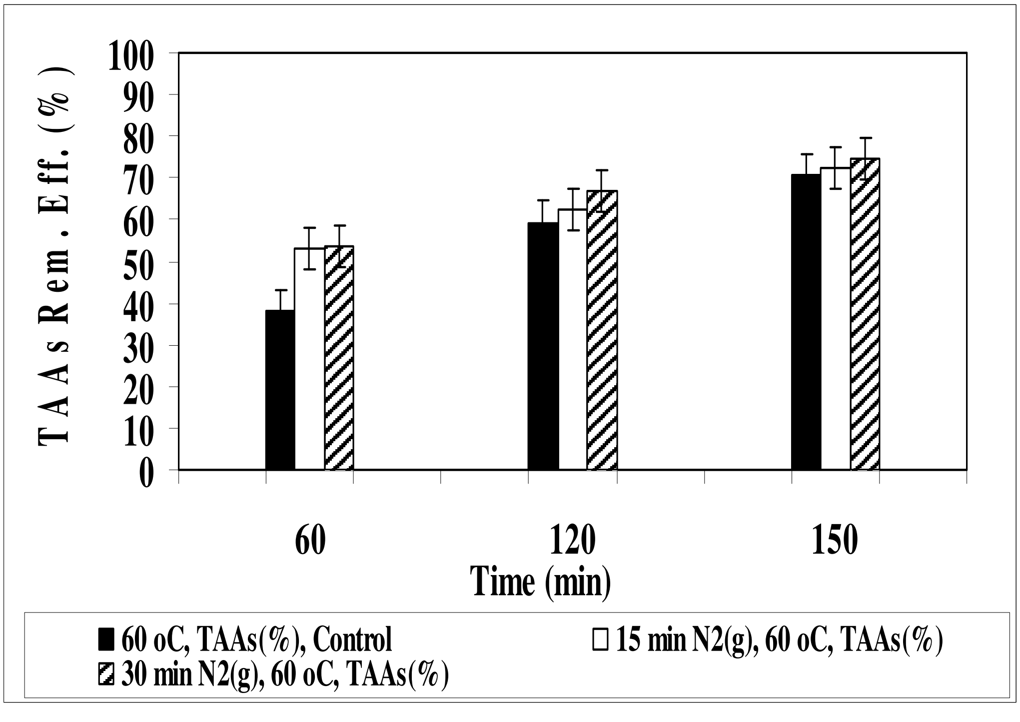
5.10.5.3 Effect of $N_2(g)$ on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

67.43% and 71.18% TAAs removals were observed under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.50a). The contribution of 15 and 30 min $N_2(g)$ (3 and 6 mg/l N_2) sparging was found as 13.83-15.26% and 6.74-10.07% to the TAAs yields, respectively, after 60 and 120 min sonication times at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C. The contribution of 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging are not significant to the TAAs yields since sonication alone provided 64.98% TAAs removal efficiencies after 150 min sonication time at pH=7.0 and at 30°C. A significant linear correlation between TAAs yields and increasing $N_2(g)$ sparging was not observed ($R^2=0.30$, F=2.64, p=0.01) (Figure 5.50a).

72.43% and 74.56% TAAs yields were found under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging after 150 min sonication time, respectively, at pH=7.0 and at 60°C (Figure 5.50b). 14.66-15.26% and 3.28-7.39% increase in TAAs removals were measured under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 60 and 120 min sonication times, compared to the control at pH=7.0 and at 60°C. An increase of 1.00-4.00% in TAAs removal was observed under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time, compared to the control (E=70.52% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 74.56% under 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing $N_2(g)$ sparging was not observed ($R^2=0.33$, F=2.41, p=0.01) (Figure 5.50b).



(a)



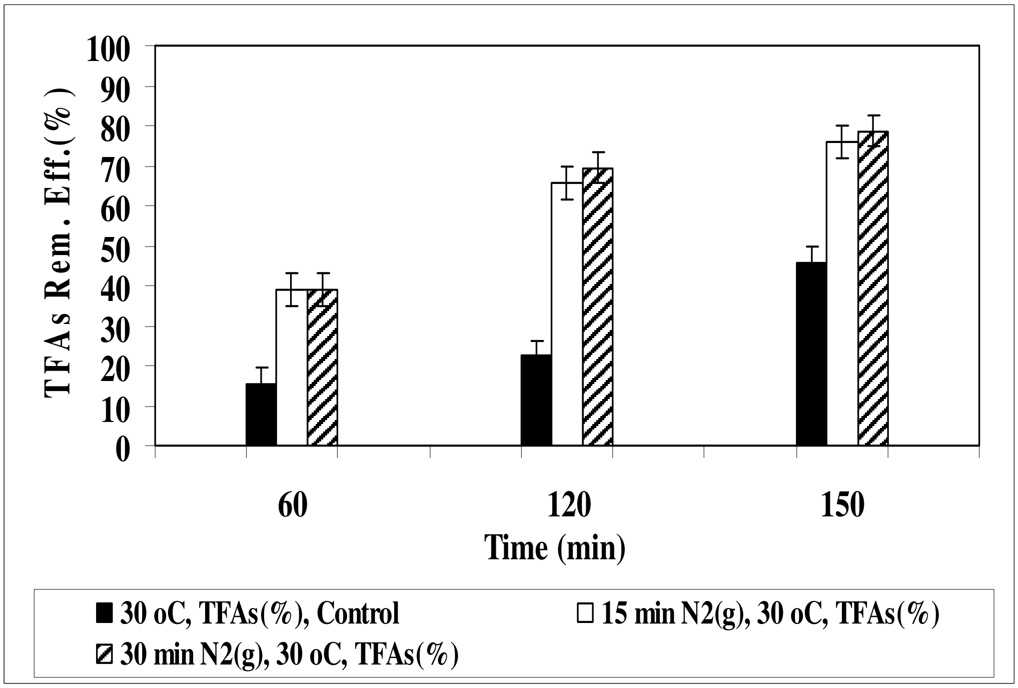
(b)

Figure 5.50 Effect of increasing N_2(g) sparging on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

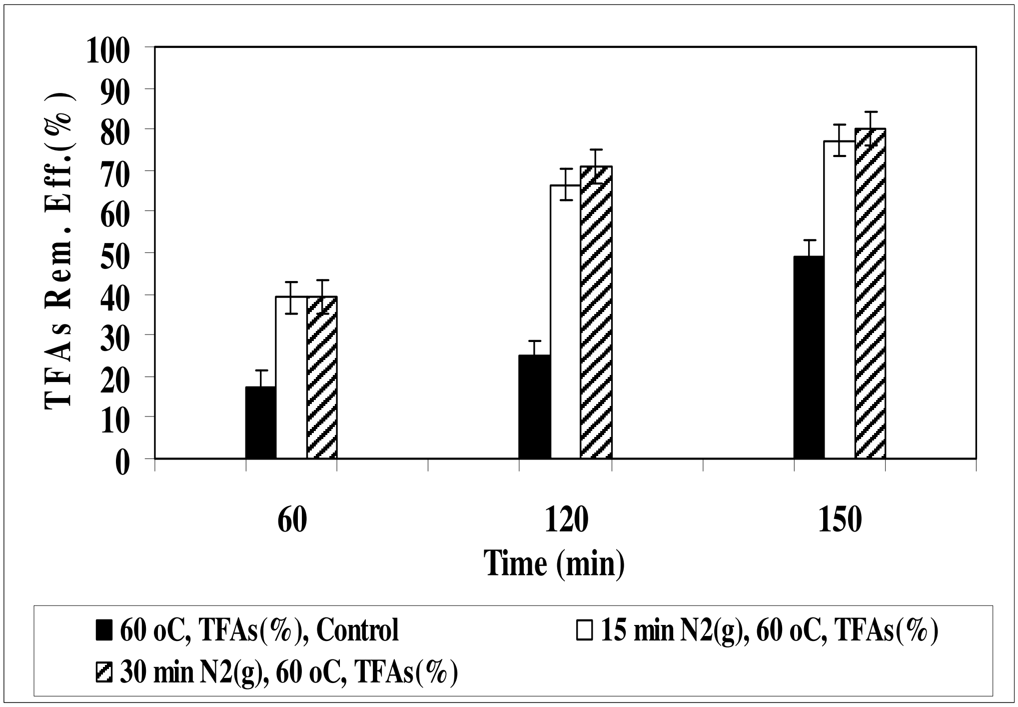
The recent literature showed that the sonochemical degradation of aromatic amines namely, 4,4–oxydianiline and aniline predominantly occurs via OH$^{\bullet}$ attack; although, a thermal reaction occurring in the vicinity of the bubble cannot be taken into consideration (Cardoso et al., 2010).

5.10.5.4 Effect of $N_2(g)$ on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

76.05% and 78.62% TFAs removals were observed under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.51a). The contribution of $N_2(g)$ sparging on the TFAs removals were 23.28-23.30% and 43.42-47.09% under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 60 and 120 min sonication times at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C. The contribution of 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging on the TFAs removals were significant ($R^2=0.78$, F=17.09, p=0.01). TFAs yields were increased from 45.66% to 76.05% and to 78.62% with 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at 30°C, compared to the control (E=45.66% TFAs at pH=7.0 and at 30°C). A significant linear correlation between TFAs yields and increasing $N_2(g)$ sparging was observed ($R^2=0.85$, F=16.63, p=0.01) (Figure 5.51a).



(a)



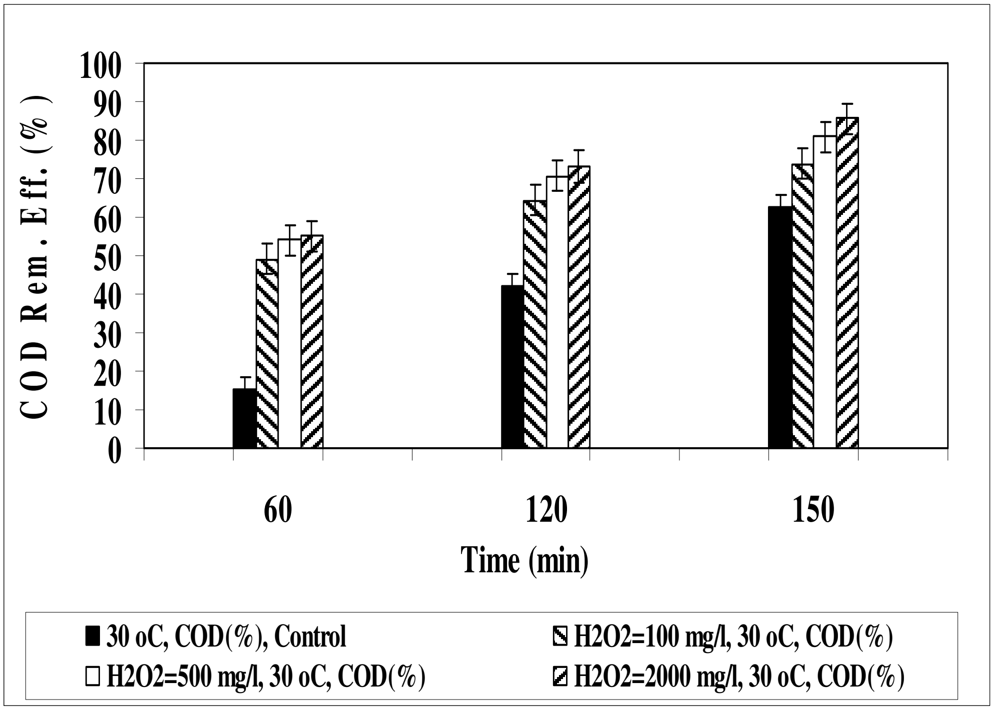
(b)

Figure 5.51 Effect of increasing N_2(g) sparging on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

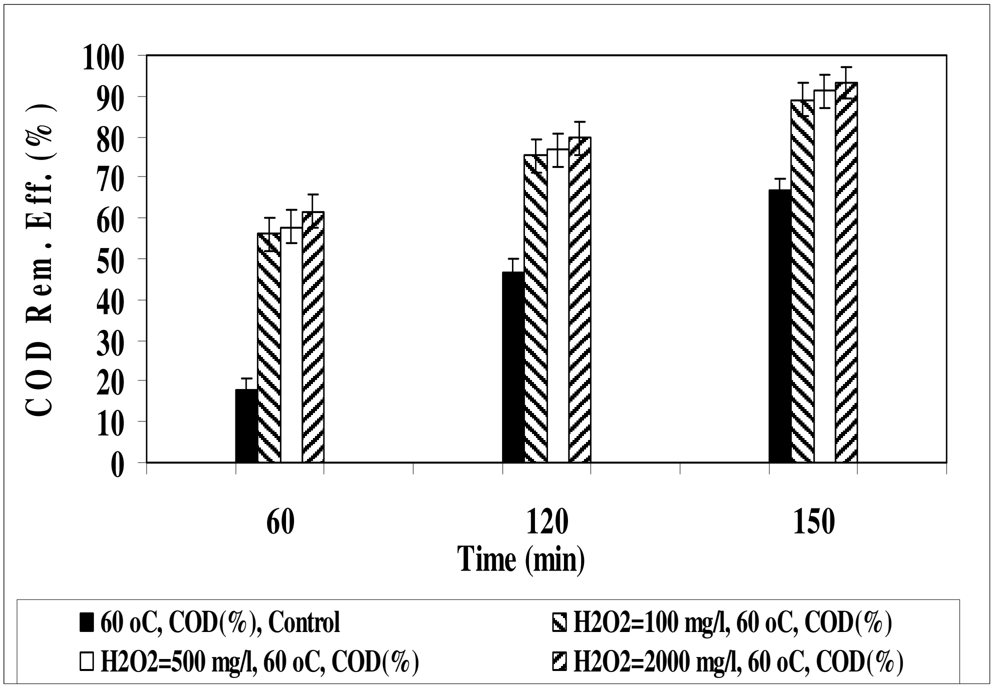
77.22% and 80.18% TFAs yields were obtained under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.51b). 21.77-21.96% and 41.73-46.09% increase in TFAs yields were found under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 60 and 120 min sonication times at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 60°C. The contribution of 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging on the TFAs removals were significant (R^2=0.76, F=17.89, p=0.01). TFAs removals increased from 48.84% to 77.22% and to 80.18% with 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=48.84% TFAs at pH=7.0 and at 60°C). The maximum TFAs removal efficiency was 80.18% under 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TFAs yields and increasing $N_2(g)$ sparging was observed (R^2=0.87, F=16.63, p=0.01) (Figure 5.51b).

5.10.6 Effect of H_2O_2 Concentrations on the Removals of COD_{dis} in OMI ww

Increasing H_2O_2 concentrations (100 - 500 and 2000 mg/l) were added in OMI ww before sonication process. 73.87%, 80.80% and 85.61% COD_{dis} removals were obtained in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.52a). 33.69-39.67% and 22.05-30.86% increase in COD_{dis} removals were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 60 and 120 min sonication times at pH=7.0 and at 30°C, compared to the control (without H_2O_2 at pH=7.0 and at 30°C). Control reactor provided 62.57% COD_{dis} yield after 150 min sonication time at pH=7.0 and at 30°C. The contribution of increasing H_2O_2 concentrations on the COD_{dis} removal were significant (R^2=0.89, F=19.09, p=0.01) (Figure 5.52a).



(a)



(b)

Figure 5.52 Effect of increasing H_2O_2 concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

89.09%, 91.13% and 93.19% COD_{dis} yields were measured in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60^oC (Figure 5.52b). The contribution of increasing H_2O_2 concentrations were found as 38.34-44.00% and 28.58-32.77% on the COD_{dis} removals in 100, 500 and 2000 mg/l H_2O_2, respectively, after 60 and 120 min sonication times at pH=7.0 and at 60^oC, compared to the control at pH=7.0 and at 60^oC. The contribution of increasing H_2O_2 concentrations on the COD_{dis} yield were significant (R^2=0.79, F=19.98, p=0.01). Sonication alone provided 66.83% COD_{dis} yield after 150 min sonication time at pH=7.0 and at 60^oC. The maximum COD_{dis} removal efficiency was 93.19% in H_2O_2=2000 mg/l after 150 min sonication time at pH=7.0 and at 60^oC. A significant linear correlation between COD_{dis} yields and increasing H_2O_2 concentrations was not observed (R^2=0.65, F=3.32, p=0.01) (Figure 5.52b).

In this study, it was found that the COD_{dis} removal increased with H_2O_2 concentration and reached the maximum 93.19% by using 2000 mg/l H_2O_2. From this, we can evaluate that 0.02 mg/l of H_2O_2 was needed to the removal of 1.00 mg/l of COD with a COD_{dis} yield of 91.37% after 150 min sonication time. Sivasankar & Moholkar (2009) estimated that the removal of 1.00 g of COD needs 2.04 g of H_2O_2. In this optimized condition, the maximum value of COD removal is at the level of 93.00% with H_2O_2 oxidation (Sivasankar & Moholkar 2009). In this study, it is clear that 2000 mg/l of H_2O_2 is the optimum amount to obtain maximum decrease (93.19%) in COD_{dis} from OMI ww after 150 min sonication time at 60^oC.

Organic compounds may be degraded either at the first two sites upon combined effects of pyrolytic decomposition and hydroxylation or in the solution bulk via oxidative degradation by H_2O_2 in OMI ww (Entezari et al., 2003). Under ultrasound irradiation, water is pyrolyzed, in which process $H^\bullet$, $OH^\bullet$, $O^\bullet$ and $O_2H^\bullet$ are produced and then react with organic pollutants measured as COD in the bulk solution or at the interface between the bubbles and the liquid phase (Goel et al., 2004). During aqueous ultrasound irradiation, $OH^\bullet$ forms during the thermolytic reactions of H_2O and self-recombine to form H_2O_2. This showed that the sono-degradation of COD_{dis} in OMI ww occurred via hydroxylation.

In a study performed by Kallel et al. (2009a) a COD removal of 78.00% was found by sonication at a power of 650 W and at a frequency of 35 kHz in OMI ww. In this study, it was found that for the sono-degradation of 1.00 g COD 0.06 M of H_2O_2 is needed. In this study, 93.19% COD_{dis} removal was observed for 2000 mg/l H_2O_2 concentration at 60°C after 150 min sonication time. In the present study the COD_{dis} yield is higher than the yield obtained by Kallel et al. (2009a) at 60°C.

5.10.6.1 Effect of H_2O_2 Concentrations on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

81.96%, 86.07% and 89.88% color removals were observed at 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.54). The contribution of 100 mg/l, 500 and 2000 mg/l H_2O_2 concentrations to the color removals were 11.82-33.56% and 19.73-30.06% after 60 and 120 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C. The contribution of increasing H_2O_2 concentrations on the color yields were found to be significant (R^2=0.76, F=15.09, p=0.01). Sonication alone provided 74.45% color removal after 150 min sonication time at pH=7.0 and at 30°C. A significant linear correlation between color yields and increasing H_2O_2 concentrations was observed (R^2=0.81, F=14.78, p=0.01) (Table 5.54).

Table 5.54 Effect of increasing H_2O_2 concentrations on the color removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
H_2O_2=100 mg/l	50.50	72.34	81.96	63.93	77.25	90.58
H_2O_2=500 mg/l	65.43	77.05	86.07	69.74	80.26	92.48
H_2O_2=2000 mg/l	72.24	82.67	89.88	73.35	86.67	93.59

90.58%, 92.48% and 93.59% color yields were measured in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.54). 19.34-28.76% and 7.51-16.93% increase in color yields were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 60 and 120 min sonication times at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 60°C. Control provided 83.77% color removal after 150 min sonication time at pH=7.0 and at 60°C. The maximum color removal efficiency was 93.59% in H_2O_2=2000 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing H_2O_2 concentrations was observed (R^2=0.83, F=15.98, p=0.01) (Table 5.54).

A non-volatile organic substance is mainly eliminated by $OH^\bullet$ outside the cavitation bubble: a hydrophobic compound at the bubble-solution interface, while hydrophilic substrates into the bulk solution. Tannins and lignins are non-volatile compounds given color in OMI ww. Therefore, these organics cannot enter inside the bubble. Additionally, the positive charge of the nitrogen atoms of the amine groups exhibiting hydrophilic properties to the benzene molecules which are giving the color to the OMI ww. As a consequence, under ultrasonic action, the removal of color must mainly occur through the reaction with $OH^\bullet$ in the bulk solution (Guzman-Duque et al., 2011).

Table 5.55 shows the effect of 2000 mg/l H_2O_2 addition on H_2O_2 and $OH^\bullet$ ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min sonication times throughout color removal in OMI ww. The H_2O_2 concentration increased to 2135.00 mg/l and accumulated in deionized water. This level increased to 2196.00 mg/l after 30 min sonication time and began to use through sonication since the H_2O_2 level decreased to 1987.00 mg/l. The sonication process ending after 150 min sonication time with decreasing of H_2O_2 concentration to 28.00 mg/l after 150 min sonication time. The $OH^\bullet$ ion concentration increased from $2.00x10^{-52}$ up to $5.00x10^{-5}$ as the sonication time increased from 30 to 150 min sonication times. This showed that color was removed with hydroxylation process in the presence of 2000 mg/l H_2O_2 in OMI ww.

Table 5.55 Effect of 2000 mg/l H_2O_2 concentration on H_2O_2 and $OH^\bullet$ ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
Addition of 2000 mg/l H_2O_2 concentration	2000.00	0.00
H_2O_2 concentration (mg/l) in deionized water (60°C)	2135.00	0.00
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 30 min sonication	2196.00	$2.00\text{x}10^{-52}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 120 min sonication	1987.00	$7.00\text{x}10^{-17}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 150 min sonication	28.00	$5.00\text{x}10^{-5}$

Under ultrasonic irradiation water sonodegraded to $OH^\bullet$ and $H^\bullet$. As a result H_2O_2 is produced according to the Eqs. (5.61) and (5.62):

$$H_2O \Leftrightarrow OH^\bullet + H^\bullet \tag{5.61}$$

$$2OH^\bullet \rightarrow H_2O_2 \tag{5.62}$$

If the solution is saturated with O_2 and O_2H, more $OH^\bullet$ are formed in the gas phase of microbubbles (upon the decomposition of molecular O_2), and the recombination of the former at the cooler sites (bubble–solution interface or the solution bulk) produces additional H_2O_2 (Ince et al., 2001) in Eqs. (5.63), (5.64), (5.65 and (5.66):

$$O_2 + H^\bullet \rightarrow O_2H^\bullet \tag{5.63}$$

$$O_2 \rightarrow O + O \tag{5.64}$$

$$O + H_2O \rightarrow 2\,OH^\bullet \tag{5.65}$$

$$2\,O_2H^\bullet \rightarrow H_2O_2 + O_2 \tag{5.66}$$

5.10.6.2 Effect of H_2O_2 Concentrations on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

79.20%, 82.30% and 84.74% total phenol removals were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.56). 20.56-21.17% and 21.89-24.73% increase in total phenol yields were found in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 60 and 120 min sonication times at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C. Sonication alone provided 59.40% total phenol after 150 min sonication time at pH=7.0 and at 30°C. The contribution of increasing H_2O_2 concentrations on total phenol removal were significant (R^2=0.79, F=19.66, p=0.01) (Table 5.56).

Table 5.56 Effect of increasing H_2O_2 concentrations on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
H_2O_2=100 mg/l	48.82	77.89	79.20	50.13	78.59	85.48
H_2O_2=500 mg/l	49.17	78.07	82.30	52.49	81.38	90.42
H_2O_2=2000mg/l	49.43	80.73	84.74	75.32	86.32	93.65

85.48%, 90.42% and 93.65% total phenol yields were found in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C

(Table 5.56). The contribution of increasing H_2O_2 concentrations were 19.93-45.12% and 20.65-28.38% in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 60 and 120 min sonication times at pH=7.0 and at 60^oC, compared to the control at pH=7.0 and at 60^oC. Control alone provided 61.24% total phenol after 150 min sonication time at 60^oC. The maximum total phenol removal efficiency was 93.65% in H_2O_2=2000 mg/l after 150 min sonication time at pH=7.0 and at 60^oC. A significant linear correlation between total phenol yields and increasing H_2O_2 concentrations was observed (R^2=0.79, F=13.95, p=0.01) (Table 5.56).

Under ultrasound irradiation, water is pyrolyzed, in which process $H^\bullet$, $OH^\bullet$, $O^\bullet$ and $O_2H^\bullet$ are produced and water then react with in the bulk solution or at the interface between the bubbles and the liquid phase (Suslick, 1988). During aqueous ultrasound irradiation, $OH^\bullet$ form during the thermolytic reactions of water and self-recombine to form H_2O_2 (Petrier & Francony, 1997). Kidak & Ince (2006) determined that the controlling mechanism of sonochemical reactors in degradation of phenol is the production of free radicals and their subsequent attack on the pollutant species. It is accepted that H_2O_2 arises from the reactions of $OH^\bullet$ and $O_2H^\bullet$ in the liquid phase around the cavitational bubble and hence can be used to quantify the efficacy of reactors in generating the desired cavitational intensity. Sivasankar & Moholkar (2009b) found that the generation of H_2O_2 increase linearly with time of ultrasonic irradiation without H_2O_2 addition while 66.00% total phenol removal was found after 100 min sonication at pH=4.8.

In this study it is important to note that in the presence of phenol under acidic conditions (at pH=3.0), the H_2O_2 values in OMI ww are much lower compared to those in distilled water (at a neutral pH=7.0) due to the fact that in the former case many of the $OH^\bullet$ produced by sonication react with phenol before they could combine to form $OH^\bullet$. In pure water, due to the absence of organic substrates, the H_2O_2 remains as formed. The results for the H_2O_2 generation in deionized water and in OMI ww containing phenol at acidic pH=3.0 is illustrated in Table 5.57. This table shows the effect of pH=3.0 on H_2O_2 and $OH^\bullet$ ion concentrations in OMI ww at 60^oC after 30 min, 120 and 150 min sonication times. The H_2O_2 concentration increased to

2147.00 mg/l and accumulated in deionized water. This level increased to 2198.00 mg/l after 30 min sonication time and began to use through sonication since the H_2O_2 level decreased to 1960.00 mg/l. The sonication process ending after 150 min sonication time with decreasing of H_2O_2 concentration to 31.00 mg/l after 150 min sonication time. The $OH^\bullet$ ion concentration increased from $1.00x10^{-51}$ up to $3.00x10^{-5}$ as the sonication time increased from 30 to 150 min sonication time. This showed that the main removal mechanism of phenol degradation in the presence of H_2O_2 is hydroxylation in OMI ww.

Table 5.57 Effect of 2000 mg/l H_2O_2 concentration at pH=3.0 on H_2O_2 and $OH^\bullet$ ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, , initial total phenol concentration=4090 mg/l, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
Addition of 2000 mg/l H_2O_2 concentration at pH=3.0	2000.00	0.00
H_2O_2 concentration (mg/l) in deionized water (60°C) at pH=7.0	2147.00	0.00
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 30 min sonication at pH=3.0	2198.00	$1.00x10^{-51}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 120 min sonication at pH=3.0	1960.00	$4.00x10^{-15}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 150 min sonication at pH=3.0	31.00	$3.00x10^{-5}$

In a study performed by Mahamuni & Pandit (2006) it was found only 7.00% phenol degradation after 90 min sonication. The attack of $OH^\bullet$ on phenol was confined through sonication. The formation of the hydrophenols through sonication can be explained by the Eqs. (5.67), (5.68) and (5.69):

$$H_2O \rightarrow H^\bullet + OH^\bullet \tag{5.67}$$

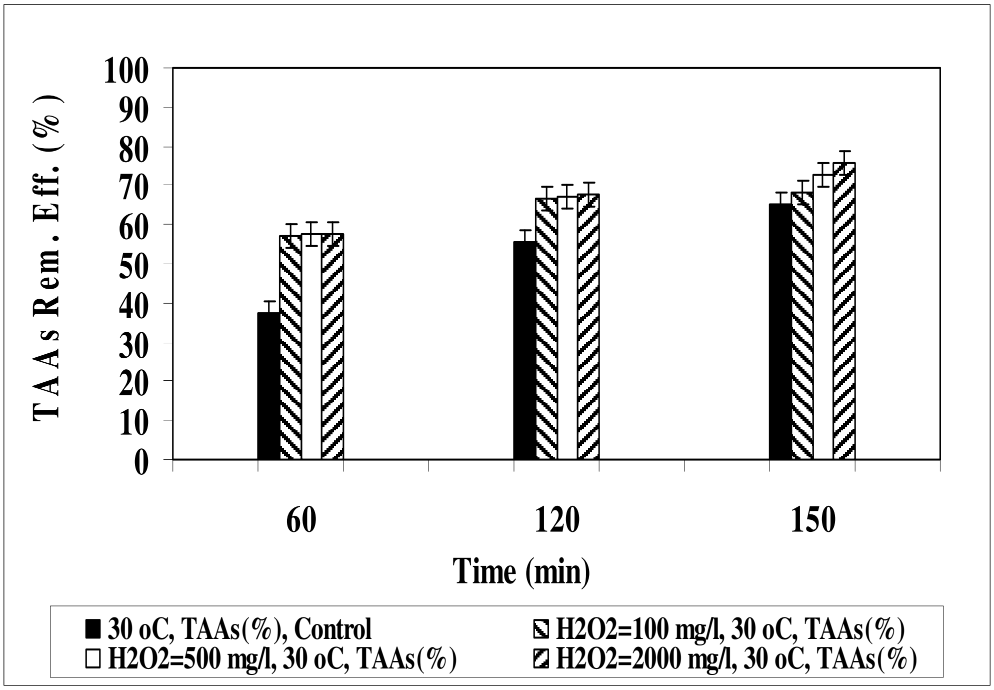
$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \tag{5.68}$$

$$Phenol + OH^{\bullet} \rightarrow Dihydroxyphenols \tag{5.69}$$

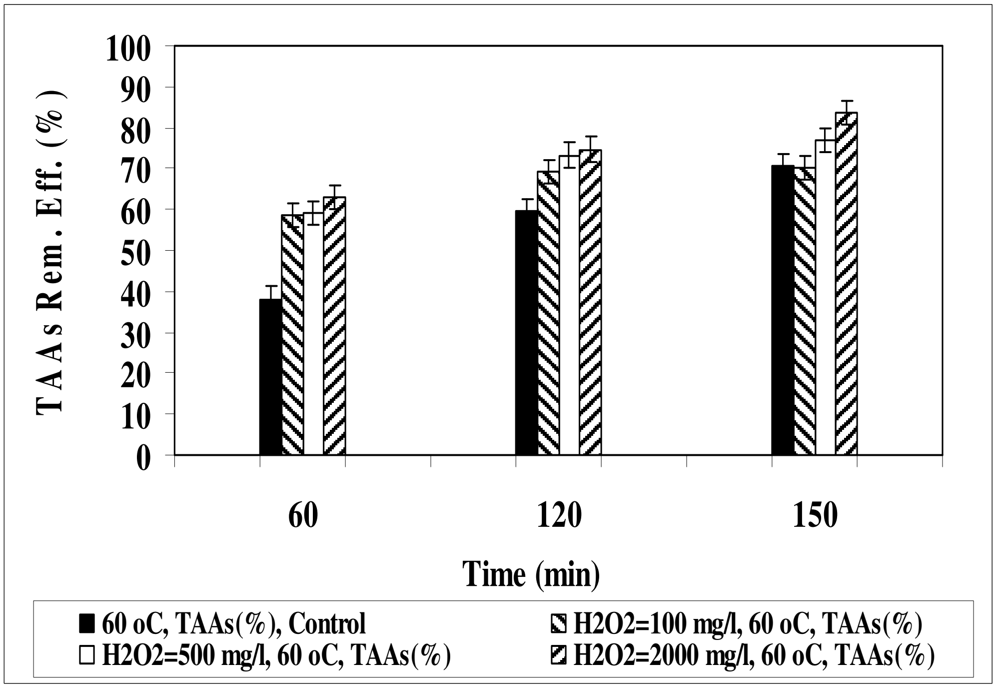
In this study, 93.65% total phenol removal was found in 2000 mg/l H_2O_2 at 60°C after 150 min sonication. The total phenol yield is higher than the yield obtained by Mahamuni & Pandit (2006) at 60°C as mentioned above.

5.10.6.3 Effect of H_2O_2 Concentrations on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

68.31%, 72.53% and 75.87% TAAs removals were obtained in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.53a). The contribution of increasing H_2O_2 concentrations on TAAs removals were 19.71-20.54% and 11.19-12.39% in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 60 and 120 min sonication times at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C. Sonication alone provided 64.98% TAAs yield after 150 min sonication time at pH=7.0 and at 30°C. A significant linear correlation between TAAs yields and increasing H_2O_2 concentrations was not observed (R^2=0.44, F=3.71, p=0.01) (Figure 5.53a).



(a)



(b)

Figure 5.53 Effect of increasing H_2O_2 concentrations on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

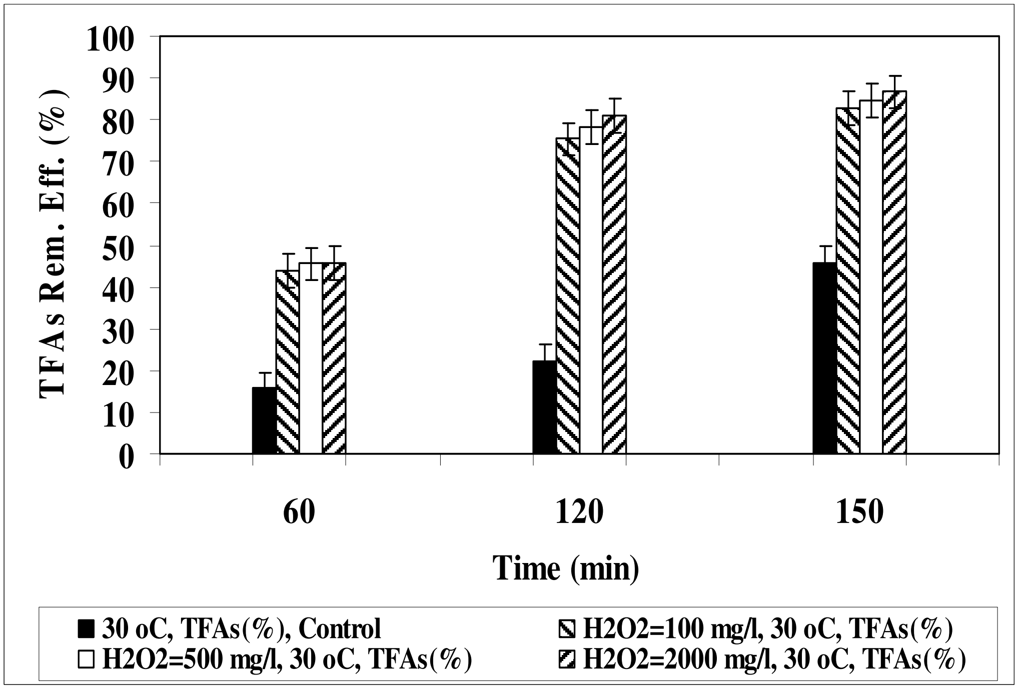
70.21%, 76.93% and 83.68% TAAs yields were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.53b). The contribution of increasing H_2O_2 concentrations on TAAs removals were 20.54-24.88% and 9.76-15.29% TAAs yields in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 60 and 120 min sonication times at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 60°C. Control provided 70.52% TAAs yield after 150 min sonication time at pH=7.0 and at 60°C. The maximum TAAs removal efficiency was 83.68% in H_2O_2=2000 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing H_2O_2 concentrations was not observed (R^2=0.49, F=4.84, p=0.01) (Figure 5.53b).

Amir et al. (2004) reported that the H_2O_2 formation in OMI ww cannot be inhibited by TAAs. If it is assumed that the first step of the TAAs degradation results from $OH^\bullet$ reaction in a site close to the surface of the bubble, it should be a competition between reactions. The low TAA yields (48.00%) throughout sonication could be attributed to the modifications of some sonodegraded aliphatic chains to generate condensed aromatic structures containing large proportions of hydroxyl, methoxyl, carboxyl and carbonyl groups. In this study, 83.68% TAAs removal obtained after 150 min sonication at 60°C. This TAAs yield is higher than the yield observed by Amir et al. (2004) at 60°C.

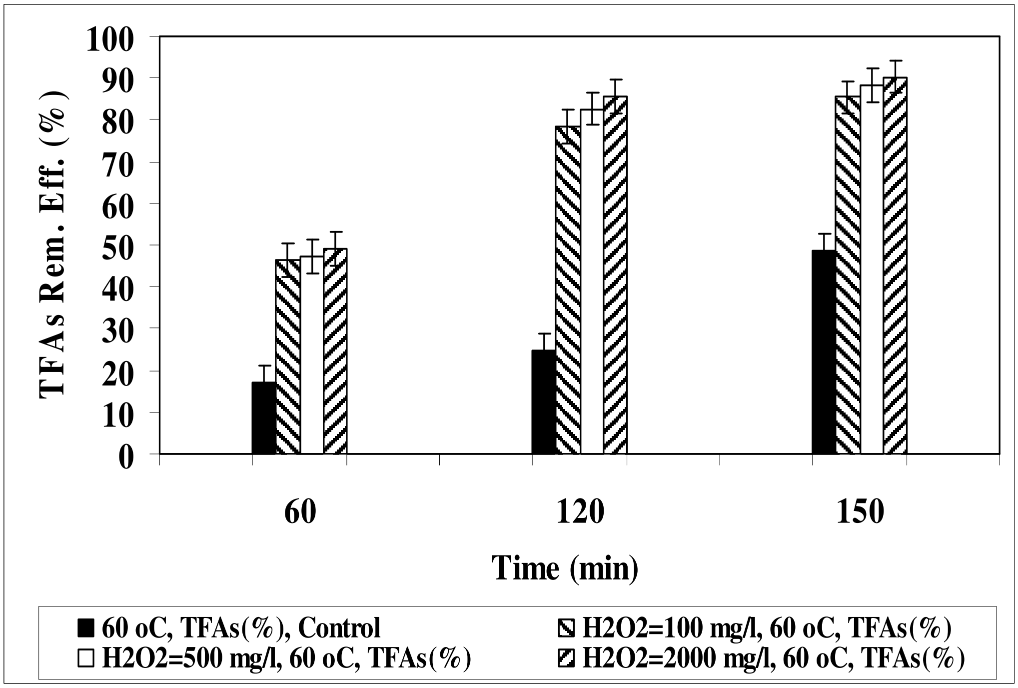
5.10.6.4 Effect of H_2O_2 Concentrations on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

82.75%, 84.75% and 86.72% TFAs removals were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.54a). The contribution of increasing H_2O_2 concentrations on TFAs removals were 28.38-30.17% and 52.99-58.66% in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 60 and 120 min sonication times at pH=7.0 and at 30°C, compared to the control reactor at pH=7.0 and at 30°C. Sonication alone provided 45.66% TFAs yield after 150 min sonication time at pH=7.0 and at 30°C. A significant linear correlation between TFAs yields and increasing H_2O_2 concentrations was observed (R^2=0.74, F=15.61, p=0.01) (Figure 5.54a).

85.41%, 88.20% and 90.30% TFAs yields were found in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.54b). The contribution of increasing H_2O_2 concentrations on TFAs removals were 29.02-31.71%, 53.77-60.96% and 36.57-41.46% in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 60, 120 and 150 min sonication times at pH=7.0 and at 60°C, compared to the control (E=48.84% TFAs after 150 min sonication time at pH=7.0 and at 60°C). The maximum TFAs removal efficiency was 90.30% in H_2O_2=2000 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TFAs yields and increasing H_2O_2 concentrations was observed (R^2=0.82, F=16.13, p=0.01) (Figure 5.54b).



(a)



(b)

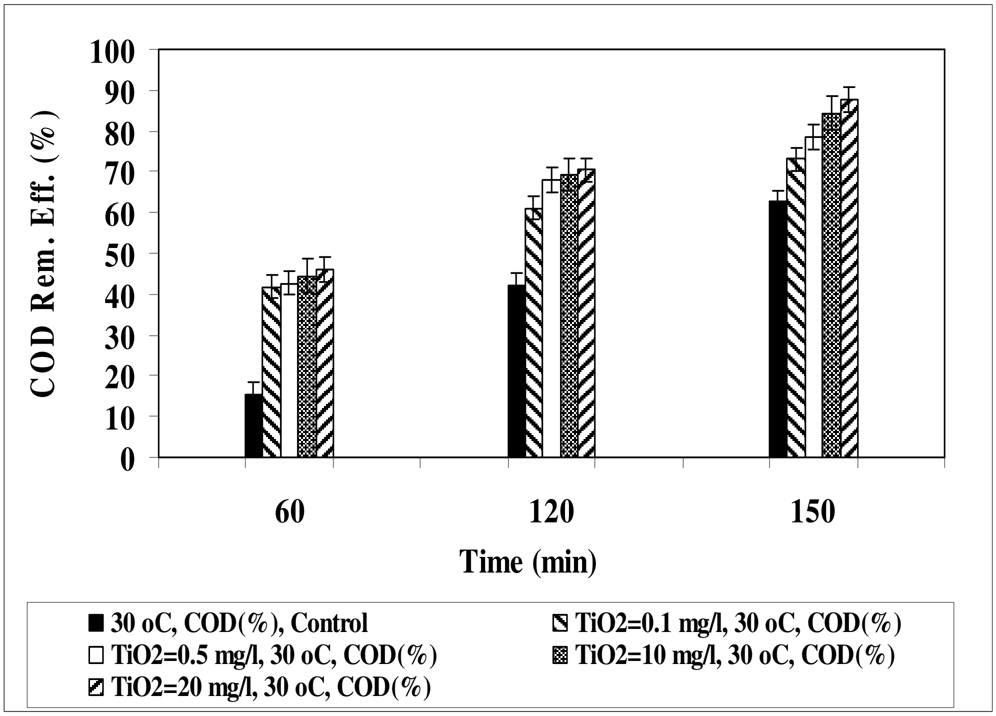
Figure 5.54 Effect of increasing H_2O_2 concentrations on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

In a study performed by Jahouach-Rabai et al. (2008) 89.00% TFAs removal was observed at 20 kHz frequency, at a 750 W ultrasonic power, after 45 min sonication time at 70°C in an OMI ww. By increasing of H_2O_2 concentrations the TFAs concentrations decreased by oxidation of oleic acid and further degradation to hexanal. In this study, 90.30% TFAs removal was observed in H_2O_2=2000 mg/l at 60°C after 150 min sonication time. The TFAs yield is higher than the yield obtained by Jahouach-Rabai et al. (2008) at 70°C as mentioned above.

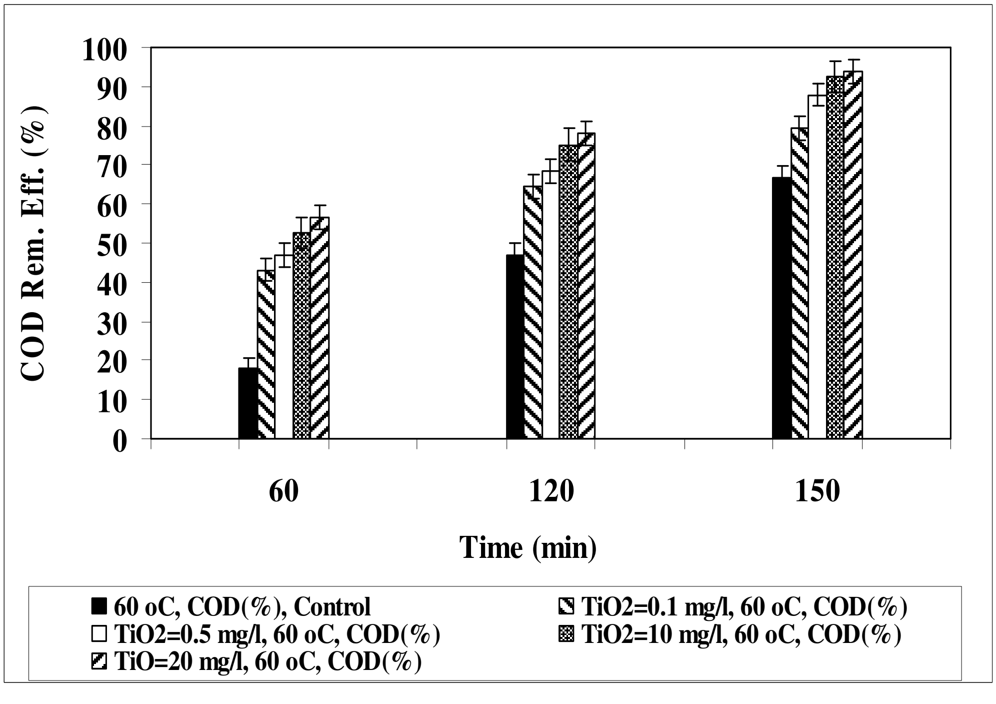
5.10.7 Effect of TiO_2 Concentrations on the Removals of COD_{dis} in OMI ww

Increasing TiO_2 concentrations (0.10-0.50-10.00 and 20.00 mg/l) were added in OMI ww before sonication experiments (Figure 5.55a). 73.08%, 78.51%, 84.42% and 87.76% COD_{dis} removals were obtained in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C. 10.51%, 15.94%, 21.85% and 25.19% increase in COD_{dis} removals were observed in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without TiO_2 while E=62.57% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing TiO_2 concentrations was observed (R^2=0.87, F=16.15, p=0.01) (Figure 5.55a).

79.38%, 87.90%, 92.44% and 93.93% COD_{dis} yields were measured in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.55b). The contribution of TiO_2 concentrations on COD_{dis} removals were 12.55%, 21.05%, 25.61% and 27.10% in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=66.83% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 93.93% in TiO_2=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing TiO_2 concentrations was observed (R^2=0.90, F=19.33, p=0.01) (Figure 5.55b).



(a)



(b)

Figure 5.55 Effect of increasing TiO_2 concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

Since the organic compounds in OMI ww are hydrophilic, its partitioning into the gas phase is unlikely and direct pyrolysis should be a very minor reaction path in a TiO_2/ultrasound system (Wang, J. et al., 2008). Accordingly, the main pathway for the destruction of COD is chemical oxidation by $OH^\bullet$ in the bulk liquid and/or the interface region of the cavitation bubbles in the ultrasound-based system (Wang, J. et al., 2008).

The H_2O_2 measurement during acoustic cavitation in the OMI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the COD treatment by sonication in OMI ww decreases with increasing sonication time at 60°C. In the deionized water samples the H_2O_2 was accumulated and its concentration was measured as 177.00 mg/l, whereas this level was 178.00 mg/l after 60 min sonication time in OMI ww. The H_2O_2 concentration was only 11.00 mg/l in OMI ww after 150 min sonication time in the samples containing 10.00 mg/l TiO_2 (Table 5.58). The $OH^\bullet$ ion concentrations also increased from $98.00x10^{-62}$ to $16.00x10^{-5}$ mg/l after 150 min sonication time in OMI ww containing 10.00 mg/l TiO_2. This showed that hydroxylation is the main mechanism for the removal of COD in OMI ww. In other words, $OH^\bullet$ ion is the major process for complete degradation of COD in OMI ww.

Table 5.58 Effect of 10.00 mg/l TiO_2 concentration at pH=3.0 on H_2O_2 and $OH^\bullet$ ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, , initial total phenol concentration=4090 mg/l, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
Addition of 10.00 mg/l TiO_2 concentration at pH=3.0	178.00	0.00
H_2O_2 concentration (mg/l) in deionized water (60°C) at pH=7.0	177.00	0.00
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 30 min sonication at pH=3.0	156.00	$98.00\text{x}10^{-62}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 120 min sonication at pH=3.0	92.00	$3.00\text{x}10^{-15}$
H_2O_2 concentration (mg/l) in OMI ww (60°C) after 150 min sonication at pH=3.0	11.00	$16.00\text{x}10^{-5}$

In this study, it was found that the percent COD removals of OMI was directly proportional to TiO_2 catalyst concentration. As expected, the removals of COD were found to increase with the increasing concentration of TiO_2. $TiO_2 \geq 25.00$ mg/l decrease the COD yields. This could be attributed to the aggregation of TiO_2 particles at high concentrations, causing a decrease in the number of active surface sites, and to the decrease in the passage of sonic waves through sonication through the OMI ww samples. At low TiO_2 concentrations the TiO_2 surfaces adsorbed additional organic molecules present in OMI ww by inhibiting direct contact between COD giving molecules and cavitation points and by suppressing the generation of $OH^\bullet$ on TiO_2 surfaces (Atanassova et al., 2005b).

5.10.7.1 Effect of TiO_2 Concentrations on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

85.07%, 88.08%, 90.08% and 91.88% color removals were found in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.59). 10.62%, 13.63%, 15.63% and 17.43% increase in color removals were observed in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=74.45% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing TiO_2 concentrations was observed (R^2=0.88, F=17.12, p=0.01) (Table 5.59).

Table 5.59 Effect of increasing TiO_2 concentrations on the color removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times, (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
TiO_2=0.10 mg/l	57.21	74.25	85.07	61.92	75.55	87.88
TiO_2=0.50 mg/l	62.12	77.15	88.08	71.04	82.06	91.38
TiO_2=10.00 mg/l	67.74	79.06	90.08	72.14	84.47	93.19
TiO_2=20.00 mg/l	72.34	83.77	91.88	74.55	87.07	95.39

87.88%, 91.38%, 93.19% and 95.39% color yields were obtained in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.59). The contribution of TiO_2 concentrations on color removals were 4.11%, 7.61%, 9.42% and 11.62% in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=83.77% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 95.39% in TiO_2=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing TiO_2 concentrations was observed (R^2=0.89, F=16.78, p=0.01) (Table 5.59).

5.10.7.2 Effect of TiO_2 Concentrations on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

79.98%, 82.52%, 85.13% and 87.88% total phenol removals were measured in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.60). 20.58%, 23.12%, 25.73% and 28.48% increase in total phenol removals were observed in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=58.25% total phenol at pH=7.0 and at 30°C). A significant linear correlation between total phenol yields and increasing TiO_2 concentrations was observed (R^2=0.92, F=19.65, p=0.01) (Table 5.60).

Table 5.60 Effect of increasing TiO_2 concentrations on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
TiO_2=0.10 mg/l	45.22	76.10	79.98	50.30	81.34	85.57
TiO_2=0.50 mg/l	47.60	78.68	82.52	50.83	82.62	88.71
TiO_2=10.00 mg/l	47.73	81.25	85.13	50.96	86.93	91.20
TiO_2=20.00 mg/l	50.30	85.41	87.88	51.39	89.37	94.77

85.57%, 88.71%, 91.20% and 94.77% total phenol yields were measured in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.60). The contributions of 0.50 mg/l, 10.00 and

20.00 mg/l TiO_2 concentrations on the total phenol removals were 24.33%, 27.47%, 29.96% and 33.53%, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=61.24% total phenol at pH=7.0 and at 60°C). The maximum total phenol removal efficiency was 94.77% in TiO_2=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between trotal phenol yields and increasing TiO_2 concentrations was observed (R^2=0.94, F=19.98, p=0.01) (Table 5.60).

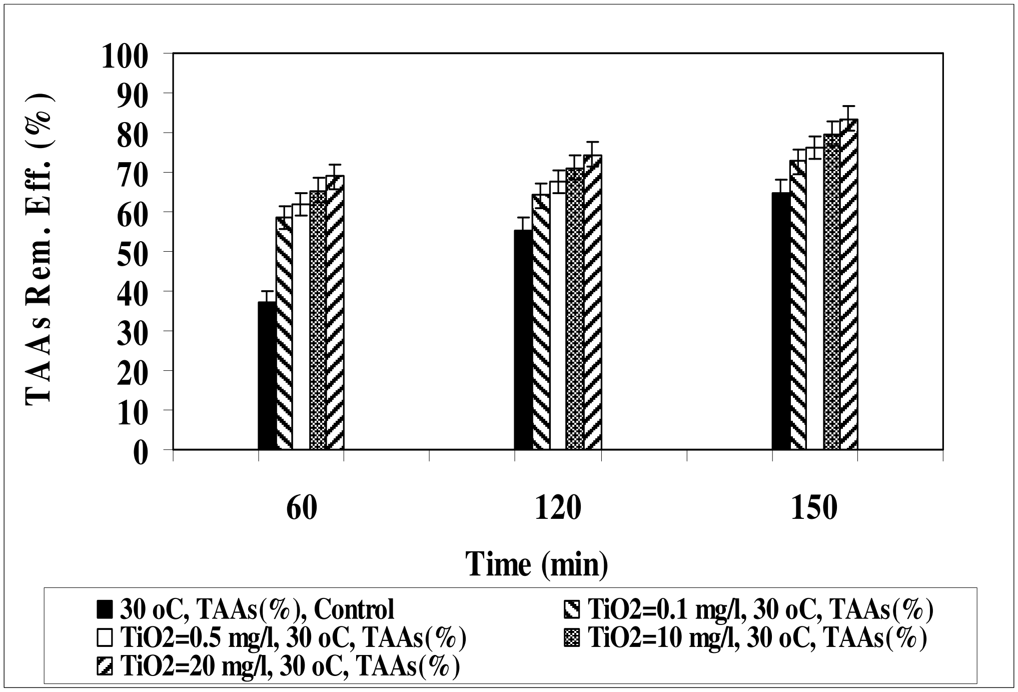
The increase in sono-destruction yields for phenol may be explained by the fragmentation of TiO_2 catalyst by the cavitation process which produces higher surface area. In this method, ultrasonic waves not only destroy the phenol compounds through cavitation process but also could increases the adsorption process by increasing the surface area of the TiO_2 catalyst as reported by Laxmi et al. (2010). During the ultrasound of OMI with TiO_2, the H_2O_2 form more active free radicals, such as $OH^\bullet$ and $O_2H^\bullet$/ $O_2^{-\bullet}$. In a study performed by Khochwala & Gogate (2010) it has been observed that 2.00 g/l TiO_2 is the optimum concentration for 78.00% phenol removal. Wu, C. et al. (2001a) and Wu, C. et al. (2001b) have reported similar results for degradation of phenol and trichloroacetic acid in a combined operation involving two 9W H-shaped UV lamps and an ultrasonic horn operating at a frequency of 30 kHz and a power of 100 W. Kidak & Ince (2007) and Shirgaonkar & Pandit (1998) have also reported similar results for degradation of phenol and 2,4,6–trichlorophenol, respectively. In this study, 94.77% the maximum total phenol yields were found at a TiO_2 concentration of 20.00 mg/l at 60°C and this result is comparable higher than the yield obtained by the other studies mentioned above.

In a study performed by Entezari & Petrier (2005) 50.00-60.00% phenol removal efficiency was obtained at a frequency of 423 kHz, after 45 min sonication time at a TiO_2 concentration of 8.00 mg/l at 60°C. They reported that the $OH^\bullet$ produced by ultrasound can react with phenol resulting in a dephenolization process. In the present study, 94.77% total phenol removal was observed in 20.00 mg/l TiO_2 at 60°C after 150 min sonication time. The total phenol yield is higher than the yield obtained by Entezari & Petrier (2005) at 60°C as mentioned above.

5.10.7.3 Effect of TiO_2 Concentrations on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

72.71%, 76.16%, 79.73% and 83.48% TAAs removals were found in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.56a). 7.73%, 11.18%, 14.75% and 18.50% increase in TAAs removals were obtained in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=64.98% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing TiO_2 concentrations was observed (R^2=0.81, F=16.82, p=0.01) (Figure 5.56a).

73.66%, 77.94%, 81.34% and 88.54% TAAs yields were obtained in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.56b). The contribution of TiO_2 concentrations on TAAs removals were 3.14%, 7.42%, 10.82% and 18.02% in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=70.52% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 88.54% in TiO_2=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing TiO_2 concentrations was observed (R^2=0.83, F=16.45, p=0.01) (Figure 5.56b).



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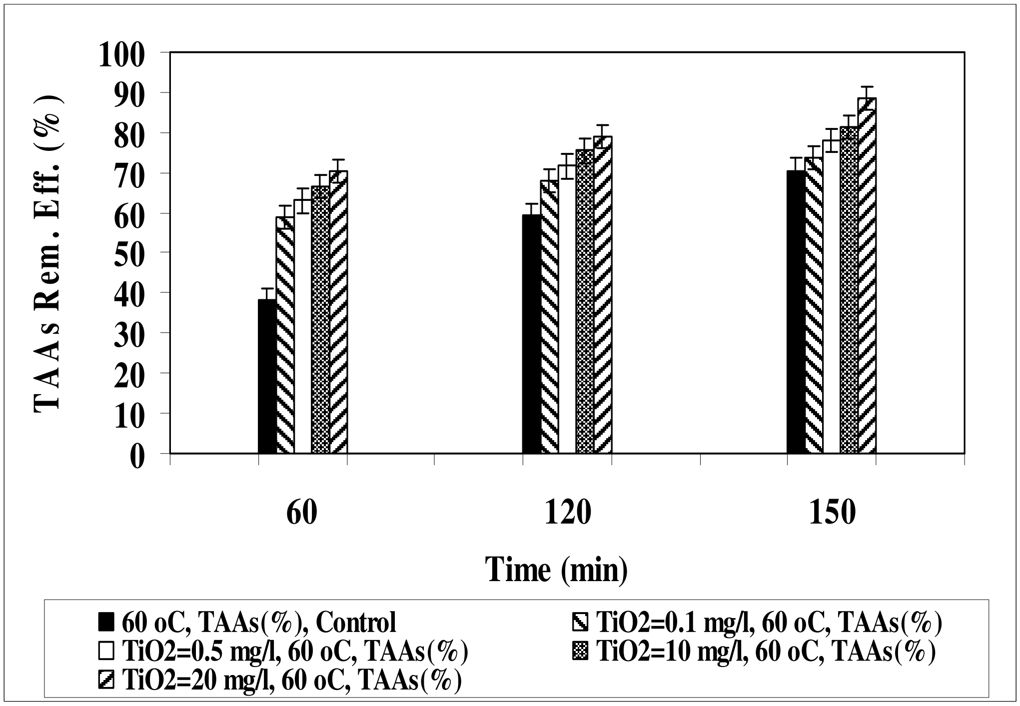


(b)

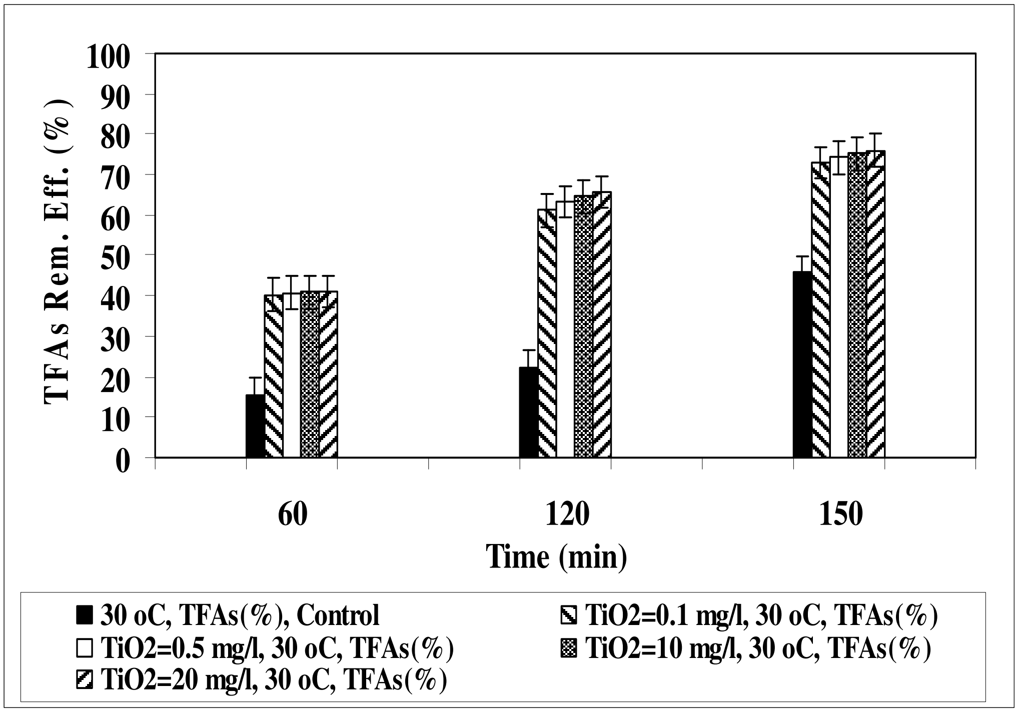
Figure 5.56 Effect of increasing TiO_2 concentrations on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

Under sonication the removal of AAs in OMI ww namely, aniline, benzene, benzidine, p–xylene, 4,4–oxydianiline, 2,4,6–trimetlyaniline, o–toluidine, etc., are attributable to the priority of hydroxylation of the cleavage of azo links in 4,4–oxydianiline, 2,4,6–trimetlyaniline AAs and cleavage of 4–nitroaniline group from aniline, benzene trough oxidation process. The $OH^{\bullet}$ initially attack azo groups and open the N=N bonds. It was reported that the N=N bonds (or cleavage of other groups) are more easily destroyed than the aromatic structures (Oussi et al., 1997).

An anatase TiO_2 was used to remove the AAs namely, 4,4–oxydianiline with a yield 85.00% from OMI ww after 120 min sonication. 87.00% mineralization of AAs was achieved in a study performed by Cardoso et al. (2010). The TAAs removal (88.54%) observed in 20.00 mg/l TiO_2 at 60°C, in this study, was higher than the yields obtained in the studies given above after 150 min sonication time.

5.10.7.4 Effect of TiO_2 Concentrations on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

72.85%, 74.28%, 75.16% and 76.05% TFAs removals were found in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.57a). 27.19%, 28.62%, 29.50% and 30.39% increase in TFAs removals were obtained in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=45.66% TFAs at pH=7.0 at 30°C). A significant linear correlation between TFAs yields and increasing TiO_2 concentrations was observed (R^2=0.87, F=16.21, p=0.01) (Figure 5.57a).



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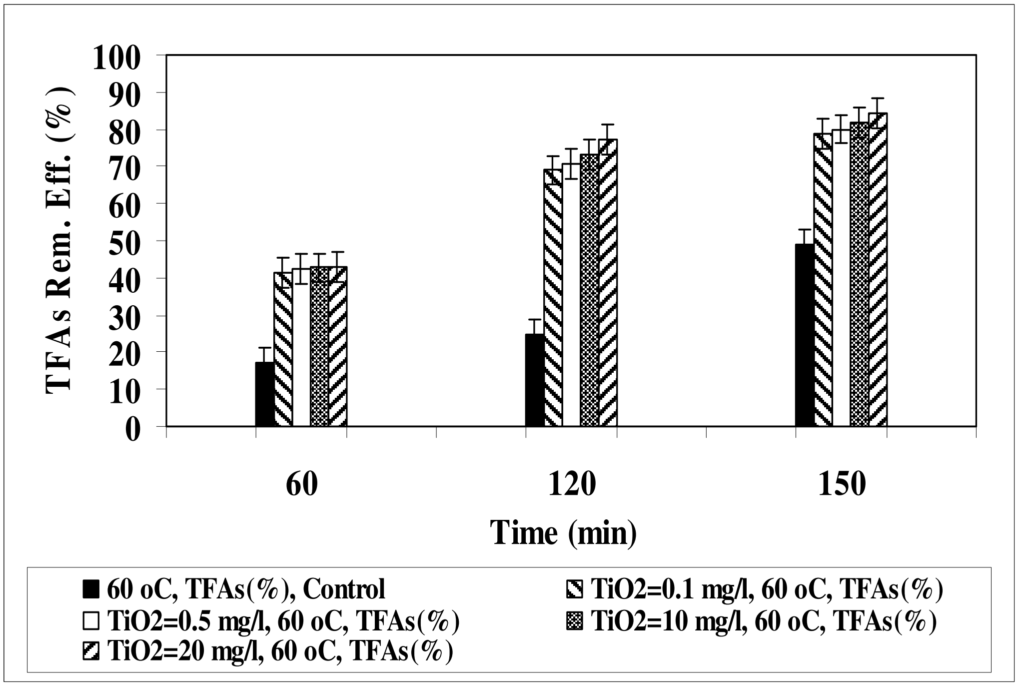


(b)

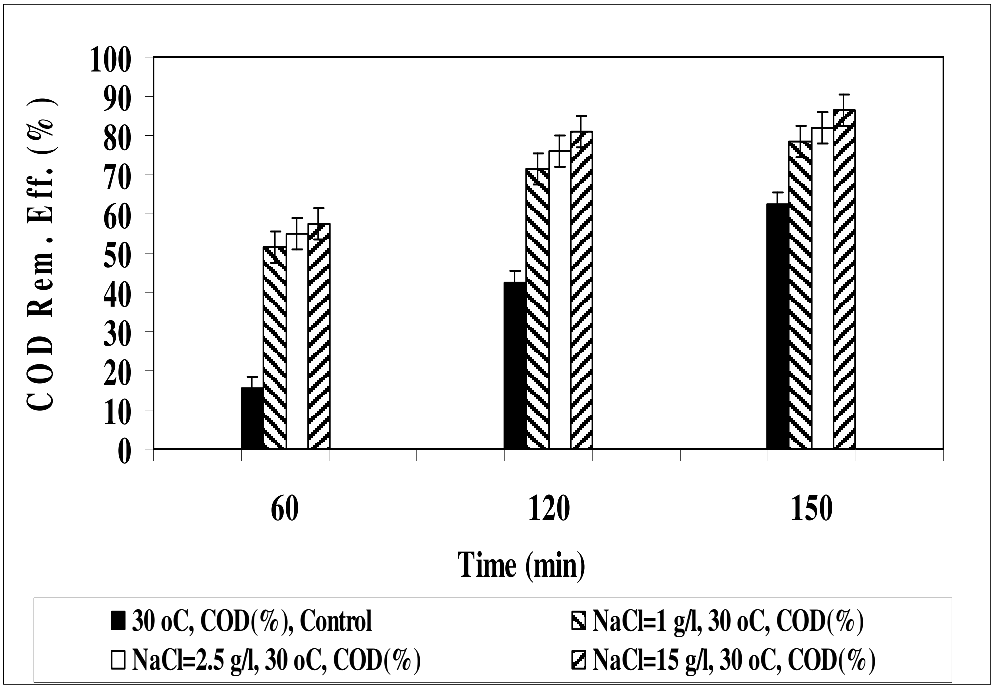
Figure 5.57 Effect of increasing TiO_2 concentrations on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

78.90%, 80.04%, 81.68% and 84.52% TFAs yields were measured in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.57b). The contribution of 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2 concentrations on TFAs removals were 30.06%, 31.20%, 32.84% and 35.68%, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=48.84% TFAs at pH=7.0 and at 60°C). The maximum TFAs removal efficiency was 84.52% in TiO_2=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TFAs yields and increasing TiO_2 concentrations was observed (R^2=0.89, F=19.05, p=0.01) (Figure 5.57b).

5.10.8 Effect of NaCl Concentrations on the Removals of COD_{dis} in OMI ww

Increasing NaCl concentrations (1.00–2.50 and 15.00 g/l) were added in OMI ww before sonication process. 78.43%, 81.85% and 86.43% COD_{dis} removals were observed in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.58a). 15.86%, 19.28% and 23.86% increase in COD_{dis} removals were obtained in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without NaCl while E=62.57% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing NaCl concentrations was observed (R^2=0.92, F=19.89, p=0.01) (Figure 5.58a).

84.85%, 90.58% and 93.15% COD_{dis} yields were found in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.58b). The contribution of 1.00 g/l, 2.50 and 15.00 g/l NaCl on COD_{dis} removals were 18.02%, 23.75% and 26.32%, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=66.83% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 93.15% in NaCl=15.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing NaCl concentrations was observed (R^2=0.94, F=19.87, p=0.01) (Figure 5.58b).



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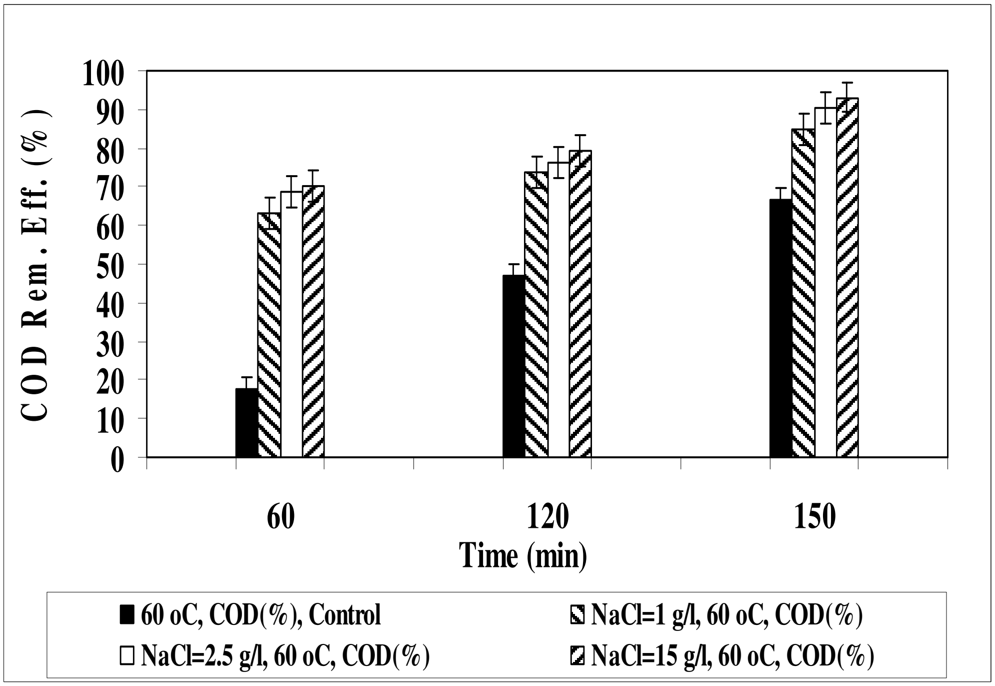


(b)

Figure 5.58 Effect of increasing NaCl concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

Addition of NaCl increases the ionic strength of the aqueous phase, driving the organic compounds to the bulk–bubble interface in ultrasound-related systems. This resulting in more COD removals in OMI ww (Goel et al., 2004). Other properties of the solution, such as viscosity and vapor pressure could affect the sonocation efficiency. The enhancement of sonication in the presence of NaCl can be attributed to the increase in partitioning of the pollutant species upon cavitation implosion in ultrasound-related system. Beyond the partitioning enhancement, the presence of salt reduces vapor pressure and increases the surface tension. All of these factors help to collapse the bubbles more violently, causing high pollutant degradation. Previous studies have yielded similar results concerning the degradation of organics in the presence of NaCl in ultrasound-based systems (Wu, C.-H. 2009).

With increasing the salt concentrations diffusion of the target OMI ww samples toward the interface becomes more and more difficult and the organic molecules in OMI ww tend to be back-diffused into the bulk solution, increasing the overall time required for their Sonochemical removal (Wu, C.-H. 2009).

In a study performed by Atanassova et al. (2005b) 50.00% COD removals was obtained in the presence of 10.00% NaCl at 24 kHz, at 75-150 W, at 25^{o}C and 60^{o}C. Addition of NaCl enhanced the reduction in antioxidant activity and this can be attributed to an increase in the partitioning of phenolic compounds in the presence of NaCl. This lead to accumulation of the reactant species ($H^{\bullet}$, $OH^{\bullet}$, $O_2^{\bullet}$, Na^+, Cl^-) at the cavitation implosion sites. This is due to the salting-out effect where fewer water molecules are available for dissolving the COD molecules, preferably forming of hydration spheres around the salt ions (Psillakis & Kalogerakis, 2003). Salt addition results in reduced vapor pressure and increased surface tension on phenolic compounds, for example in caffeic acid (Seymour & Gupta, 1997), thus promoting a more violent collapse of the cavitations bubbles. In this study, 93.15% COD_{dis} removal was found for 15.00 g/l NaCl at 60^{o}C after 150 min sonication time. The COD_{dis} yield is higher than the COD_{dis} yield obtained by Atanassova et al. (2005b) at 60^{o}C as mentioned above.

5.10.8.1 Effect of NaCl Concentrations on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

87.37%, 89.08% and 92.18% color removals were observed in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.61). 12.92%, 14.63% and 17.73% increase in color removals were obtained in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=74.45% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing NaCl concentrations was observed (R^2=0.73, F=14.45, p=0.01) (Table 5.61).

Table 5.61 Effect of increasing NaCl concentrations on the color removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
NaCl=1.00 g/l	57.31	74.85	87.37	62.02	78.76	93.39
NaCl=2.50 g/l	68.34	77.35	89.08	65.63	80.86	94.29
NaCl=15.00 g/l	72.04	80.86	92.18	74.65	83.57	96.09

93.39%, 94.29% and 96.09% color yields were found in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.61). The contribution of NaCl concentrations on color removals were 9.62%, 10.52% and 12.32% in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=83.77% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 96.09% in NaCl=15.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing NaCl concentrations was observed (R^2=0.76, F=14.24, p=0.01) (Table 5.61).

In this study, it was found that the decolorization degree of OMI ww (color removals) increased by increasing the NaCl concentration. NaCl addition increases the ionic strength of the aqueous phase, driving the organic compounds to the bulk-bubble interface (Goel et al., 2004). The enhancement of the color yields in the presence of NaCl can be attributed to the increase in partitioning of the COD in OMI ww upon cavitation implosion. Beyond the partitioning enhancement, the presence of salt reduces the vapor pressure and increases the surface tension of some color giving organics like lignin and tannins. All of these factors help to collapse the bubbles more violently, causing high color removals (83.77%) by sonodegradation of colorful organics (lignin, tannins, ferrous humates, polyphenols, etc.) in OMI ww. Previous studies yielded similar results for (69.00% color removal) the degradation of some organic pollutants giving color to the OMI ww in the presence of NaCl in ultrasound-based systems (Mahamuni & Pandit, 2006).

5.10.8.2 Effect of NaCl Concentrations on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

80.33%, 82.82% and 85.66% total phenol removals were observed in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.62). 20.93%, 23.42% and 26.26% increase in total phenol removals were obtained in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=59.40% total phenol at pH=7.0 and at 30°C). A significant linear correlation between total phenol yields and increasing NaCl concentrations was observed (R^2=0.70, F=14.25, p=0.01) (Table 5.62).

88.49%, 91.77% and 93.72% total phenol yields were found in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.62). The contributions of increasing NaCl concentrations on total phenol removals were 27.25%, 30.53% and 32.48%, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=61.24% Total Phenol at pH=7.0 and at 60°C). The maximum total phenol removal efficiency was 93.72% in NaCl=15.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between total phenol yields and increasing NaCl concentrations was observed (R^2=0.76, F=14.54, p=0.01) (Table 5.62).

Table 5.62 Effect of increasing NaCl concentrations on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
NaCl=1.00 g/l	42.89	73.44	80.33	49.43	79.03	88.49
NaCl=2.50 g/l	43.19	75.57	82.82	50.26	79.94	91.77
NaCl=15.00 g/l	48.17	76.15	85.66	51.04	82.34	93.72

High phenol yields in OMI ww can be explained by the salting out effect created by the presence of NaCl on phenol in the OMI ww. As proved by Seymour & Gupta (2001) the hydrophobicity of phenol increases when NaCl is added to the aqueous phenol solution. This causes the phenol molecules to move towards the interface of the cavities created by sonication. This increases the possibility of $OH^\bullet$ attack on phenol. They conclude that NaCl is responsible for only physically pushing the phenol towards the cavity/water interface and is not taking part in any chemical reaction. Thus, the mechanism of phenol degradation in this case remains the same as that in case of ultrasound alone and NaCl just increases the interfacial phenol concentration (Kidak & Ince, 2006).

Additives such as H_2O_2 and NaCl (1.00% in concentration) were used to intensify the sono-degradation process in OMI ww (Atanassova et al., 2005a). Use of H_2O_2

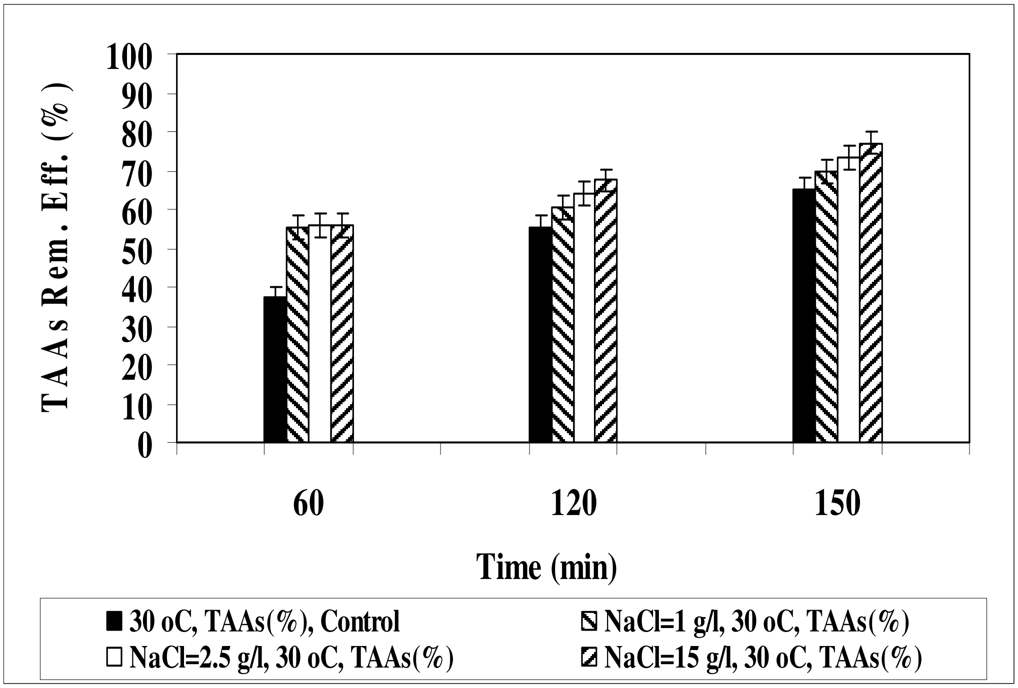
provides additional source of free radicals whereas use of salts alters the distribution of the pollutants selectively at the site of radical generation and possibly result in enhanced degradation.

Higher percentage (8.00%) of NaCl in OMI ww decrease the phenol yields by the fact that higher amount of NaCl will create more salting out effect than the lower amount and thus increase the interfacial concentration of the phenol (Sivasankar & Moholkar, 2009b). Atanassova et al. (2005b) 24.00% and 28.00% total phenol yields were obtained in the samples contained 14.00%, 19.00% NaCl after 240 min sonication time at 80 kHz frequency and at 150 W power at 60^{o}C. In this study, 93.72% total phenol removal was measured in 15.00 g/l NaCl at 60^{o}C after 150 min sonication. In the present study, the total phenol yield is higher than the yield obtained by Atanassova et al. (2005b) at 60^{o}C as mentioned above.

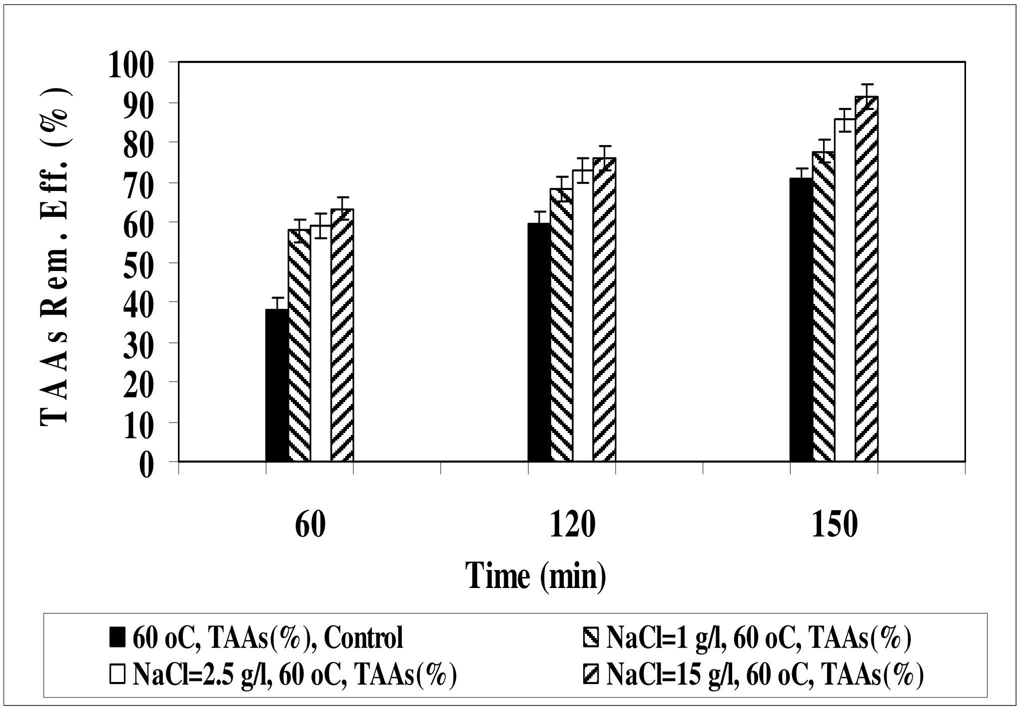
In a study performed by Mahamuni & Pandit (2006) in the presence of 2.00% NaCl the phenol in OMI ww removed with a yield of 40.00% while 50.00% phenol removal was obtained in the presence of 8.00% NaCl. In this study, 93.72% total phenol removal was measured in 15.00 g/l NaCl at 60^{o}C after 150 min sonication time. The total phenol yield is higher than the yield obtained by Mahamuni & Pandit (2006) at 60^{o}C.

5.10.8.3 Effect of NaCl Concentrations on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

69.85%, 73.25% and 77.11% TAAs removals were observed in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.59a). 4.87%, 8.27% and 12.13% increase in TAAs removals were obtained in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=64.98% TAAs at pH=7.0 and at 30^{o}C). A significant linear correlation between TAAs yields and increasing NaCl concentrations was observed (R^2=0.65, F=11.82, p=0.01) (Figure 5.59a).



(a)



(b)

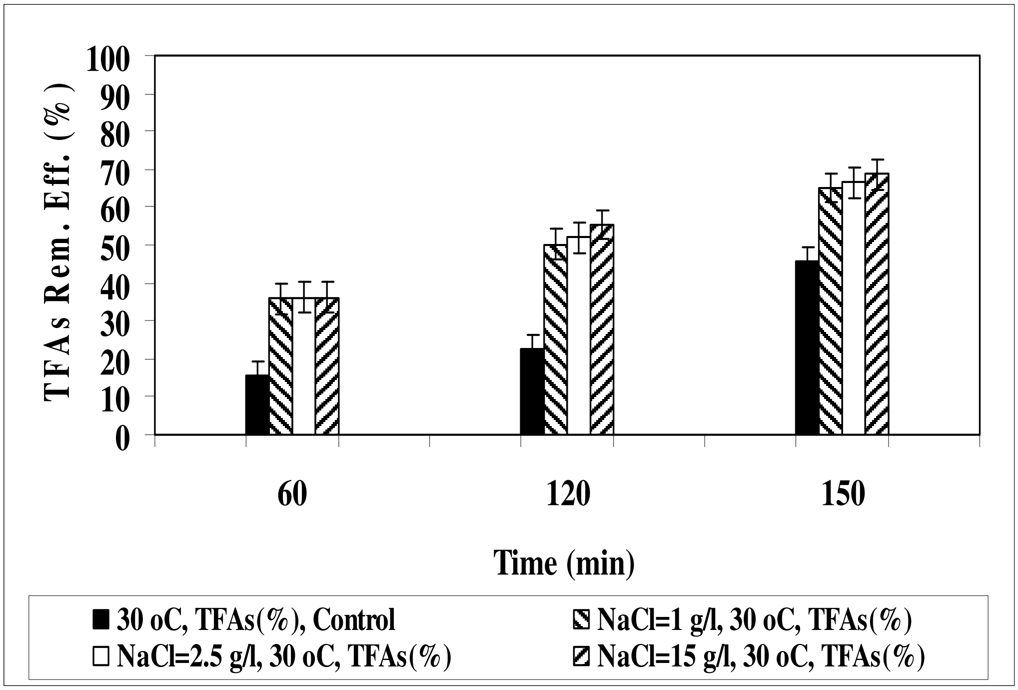
Figure 5.59 Effect of increasing NaCl concentrations on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

77.65%, 85.44% and 91.44% TAAs yields were found in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.59b). The contributions of increasing NaCl concentrations on TAAs removals were 7.13%, 14.92% and 20.92%, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=70.52% TAAs at pH=7.0 and at 60^{o}C). The maximum TAAs removal efficiency was 91.44% in NaCl=15.00 g/l after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between TAAs yields and increasing NaCl concentrations was observed (R^2=0.69, F=11.78, p=0.01) (Figure 5.59b).

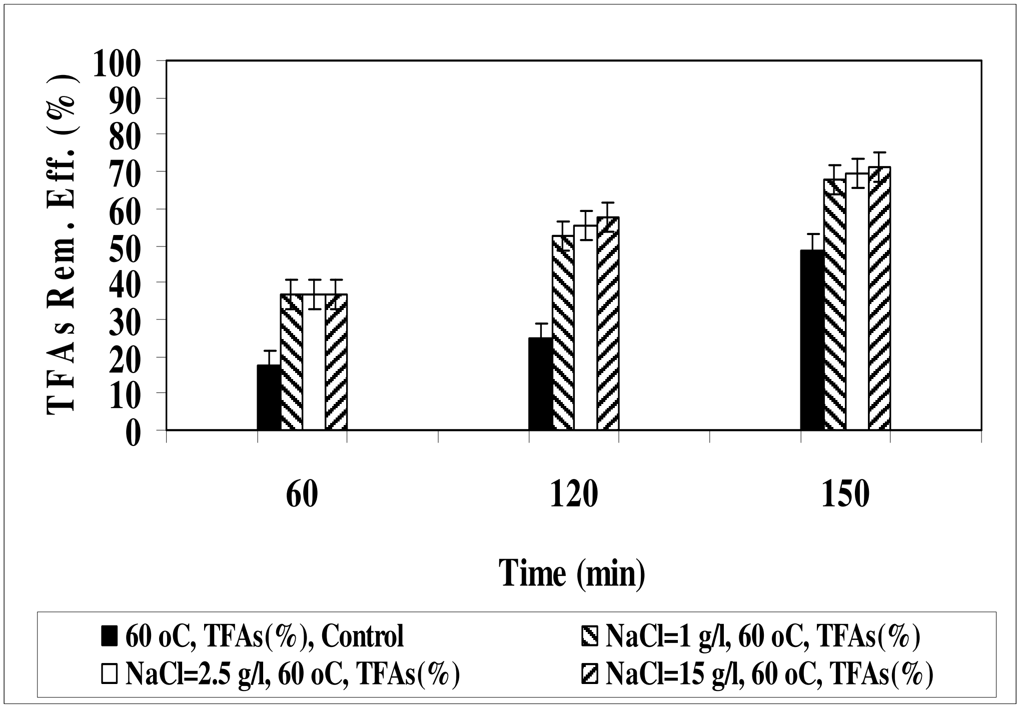
During the hydroxylation of TAAs the $OH^{\bullet}$ most effectively attack the azo-links and other double N=N bonds. The decay of the TAAs absorbance is considered to indicate aromatic fragment degradation in the molecules producing color (aniline, benzidine, benzene, etc.) and its intermediates (Ince & Tezcanli, 2001).

5.10.8.4 Effect of NaCl Concentrations on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

65.04%, 66.48% and 68.77% TFAs removals were observed in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.60a). 19.38%, 20.82% and 23.11% increase in TFAs removals were obtained in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=45.66% TFAs at pH=7.0 and at 30^{o}C). A significant linear correlation between TFAs yields and increasing NaCl concentrations was observed (R^2=0.68, F=11.43, p=0.01) (Figure 5.60a).



(a)



(b)

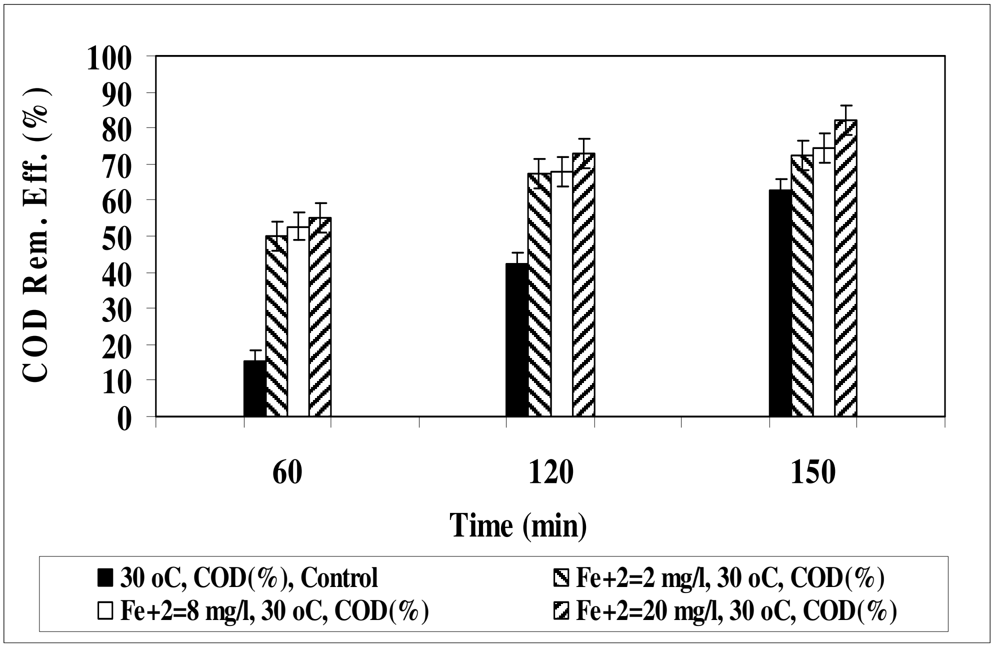
Figure 5.60 Effect of increasing NaCl concentrations on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

67.70%, 69.49% and 71.23% TFAs yields were found in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.60b). The contributions of increasing NaCl concentrations on TFAs removals were 18.86%, 20.65% and 22.39%, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=48.84% TFAs at pH=7.0 and at 60^{o}C). The maximum TFAs removal efficiency was 71.23% in NaCl=15.00 g/l after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between TFAs yields and increasing NaCl concentrations was observed (R^2=0.73, F=13.75, p=0.01) (Figure 5.60b).

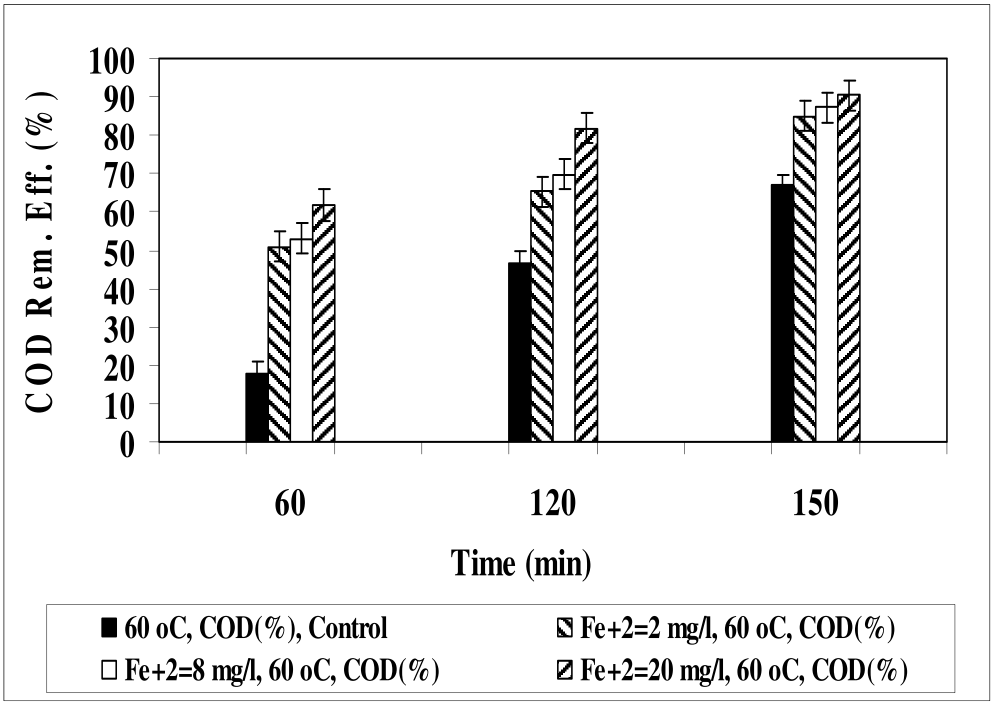
5.10.9 Effect of Fe^{+2} Concentrations on the Removals of COD_{dis} in OMI ww

Increasing Fe^{+2} concentrations (2.00–8.00 and 20.00 mg/l) were added in OMI ww before sonication experiments. 72.48%, 74.38% and 82.24% COD_{dis} removals were observed in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.61a). 9.91%, 11.81% and 19.67% increase in COD_{dis} removals were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (without Fe^{+2} while E=62.57% COD_{dis} at pH=7.0 and at 30^{o}C). A significant linear correlation between COD_{dis} yields and increasing Fe^{+2} concentrations was observed (R^2=0.80, F=6.14, p=0.01) (Figure 5.61a).

84.95%, 87.33% and 90.36% COD_{dis} yields were measured in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.61b). The contribution of 2.00, 8.00 and 20.00 mg/l Fe^{+2} concentrations on COD_{dis} removals were 18.12%, 20.50% and 23.53% respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=66.83% COD_{dis} at pH=7.0 and at 60^{o}C). The maximum COD_{dis} removal efficiency was 90.36% in Fe^{+2}=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between COD_{dis} yields and increasing Fe^{+2} concentrations was observed (R^2=0.81, F=15.93, p=0.01) (Figure 5.61b).



(a)



(b)

Figure 5.61 Effect of increasing Fe^{+2} concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

Bremmer et al. (2008) investigated to the effects of various additives such as Fe^{+2} (elemental, bivalent and trivalent) on the sonochemical destruction of OMI ww. 40.00% COD removals were found at 240 min sonication time, 40 kHz frequency, 500 W power at pH=7.0 with 20.00 mg/l Fe^{+2} addition at 30°C. In this study, 82.24% COD_{dis} removal was observed in 20.00 mg/l Fe^{+2} at 30°C after 150 min sonication time. The COD_{dis} yield is higher than the yield obtained by Bremmer et al. (2008) at 30°C.

Ginos et al. (2006) showed that COD removals in OMI ww were between 10.00% and 30.00% after addition of ferrous sulfate and cationic polyelectrolytes in the range of 200–300 mg/l. In the presence of H_2O_2 and fenton, COD reduction was measured as 60%. In this study, 90.36% COD_{dis} removal was measured in 20.00 mg/l Fe^{+2} at 60°C after 150 min sonication time. In the present study the COD_{dis} yield is higher than the yield obtained by Ginos et al. (2006) at 60°C.

Enhancement of sonochemical degradation of organic compounds can be occurred by the presence of Fe^{+2} (Adewuyi, 2005a; Torres et al., 2007, 2008a). This ion, which are commonly present in the composition of OMI ww, result in H_2O_2 decomposition and $OH^{\bullet}$ generation through the sonication and fenton reactions (Walling et al., 1975) given in Eq. (5.70):

$$Fe^{+2} + H_2O_2 \quad \rightarrow \quad Fe^{+3} + OH^{\bullet} + OH^{-1} \qquad (5.70)$$

5.10.9.1 Effect of Fe^{+2} Concentrations on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

82.77%, 85.57% and 87.07% color removals were found in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.63). 8.32%, 11.12% and 12.62% increase in color removals were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=74.45% color at pH=7.0 and at

30^{o}C). A significant linear correlation between color yields and increasing Fe^{+2} concentrations was observed (R^2=0.75, F=13.97, p=0.01) (Table 5.63).

Table 5.63 Effect of increasing Fe^{+2} concentrations on the color removal efficiencies in OMI ww at 30^{o}C and at 60^{o}C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30^{o}C			**60^{o}C**		
	60. min	**120. min**	**150. Min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
Fe^{+2}=2.00 mg/l	60.42	74.45	82.77	64.63	75.25	87.58
Fe^{+2}=8.00 mg/l	63.43	77.66	85.57	71.34	78.86	89.18
Fe^{+2}=20.00 mg/l	65.13	81.26	87.07	73.85	82.97	93.89

87.58%, 89.18% and 93.89% color yields were measured in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Table 5.63). The contributions of increasing Fe^{+2} concentrations on color removals were 3.81%, 5.41% and 10.12%, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=84.00% color at pH=7.0 and at 60^{o}C). The maximum color removal efficiency was 93.89% in Fe^{+2}=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between color yields and increasing Fe^{+2} concentrations was observed (R^2=0.77, F=13.93, p=0.01) (Table 5.63).

The results performed by Guzman-Duque et al. (2011) showed that the generation of additional $OH^{\bullet}$ in the presence of Fe^{+2} significantly increased the degradation rate of color in OMI ww. In the study performed by Guzman-Duque et al. (2011) after 180 min irradiation more than 60.00% color removal was observed. The reaction of Fe^{+2} with H_2O_2 produces additional $OH^{\bullet}$ Eq. (5.70) which is supported by a lower accumulation of H_2O_2 during the sonochemical degradation of colorful compounds in the presence of Fe^{+2}. On the other hand, when H_2O_2 was present in the reaction system, and Fe^{+3} is dissolved in acid solution to produce Fe^{+2}, the latter would react with H_2O_2 to generate $OH^\bullet$ in Eqs. (5.71) and (5.72):

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + O_2H^\bullet + H^+ \tag{5.71}$$

$$Fe^{+2} + OH^\bullet \rightarrow Fe^{+3} + OH^- \tag{5.72}$$

The generation of $OH^\bullet$ was dependent on H_2O_2 concentration based on Eqs. (5.70) and (5.72). Consequently, the decolorization rate increased with H_2O_2 concentration (Svitelska et al., 2004). For the combined Fe^{+2}/ultrasound experiments, the enhancement of degradation rate by Fe^{+2} additions was mainly due to the highly produced $OH^\bullet$ concentration. Sonochemically generated H_2O_2 can be effectively utilized when Fe^{+2} is added to the system, because additional $OH^\bullet$ generation is achieved in Eqs. (5.73), (5.74) and (5.75). If Eq. (5.70) proceeds at a high rate, the reduction of Fe^{+3} to Fe^{+2} by H_2O_2 occurs at a lower rate. Then, the initial degradation rate in the Fe^{+2}/ultrasound process is higher than that observed in the case of ultrasound alone. This is due to the fact that at high Fe^{+2} concentrations, the solution undergoes self-quenching of $OH^\bullet$ by the added amounts of Fe^{+2} to produce Fe^{+3}, (Ghodbane & Hamdaoui, 2009) given in Eqs. (5.73), (5.74) and (5.75).

$$Fe^{+3} + H_2O_2 \rightarrow Fe-O_2H^{+2} + H^+ \tag{5.73}$$

$$Fe-O_2H^{+2} \rightarrow Fe^{+2} + O_2H^\bullet \tag{5.74}$$

$$Fe^{+3} + O_2H^\bullet \rightarrow Fe^{+2} + O_2 + H^+ \tag{5.75}$$

5.10.9.2 Effect of Fe^{+2} Concentrations on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

78.42%, 81.22% and 84.75% total phenol removals were observed in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Table 5.64). 19.02%, 21.82% and 25.35% increase in total phenol removals were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=59.40% total phenol at pH=7.0 and at 30^{o}C). A significant linear correlation between total phenol yields and increasing Fe^{+2} concentrations was observed (R^2=0.69, F=12.11, p=0.01) (Table 5.64).

Table 5.64 Effect of increasing Fe^{+2} concentrations on the total phenol removal efficiencies in OMI ww at 30^{o}C and at 60^{o}C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30^{o}C			**60^{o}C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
Fe^{+2}=2.00 mg/l	41.32	74.76	78.42	42.54	75.41	82.35
Fe^{+2}=8.00 mg/l	42.45	77.69	81.22	47.61	78.08	84.88
Fe^{+2}=20.00 mg/l	47.21	80.37	84.75	47.78	82.88	89.64

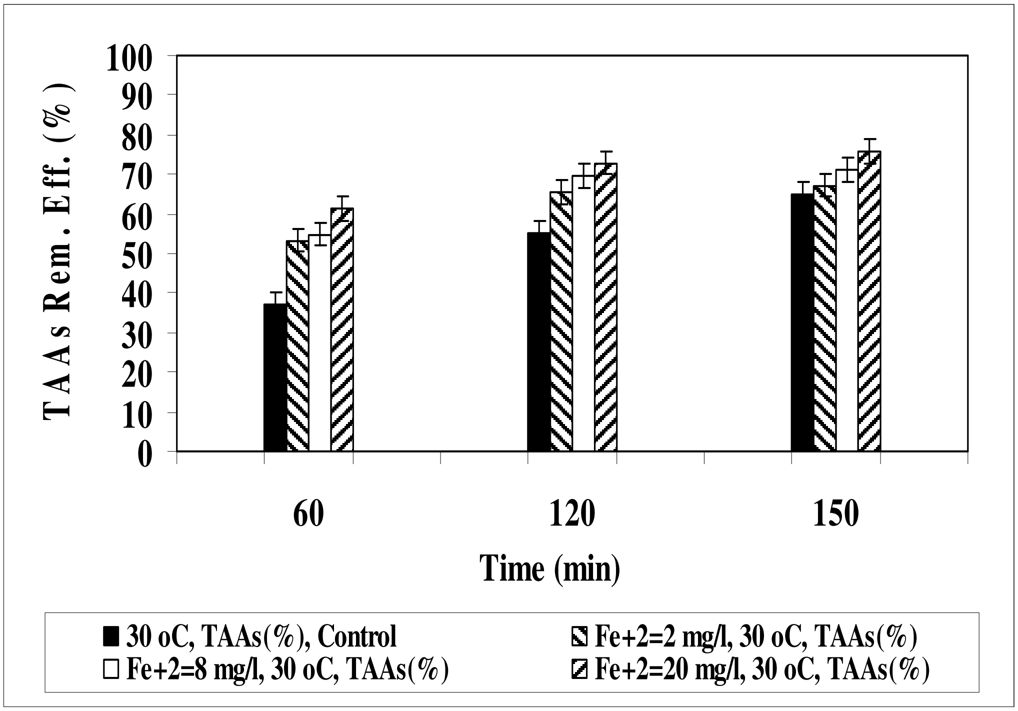
82.35%, 84.88% and 89.64% total phenol yields were found in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Table 5.64). The contributions of increasing Fe^{+2} concentrations on the total phenol removals were 21.11%, 23.64% and 28.40% in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=61.24% total phenol at pH=7.0 and at 60^{o}C). The maximum total phenol removal efficiency was 89.64% in Fe^{+2}=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between total phenol yields and increasing Fe^{+2} concentrations was observed (R^2=0.76, F=14.50, p=0.01) (Table 5.64).

It is revealed that sonochemical degradation of phenol is governed by the extent of radical scavenging, both inside and outside the bubble. Phenomenon of radical scavenging influences the probability of interaction between the phenol molecules and radicals. The extent of degradation in the presence of Fe^{+2} has been much higher. This result has been attributed to higher reactivity and uniform concentration of the Fe^{+2} in the medium, as a result of which they can effectively scavenge the radicals generated by cavitations bubbles (Sivasankar & Moholkar, 2009b).

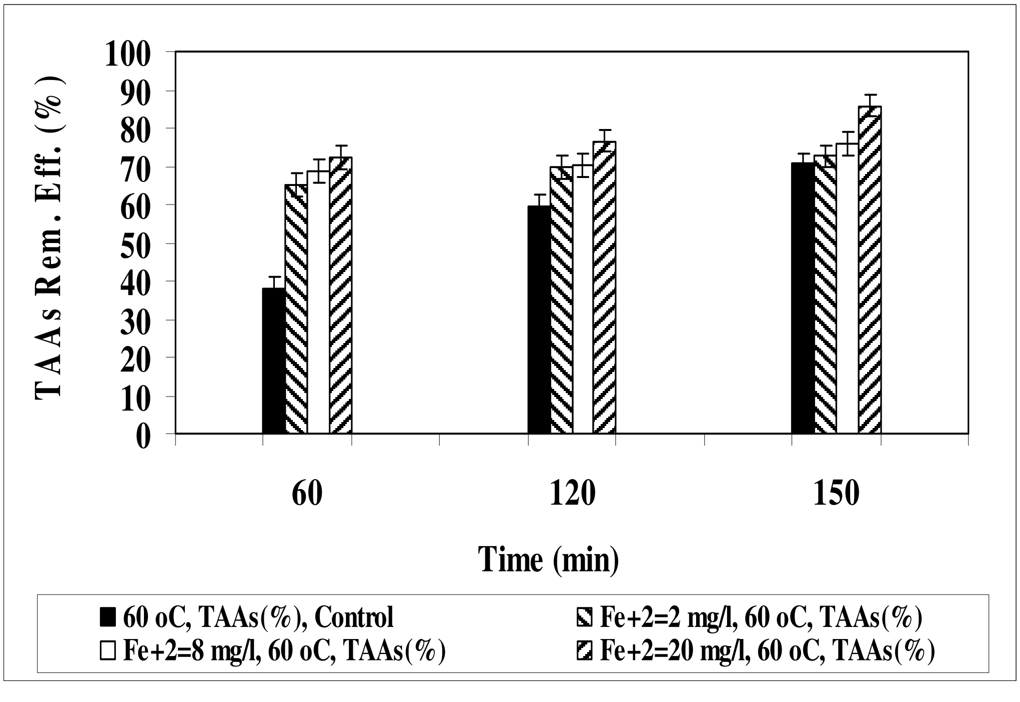
5.10.9.3 Effect of Fe^{+2} Concentrations on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

67.25%, 71.06% and 75.88% TAAs removals were measured in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.62a). 2.27%, 6.08% and 10.90% increase in TAAs removals were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=64.98% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing Fe^{+2} concentrations was not observed (R^2=0.36, F=4.03, p=0.01) (Figure 5.62a).

72.60%, 76.06% and 85.88% TAAs yields were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.62b). The contribution of Fe^{+2} concentrations on TAAs removals were 2.08%, 5.54% and 15.36% in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=70.52% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 85.88% in Fe^{+2}=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing Fe^{+2} concentrations was not observed (R^2=0.38, F=3.97, p=0.01) (Figure 5.62b).



(a)



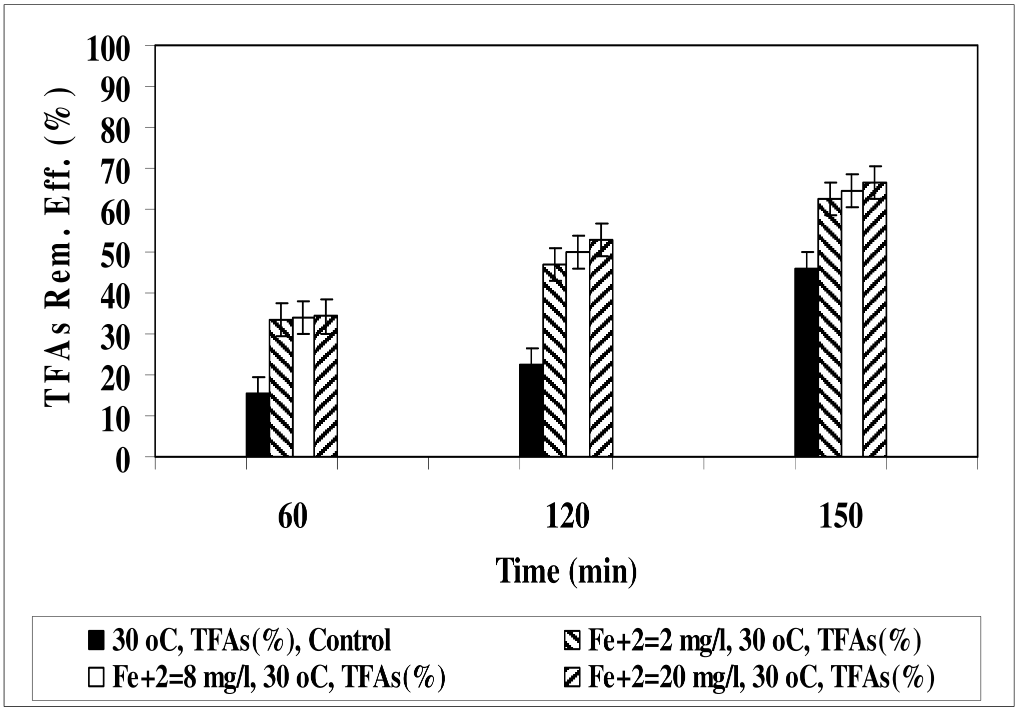
(b)

Figure 5.62 Effect of increasing Fe^{+2} concentrations on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

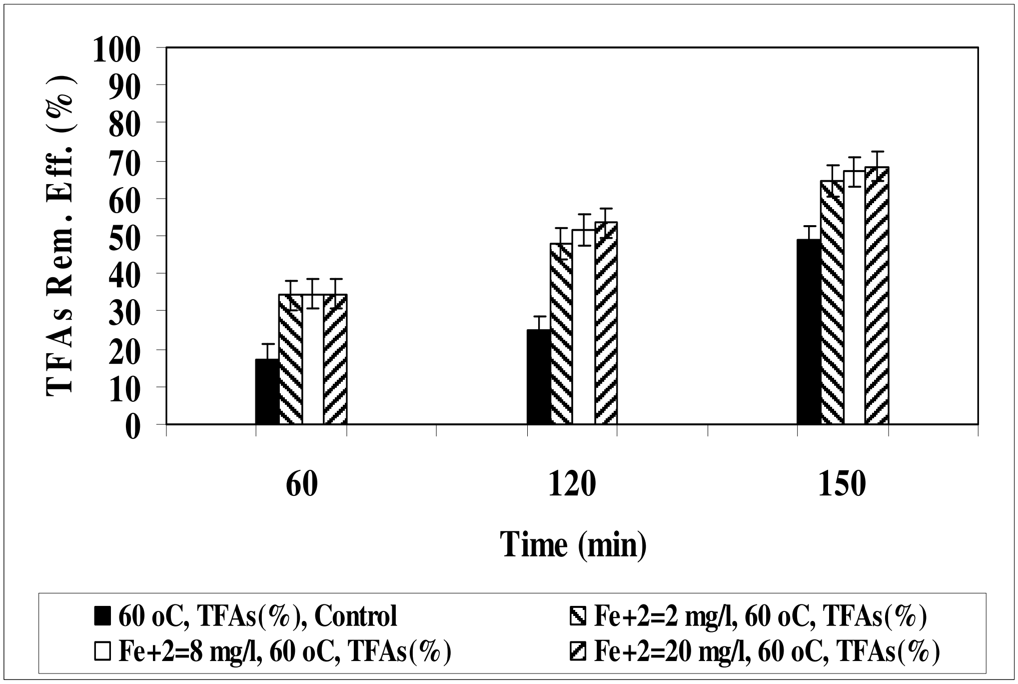
5.10.9.4 Effect of Fe^{+2} Concentrations on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

62.74%, 64.70% and 66.78% TFAs removals were observed in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.63a). 17.08%, 19.04% and 21.12% increase in TFAs removals were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=45.66% TFAs at pH=7.0 and at 30^{o}C). A significant linear correlation between TFAs yields and increasing Fe^{+2} concentrations was observed (R^2=0.85, F=16.36, p=0.01) (Figure 5.63a).

64.63%, 67.04% and 68.40% TFAs yields were measured in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.63b). The contribution of 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2} concentrations on TFAs removals were 15.79%, 18.20% and 19.56%, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=48.84% TFAs at pH=7.0 and at 60^{o}C). The maximum TFAs removal efficiency was 68.40% in Fe^{+2}=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between TFAs yields and increasing Fe^{+2} concentrations was observed (R^2=0.88, F=17.41, p=0.01) (Figure 5.63b).



(a)



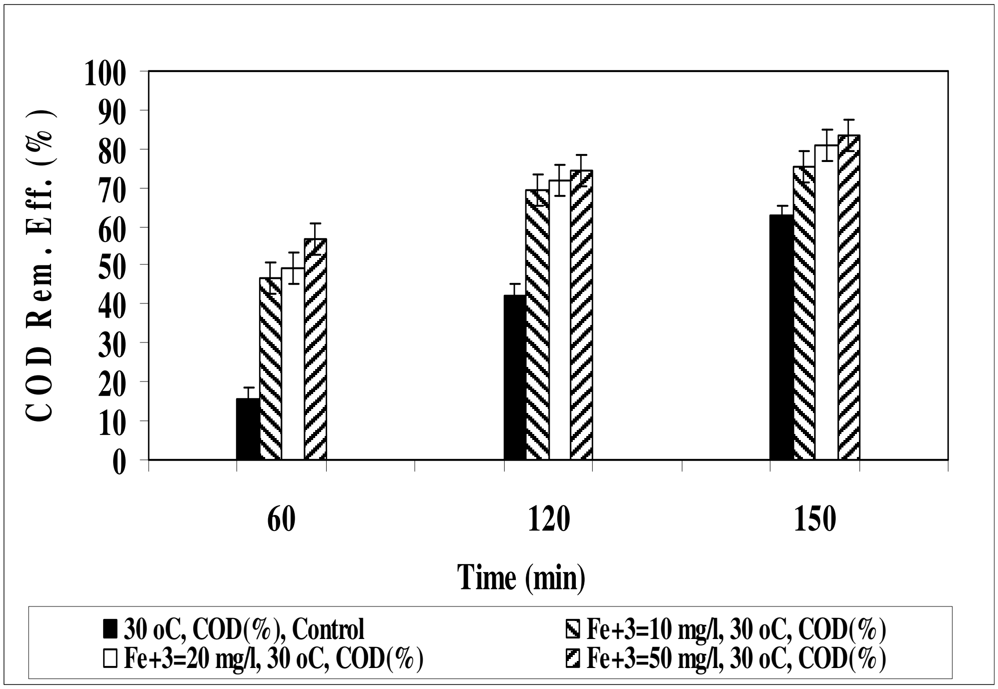
(b)

Figure 5.63 Effect of increasing Fe^{+2} concentrations on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

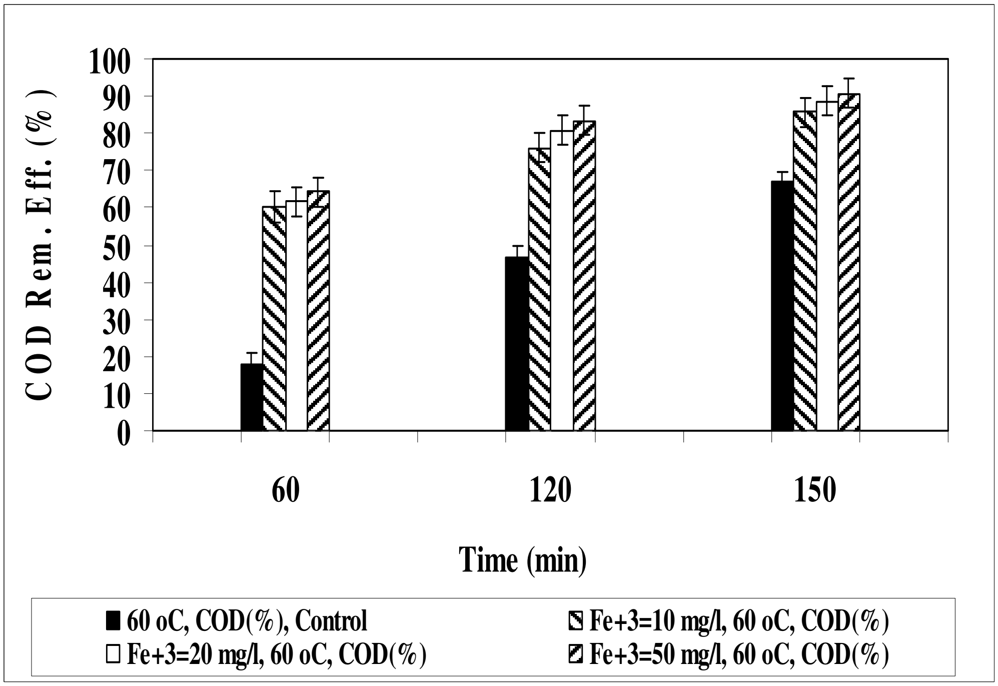
5.10.10 Effect of Fe^{+3} Concentrations on the Removals of COD_{dis} in OMI ww

Increasing Fe^{+3} concentrations (10.00–20.00 and 50.00 mg/l) were added in OMI ww before sonication process. 75.24%, 81.08% and 83.42% COD_{dis} removals were found in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.64a). 12.67%, 18.51% and 20.85% increase in COD_{dis} removals were obtained in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (without Fe^{+3} while E=62.57% COD_{dis} at pH=7.0 and at 30^{o}C). A significant linear correlation between COD_{dis} yields and increasing Fe^{+3} concentrations was observed (R^2=0.90, F=18.94, p=0.01) (Figure 5.64a).

85.70%, 88.61% and 90.75% COD_{dis} yields were observed in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.64b). The contributions of increasing Fe^{+3} concentrations on COD_{dis} removals were 18.87%, 21.78% and 23.92%, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=66.83% COD_{dis} at pH=7.0 and at 60^{o}C). The maximum COD_{dis} removal efficiency was 90.75% in Fe^{+3}=50.00 mg/l after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between COD_{dis} yields and increasing Fe^{+3} concentrations was observed (R^2=0.94, F=19.77, p=0.01) (Figure 5.64b).



(a)



(b)

Figure 5.64 Effect of increasing Fe^{+3} concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

An important step in the degradation of OMW is the breakdown of colorful polymeric phenolics via decolorization to monomers which can subsequently be mineralized (Sayadi & Ellouz, 1992; Vinciguerra et al., 1995). It has been shown that there is a significant correlation between OMW decolorization, reduction of COD, TOC and phenolic compounds and Fe^{+3} (Boominathan et al., 1993; Morrison & Mulder, 1994; Sayadi & Ellouz, 1995; Vinciguerra et al., 1995). In the present study also, a significant linear correlation between COD_{dis} removals and Fe^{+3} was observed in OMI ww throughout sonication experiments (R^2=0.86, F=15.98, p=0.01).

5.10.10.1 Effect of Fe^{+3} Concentrations on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

84.27%, 86.67% and 88.08% color removals were measured in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.65). An increase of 9.82%, 12.22% and 13.63% color removals were obtained in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=74.45% Color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing Fe^{+3} concentrations was not observed (R^2=0.36, F=0.48, p=0.01) (Table 5.65).

85.17%, 88.28% and 91.08% color yields were observed in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.65). The contribution of increasing Fe^{+3} concentrations on color removals were 1.40%, 4.51% and 7.31% in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=83.77% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 91.08% in Fe^{+3}=50.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C). A significant linear correlation between color yields and increasing Fe^{+3} concentrations was not observed (R^2=0.39, F=4.51, p=0.01) (Table 5.65).

Table 5.65 Effect of increasing Fe^{+3} concentrations on the color removal efficiencies in OMI ww at 30^{o}C and at 60^{o}C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30^{o}C			**60^{o}C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
Fe^{+3}=10.00 mg/l	40.28	73.65	84.27	63.34	76.55	85.17
Fe^{+3}=20.00 mg/l	42.08	75.15	86.67	70.44	80.76	88.28
Fe^{+3}=50.00 mg/l	50.30	77.56	88.08	75.05	82.46	91.08

The effect of the sonication in the reaction medium in the presence of the heterogeneous Fe^{+3} catalysts and H_2O_2 could be explained as follows. The reaction of ultrasound coupled with the fenton-like reagent can be described by the Eqs. (5.76), (5.77), (5.78) and (5.79) where the symbol ≡ represents the Fe^{+3} species bound to the surface of the Fe^{+3} catalyst.

$$\equiv Fe^{+3} + H_2O_2 \quad \rightarrow \quad \equiv Fe(O_2H)^{+2} + H^{+} \tag{5.76}$$

$$\equiv Fe(O_2H)^{+2} \quad \rightarrow \quad \equiv Fe^{+2} + O_2H^{\bullet} \tag{5.77}$$

$$\equiv Fe(O_2H)^{+2} + Ultrasound \quad \rightarrow \quad \equiv Fe^{+2} + O_2H^{\bullet} \tag{5.78}$$

$$\equiv Fe^{+2} + H_2O_2 \quad \rightarrow \quad \equiv Fe^{+3} + OH^{-} + OH^{\bullet} \tag{5.79}$$

5.10.10.2 Effect of Fe^{+3} Concentrations on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

82.83%, 85.97% and 88.59% total phenol removals were found in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.66). An increase of 23.43%, 26.57% and 29.19% total phenol removals were obtained in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=59.40% total phenol at pH=7.0 and at 30°C). A significant linear correlation between total phenol yields and increasing Fe^{+3} concentrations was observed (R^2=0.87, F=16.49, p=0.01) (Table 5.66).

Table 5.66 Effect of increasing Fe^{+3} concentrations on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

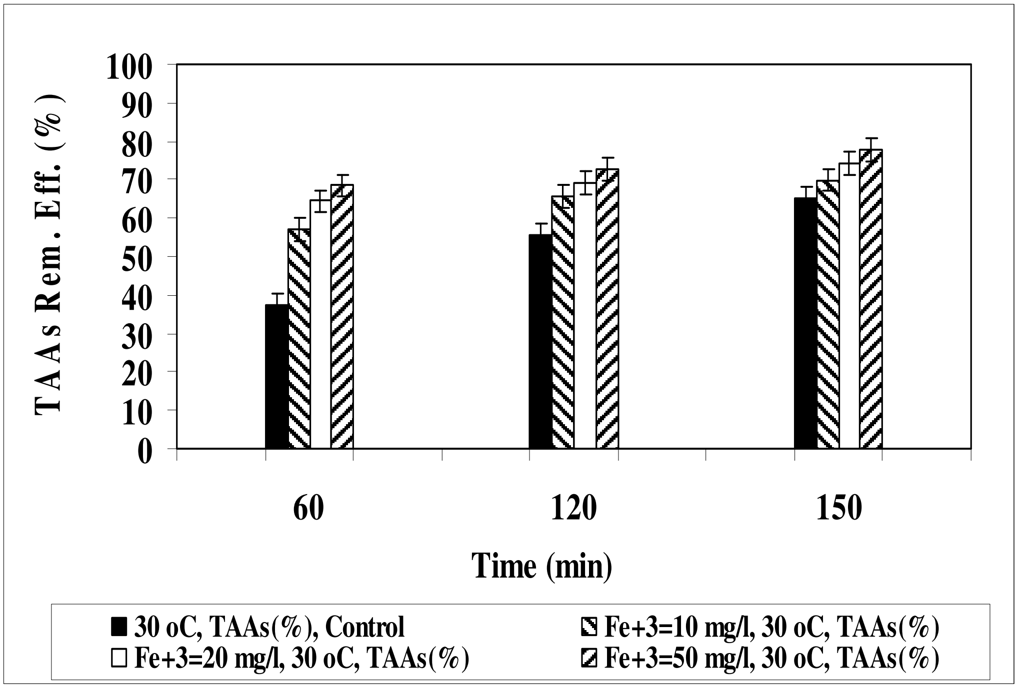
Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
Fe^{+3}=10.00 mg/l	44.02	77.33	82.83	45.28	82.57	86.10
Fe^{+3}=20.00 mg/l	49.43	79.95	85.97	50.04	82.78	88.85
Fe^{+3}=50.00 mg/l	51.67	82.44	88.59	52.75	85.49	92.58

86.10%, 88.85% and 92.58% total phenol yields were measured in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.66). The contribution of Fe^{+3} concentrations on total phenol removals were 24.86%, 27.61% and 31.34% in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=61.24% total phenol at pH=7.0 and at 60°C). The maximum total phenol removal efficiency was 92.58% in Fe^{+3}=50.00 mg/l after 150 min sonication at pH=7.0 and at 60°C. A significant linear correlation between total phenol yields and increasing Fe^{+3} concentrations was observed (R^2=0.88, F=16.32, p=0.01) (Table 5.66).

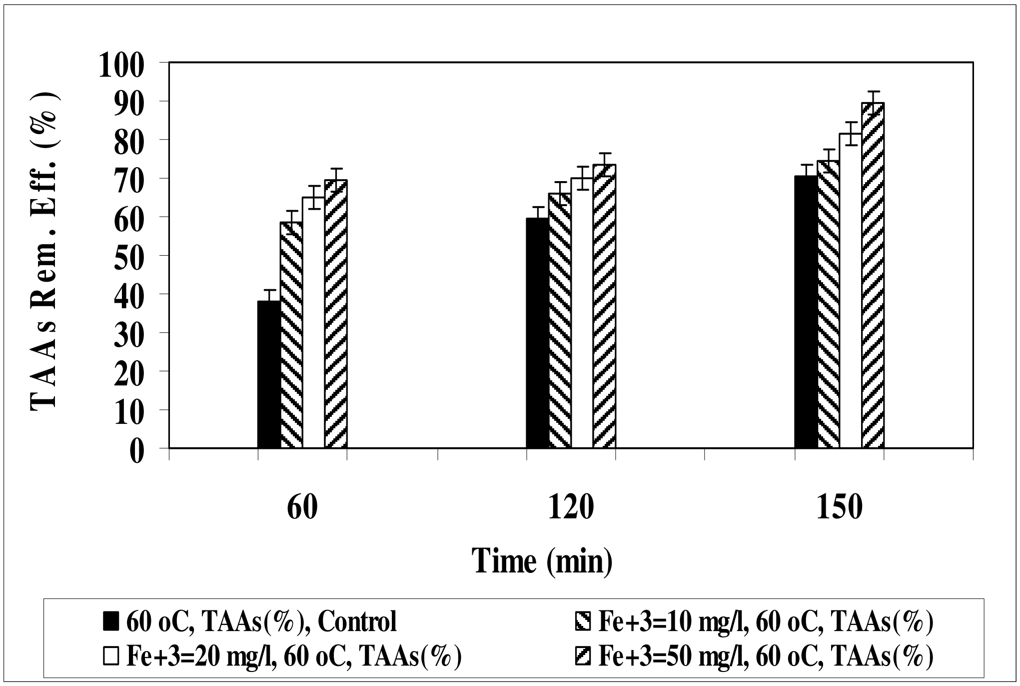
5.10.10.3 Effect of Fe^{+3} Concentrations on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

69.92%, 74.21% and 77.78% TAAs removals were obtained in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.65a). An increase of 4.94%, 9.23% and 12.80% TAAs removals were observed in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=64.98% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing Fe^{+3} concentrations was not observed (R^2=0.33, F=3.47, p=0.01) (Figure 5.65a).

74.38%, 81.47% and 89.56% TAAs yields were found in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.65b). The contributions of increasing Fe^{+3} concentrations on TAAs removals were 3.86%, 10.95% and 19.04% in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=70.52% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 89.56% in Fe^{+3}=50.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing Fe^{+3} concentrations was observed (R^2=0.78, F=13.89, p=0.01) (Figure 5.65b).



(a)



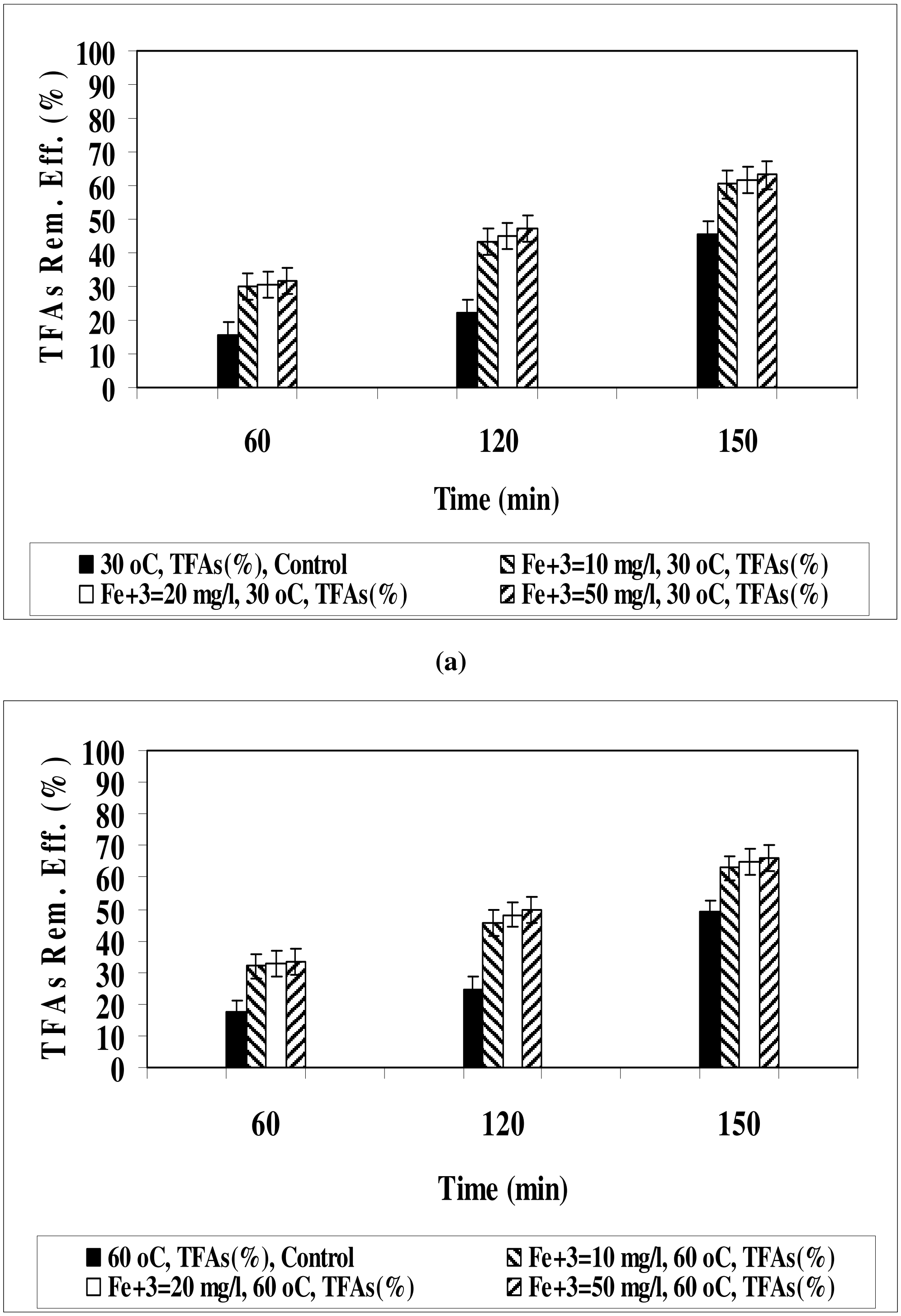
(b)

Figure 5.65 Effect of increasing Fe^{+3} concentrations on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

5.10.10.4 Effect of Fe^{+3} Concentrations on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

60.31%, 61.51% and 63.12% TFAs removals were observed in 10.00 mg/l, 20 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.66a). 14.65%, 15.85% and 17.46% increase in TFAs removals were obtained in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=45.66% TFAs at pH=7.0 and at 30°C). A significant linear correlation between TFAs yields and increasing Fe^{+3} concentrations was observed ($R^2=0.75$, F=14.11, p=0.01) (Figure 5.66a).

62.96%, 64.78% and 65.93% TFAs yields were measured in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.66b). The contributions of increasing Fe^{+3} concentrations on TFAs removals were 14.12%, 15.94% and 17.09% in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=48.84% TFAs at pH=7.0 and at 60°C). The maximum TFAs removal efficiency was 65.93% in Fe^{+3}=50.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TFAs yields and increasing Fe^{+3} concentrations was observed ($R^2=0.73$, F=14.94, p=0.01) (Figure 5.66b).



(a)

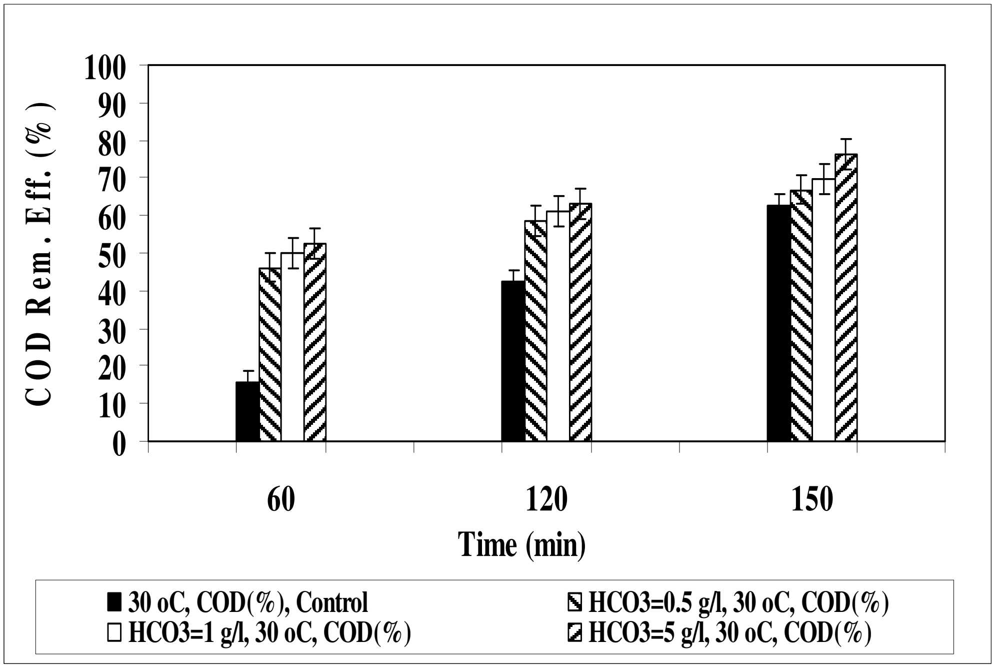
(b)

Figure 5.66 Effect of increasing Fe^{+3} concentrations on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

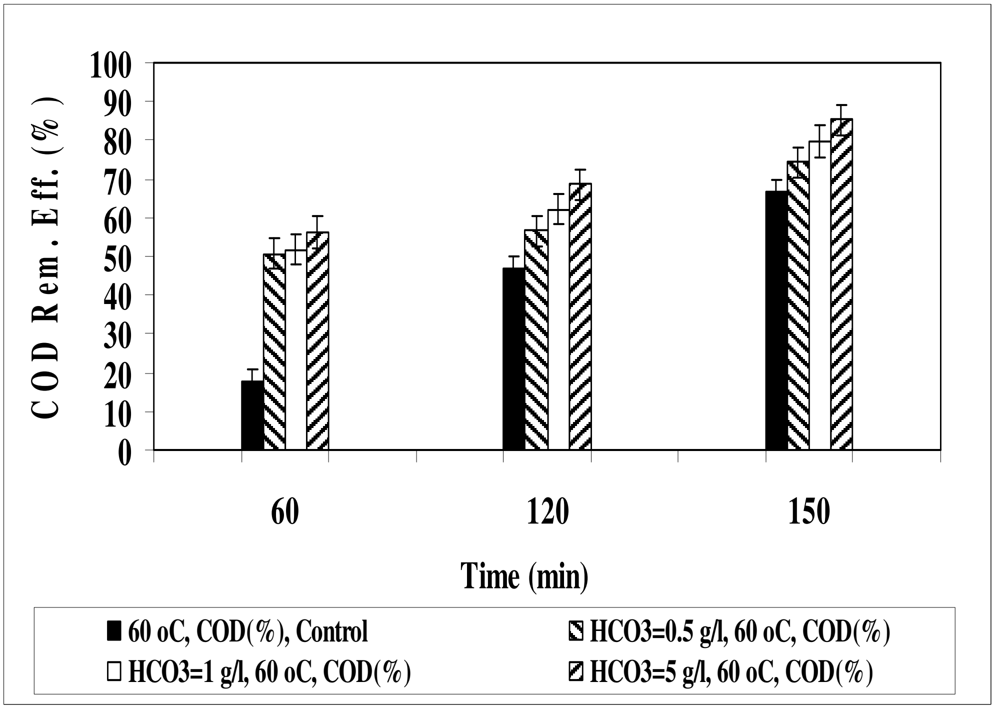
5.10.11 Effect of HCO_3^{-1} Concentrations on the Removals of COD_{dis} in OMI ww

Increasing HCO_3^{-1} (0.50 g/l, 1.00 and 5.00 g/l) concentrations were added in OMI ww before sonication experiments. 66.92%, 69.66% and 76.06% COD_{dis} removals were observed in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.67a). 4.35%, 7.09% and 13.49% increase in COD_{dis} removals were obtained in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without HCO_3^{-1} while E=62.57% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.31, F=2.23, p=0.01) (Figure 5.67a).

74.23%, 79.72% and 85.21% COD_{dis} yields were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.67b). The contributions of increasing HCO_3^{-1} concentrations on COD_{dis} removals were 7.40%, 12.89% and 18.38% in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=66.83% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 85.21% in HCO_3^{-1}=5.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.44, F=4.28, p=0.01) (Figure 5.67b).



(a)



(b)

Figure 5.67 Effect of increasing HCO_3^{-1} concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

The scavenging of $OH^{\bullet}$ by the anions would yield radical species such as $CO_3^{\bullet\,-}$, (Minero et al., 2008) in Eqs. (5.80) and (5.81):

$$OH^{\bullet} + HCO_3^{-} \rightarrow H_2O + CO_3^{\bullet\,-} \tag{5.80}$$

$$OH^{\bullet} + CO_3^{-2} \rightarrow OH^{-} + CO_3^{\bullet\,-} \tag{5.81}$$

The study performed by Gogate et al. (2004b) showed 80.00% COD removal in OMI ww with 1.50 g/l HCO_3^{-1} concentration at 40 kHz frequency and at a sonication power of 500 W after 100 min sonication time at 60°C. In this study, 85.21% COD_{dis} removal was found in 5.00 g/l HCO_3^{-1} at 60°C after 150 min sonication time. In the present study, the COD_{dis} yield is higher than the yield observed by Gogate et al. (2004b) at 60°C as mentioned above.

5.10.11.1 Effect of HCO_3^{-1} Concentrations on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

80.96%, 82.97% and 85.17% color removals were observed in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.67). 6.51%, 8.52% and 10.72% increase in color removals were obtained in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=74.45% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.37, F=3.92, p=0.001) (Table 5.67).

87.47%, 89.18% and 91.78% color yields were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.67). The contributions of increasing HCO_3^{-1} concentrations on the color removals were 3.7%, 5.41% and 8.01% in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=83.77% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 91.78% in HCO_3^{-1}=5.00 g/l after 150 min sonication time at pH=7.0 and at 60°C.

A significant linear correlation between color yields and increasing HCO_3^{-1} concentration was not observed at 60°C ($R^2=0.41$, F=5.02, p=0.001) (Table 5.67).

Table 5.67 Effect of increasing HCO_3^{-1} concentrations on the color removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
HCO_3^{-1}=0.50 g/l	61.52	73.75	80.96	73.85	79.96	87.47
HCO_3^{-1}=1.00 g/l	64.43	75.85	82.97	77.45	82.57	89.18
HCO_3^{-1}=5.00 g/l	67.64	77.76	85.17	81.06	83.87	91.78

The presence of HCO_3^{-1} increased the yields of color originating from the phenolic compounds, lignin, tannins, etc. In the presence of HCO_3^{-1}, the organic compounds given the color mentioned above are sono-degraded by the $OH^{\bullet}$ and these can reach to the steady-state in the bulk solution (Guzman-Duque et al., 2011). Petrier et al. (2010) and Merouani et al. (2010b) found that when 183.00 mg/l HCO_3^{-1} are added to the OMI ww, HCO_3 react with $OH^{\bullet}$ to produce the $CO_3^{\bullet}$, which unlike the $OH^{\bullet}$, can migrate to the bulk solution an induce the degradation of the organic molecules given the color in OMI ww through sonication. In this study, 91.78% color removal was observed at a HCO_3^{-1} concentration of 5.00 g/l after 150 min sonication time at 60°C.

The H_2O_2 measurement during acoustic cavitation in the OMI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the color treatment by sonication in OMI ww decreases with increasing sonication time at 60°C (Table 5.68). In deionized water samples the H_2O_2 was accumulated and its concentration was measured as 165.00 mg/l, whereas this level was 166.00 mg/l after 60 min sonication time in OMI ww. The H_2O_2 concentration was only 18.00 mg/l in OMI ww after 150 min sonication time in the samples containing 5.00 g/l HCO_3^{-1} (Table 5.68). The $OH^{\bullet}$ ion concentrations also increased from $73.00 x 10^{-60}$ to $31.00 x 10^{-8}$ mg/l after 150 min sonication time in OMI ww containing 5.00 g/l HCO_3^{-1}. This showed that hydroxylation is the main mechanism for the removal of color in OMI ww. In other words, $OH^{\bullet}$ is the major process for complete degradation of color in OMI ww.

Table 5.68 Effect of 5.00 g/l HCO_3^{-1} on H_2O_2 production and $OH^{\bullet}$ ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^{\bullet}$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	165.00	0.00
H_2O_2 concentration (mg/l) for color (60°C) after 30 min sonication	166.00	$73.00 x 10^{-60}$
H_2O_2 concentration (mg/l) for color (60°C) after 120 min sonication	79.00	$46.00 x 10^{-42}$
H_2O_2 concentration (mg/l) for color (60°C) after 150 min sonication	18.00	$31.00 x 10^{-8}$

Petrier et al. (2010) found that at high HCO_3^{-1} concentrations such as 20.00 g/l all of the $OH^{\bullet}$ sonochemically generated is scavenged by these ions to produce $CO_3^{\bullet}$. Because of the high relative concentration of the $CO_3^{\bullet}$ obtained, the efficiency of the color removal decreased (Petrier et al., 2010). The studies performed by Guzman-Duque et al. (2011) showed that the effect of HCO_3^{-1} on the sonochemical degradation of the color is dependent on the initial pollutant concentration. When a concentration of 20.00 mg/l of dyestuff was sonicated, the color yield increased to 60.00% in the presence of low HCO_3^{-1} concentrations. The color yields decreased to 20.00% in the presence of high HCO_3^{-1} concentrations. Therefore, it can be concluded that high $NaHCO_3$ concentrations have detrimental effect on the color removal in OMI ww (Guzman-Duque et al., 2011). In this study, as the HCO_3^{-1} concentration increased from 0.50 to 5.00 g/l, the color yields increased as the temperature and the sonication times increased. A significant multiple linear regression was obtained between color yields, increasing HCO_3^{-1} concentrations, sonication temperatures and times ($R^2=0.84$, $F=19.01$, $p=0.01$). Maximum 91.78% color removal was measured in 5.00 g/l HCO_3^{-1} at 60°C after 150 min sonication time. The color yield is higher than the yield obtained by Guzman-Duque et al. (2011) at 60°C as mentioned above.

5.10.11.2 Effect of HCO_3^{-1} Concentrations on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

80.33%, 82.82% and 85.66% total phenol removals were observed in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.69). 20.93%, 23.42% and 26.26% increase in total phenol removals were obtained in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=59.40% total phenol at pH=7.0 and at 30°C). A significant linear correlation between total phenol yields and increasing HCO_3^{-1} concentrations was observed ($R^2=0.81$, $F=17.76$, $p=0.001$) (Table 5.69).

88.49%, 91.77% and 93.72% total phenol yields were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.69). The contribution of HCO_3^{-1} concentrations on total phenol removals were 27.25%, 30.53% and 32.48% in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=61.24% total phenol at pH=7.0 and at 60°C). The maximum total phenol removal efficiency was 93.72% in HCO_3^{-1}=5.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between total phenol yields and increasing HCO_3^{-1} concentration was observed ($R^2=0.84$, $F=17.89$, $p=0.001$) (Table 5.69).

Table 5.69 Effect of increasing HCO_3^{-1} concentrations on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
HCO_3^{-1}=0.50 g/l	42.89	73.44	80.33	44.54	79.03	88.49
HCO_3^{-1}=1.00 g/l	48.08	76.06	82.82	50.26	82.39	91.77
HCO_3^{-1}=5.00 g/l	50.86	81.04	85.66	55.93	87.23	93.72

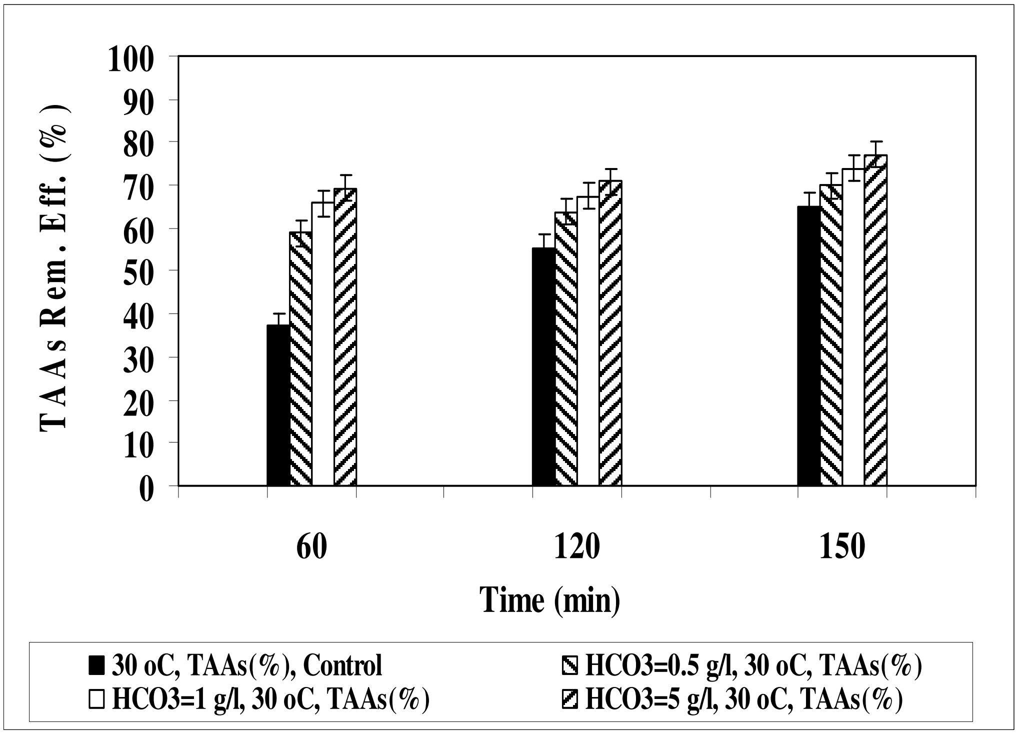
In a study performed by Petrier et al. (2010) 72.00% phenol removal was achieved at 40 kHz frequency, at 300 W power, after 120 min sonication time at 60°C. Several papers have reported similar positive and negative effects of low and high CO_3/ HCO_3^{-1} ion concentration on the sonochemical degradation of bisphenol A (Petrier et al., 2010) and some organic compounds given the color to the OMI ww (Merouani et al., 2010b). In this study, it was found that as the HCO_3^{-1}concentration increased from 0.50 to 5.00 g/l, the total phenol yields increased as the temperature and the sonication times increased. A significant multiple linear regressions were obtained between total phenol yields, increasing HCO_3^{-1} concentrations, sonication temperatures and times (R^2=0.88, F=1998, p=0.01). Maximum 93.72% total phenol removal was measured in 5.00 g/l HCO_3^{-1} at 60°C after 150 min sonication time. In this study the total phenol yield is higher than the yield obtained by Petrier et al. (2010) at 60°C as mentioned above.

The study by Kiril Mert et al. (2010) showed 85.00% total phenol removal in OMI ww by fenton-like processing following the acid cracking and coagulation processes. In this study, 93.72% total phenol removal was measured in 5.00 g/l HCO_3^{-1} at 60°C after 150 min sonication time. In this study, the total phenol yield is higher than the yield observed by Kiril Mert et al. (2010) at 60°C.

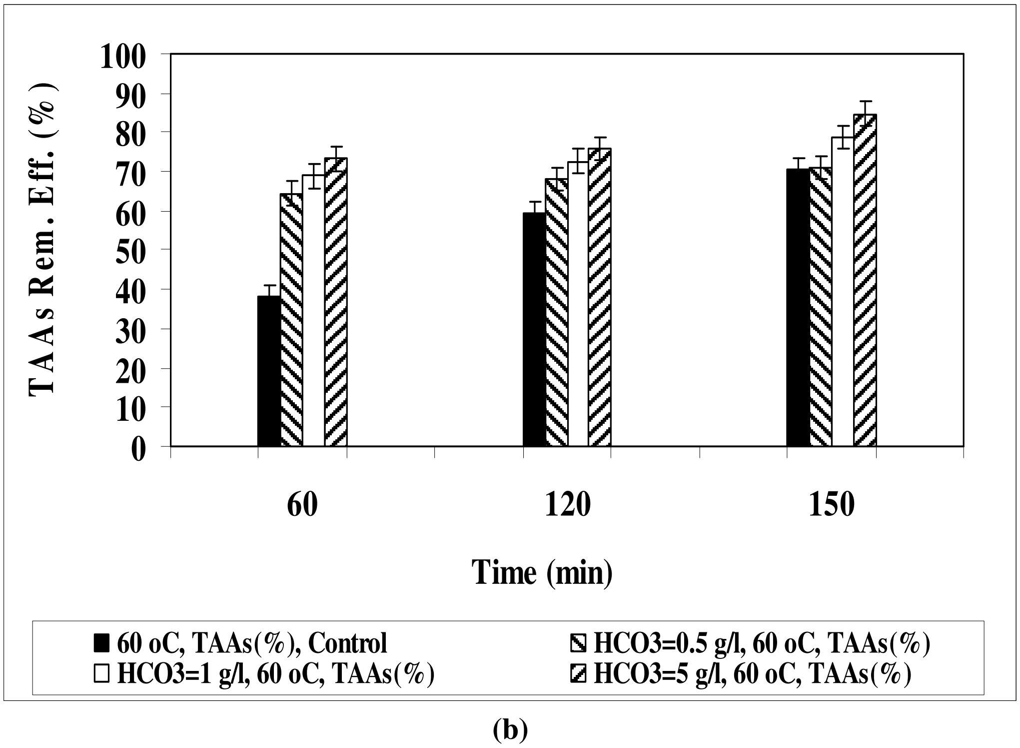
5.10.11.3 Effect of HCO_3^{-1} Concentrations on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

69.85%, 73.91% and 77.11% TAAs removals were observed in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.68a). 4.87%, 8.93% and 12.13% increase in TAAs removals were obtained in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (64.98% TAAs yield at pH=7.0 and at 30^{o}C). A significant linear correlation between TAAs yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.38, F=4.76, p=0.001) (Figure 5.68a).

70.98%, 78.77% and 84.78% TAAs yields were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.68b). The contribution of HCO_3^{-1} concentrations on TAAs removals were 8.25% and 14.26% in 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=70.52% TAAs at pH=7.0 and at 60^{o}C). The maximum TAAs removal efficiency was 84.78% in HCO_3^{-1}=5.00 g/l after 150 min sonication time at 60^{o}C. A significant linear correlation between TAAs yields and increasing HCO_3^{-1} concentration was not observed (R^2=0.37, F=3.70, p=0.001) (Figure 5.68b).



(a)



(b)

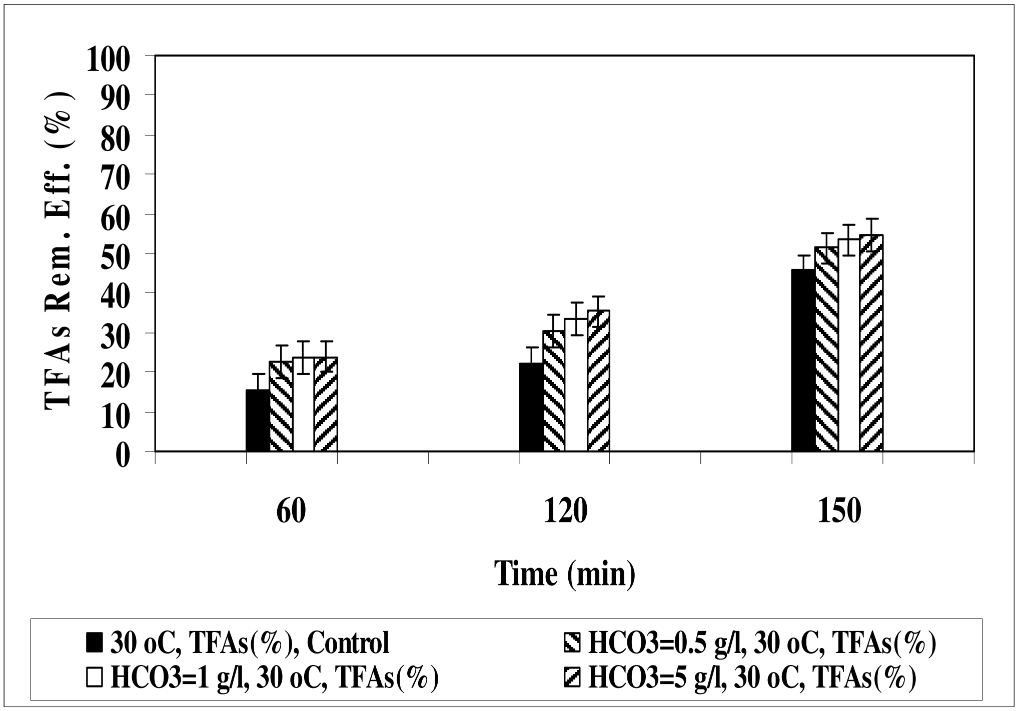
Figure 5.68 Effect of increasing HCO_3^{-1} concentrations on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

HCO_3^{-1} increase the removal yield of TAAs by enhancing the effective mass transfer between aromatic amines and $OH^{\bullet}$ ions near the cavitation bubbles through sonodegradation of OMI ww (Mecciarovas et al., 2003). Tang & Isacsson (2005) found 43.00% TAAs (toluene, ethylbenzene, m–xylene, p–xylene, o–xylene, 3–ethyltoluene, 1,3,5–trimethylbenzene, 2–ethyltoluene, 1,2,4–trimethylbenzene, 1,2,3–trimethylbenzene, 1,2,3,4–tetramethylbenzene) removals in OMI ww after 60 min sonication time at 30°C at a HCO_3^{-1} concentration of 4.00 g/l. In this study, 69.34% TAAs removal was observed at 30°C after 60 min sonication time with 5.00 g/l HCO_3^{-1} addition. The TAAs removal was obtained by Tang & Isacsson (2005) is lower than the present study at 30°C after 60 min sonication.

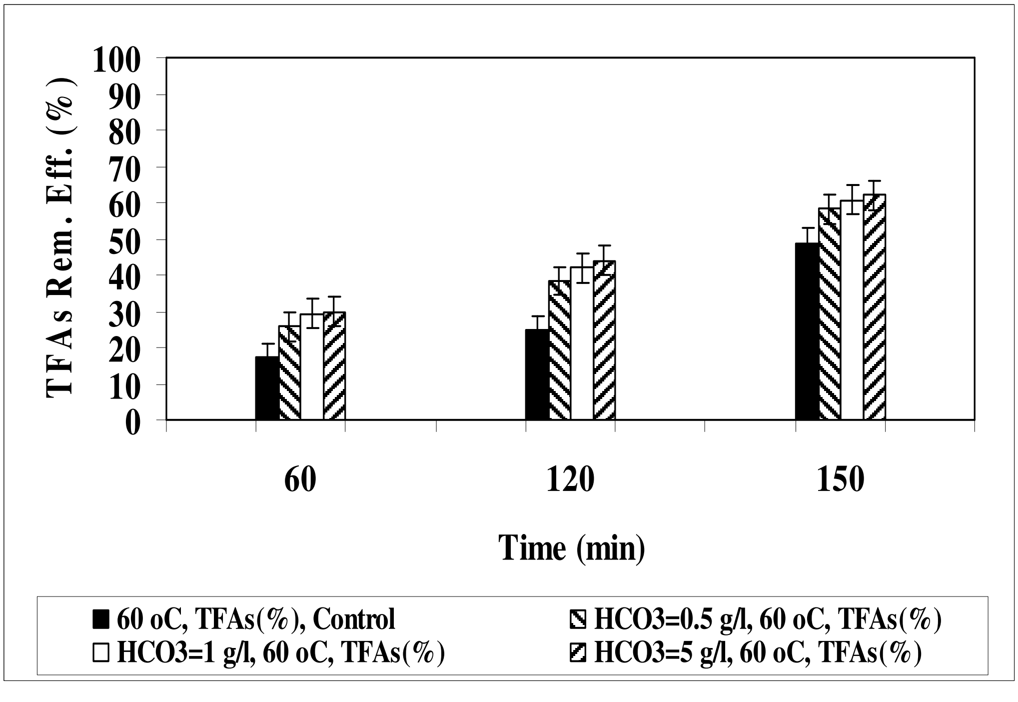
5.10.11.4 Effect of HCO_3^{-1} Concentrations on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

51.31%, 53.47% and 54.73% TFAs removals were observed in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.69a). 5.65%, 7.81% and 9.07% increase in TFAs removals were obtained in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=45.66% TFAs at pH=7.0 and at 30°C). A significant linear correlation between TFAs yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.38, F=4.03, p=0.001) (Figure 5.69a).

58.12%, 60.61% and 61.91% TFAs yields were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.69b). The contribution of HCO_3^{-1} concentrations on TFAs removals were 9.28%, 11.77% and 13.07% in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=48.84% TFAs at pH=7.0 and at 60°C). The maximum TFAs removal efficiency was 61.91% in HCO_3^{-1}=5.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TFAs yields and HCO_3^{-1} concentration was not observed (R^2=0.43, F=5.34, p=0.001) (Figure 5.69b).



(a)



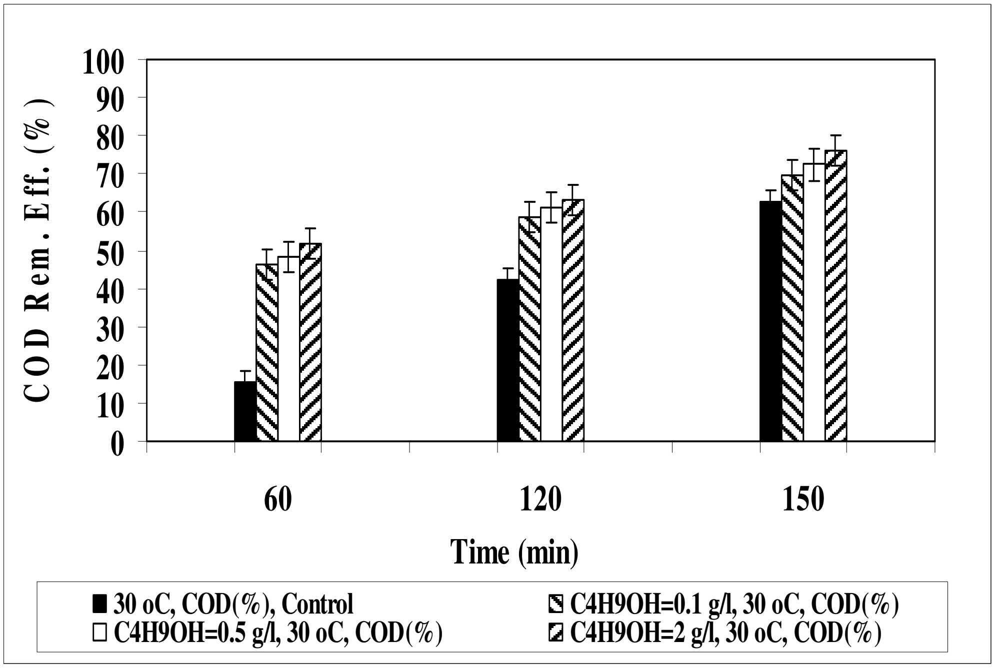
(b)

Figure 5.69 Effect of increasing HCO_3^{-1} concentrations on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

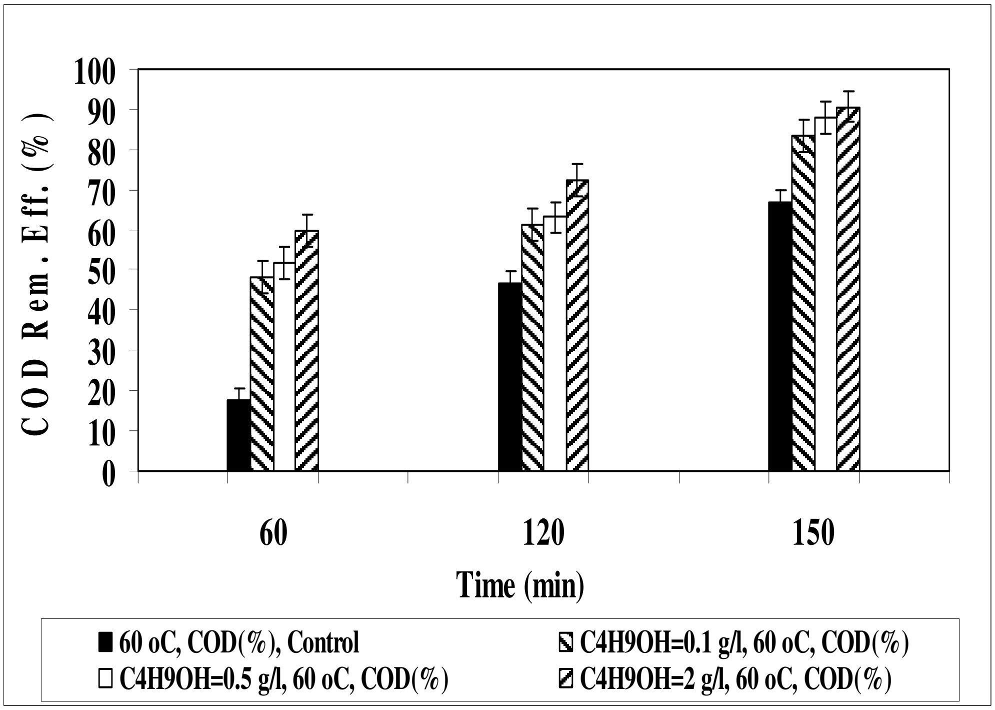
5.10.12 Effect of C_4H_9OH (1-Butanol) Concentrations on the Removals of COD_{dis} in OMI ww

Increasing C_4H_9OH concentrations (0.10–0.50 and 2.00 g/l) were added in OMI ww before sonication process. 69.66%, 72.41% and 76.07% COD_{dis} removals were observed in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.70a). 7.09%, 9.84% and 13.50% increase in COD_{dis} removals were obtained in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without C_4H_9OH while E=62.57% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing 1-butanol concentrations was not observed ($R^2=0.44$, F=5.29, p=0.001) (Figure 5.70a).

83.38%, 87.95% and 90.70% COD_{dis} yields were found in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.70b). The contribution of C_4H_9OH concentrations on COD_{dis} removals were 16.55%, 21.12% and 23.87% in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=66.83% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 90.70% in C_4H_9OH=2.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing 1-butanol concentrations was not observed ($R^2=0.40$, F=5.22, p=0.001) (Figure 5.70b).



(a)



(b)

Figure 5.70 Effect of increasing C_4H_9OH concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

Although, Ghodbane & Hamdaoui (2009a) found that the COD_{dis} degradation was partially quenched by the addition of 1-butanol in OMI ww in this study addition of 1-butanol increased slightly the COD_{dis} yields. This could be attributed to different 1-butanol concentrations, the COD_{dis} concentration in OMI ww, sonication frequency, sonication power and to different temperatures used in this study. In a study performed by Petrier & Francony (1997) it was found a COD yield of 76.00% after 120 min of sonication time at a power of 350 W and a frequency of 20 kHz at 60°C with 1.70 g/l C_4H_9OH. In this study, 90.70% COD_{dis} yield was observed at 60°C after 150 min sonication time in 2.00 g/l C_4H_9OH. In the present study, the COD_{dis} removal is higher than the yield found by Petrier & Francony (1997) at 60°C as mentioned above.

5.10.12.1 Effect of C_4H_9OH Concentrations on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

82.6%, 84.47% and 87.98% color removals were observed in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.70). 7.81%, 10.02% and 13.53% increase in the color removals were obtained in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=74.45% Color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing 1-butanol concentrations was not observed (R^2=0.42, F=4.19, p=0.001) (Table 5.70).

85.17%, 87.07% and 89.78% color yields were found in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.70). The contribution of C_4H_9OH concentrations on color removals were 1.40%, 3.30% and 6.01% in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=83.77% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 89.78% in C_4H_9OH=2.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing 1-butanol concentrations was not observed (R^2=0.39, F=3.78, p= 0.001) (Table 5.70).

Table 5.70 Effect of increasing C_4H_9OH concentrations on the color removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial Color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
C_4H_9OH=0.10 g/l	49.30	70.34	82.26	62.49	74.25	85.17
C_4H_9OH=0.50 g/l	52.61	78.06	84.47	63.98	80.96	87.07
C_4H_9OH=2.00 g/l	68.14	79.96	87.98	69.74	82.06	89.78

An extensive work on the sonochemistry of iso-butyl alcohol has been reported by Tauber et al. (1999b). The iso-butyl alcohol is able to scavenge $OH^\bullet$ in the bubble and prevent the accumulation of $OH^\bullet$ at the interface of the bubble. At low iso-butyl alcohol concentrations (7.00 and 20.00 mg/l), the rate of color degradation was accelerated. This enhancement may be attributed to the relatively low dose of tert-butyl alcohol, at which competition for $OH^\bullet$ is unlikely and the rapid decomposition of the additive to produce reactive $CH_3^\bullet$, which are the main products of high-temperature pyrolysis of the iso-butanol (Ince et al., 2009). Additionally, alcohol, a surfactant substance, can reduce the surface tension of the liquid and thus reduce the cavitation threshold and facilitate the generation of bubbles and therefore, the production of $OH^\bullet$ (Ince et al., 2009). At high iso-butyl alcohol concentrations (250–2500 mg/l), the degradation was effectively quenched, but not completely, by the addition of iso-butyl alcohol, suggesting that the main mechanism of color destruction is chemical oxidation by $OH^\bullet$ (Ince et al., 2009). The degradation efficiency of color decreased with the increase of concentration of iso-butyl alcohol in solution. Another factor that also affects the rate of color degradation is the formation of volatile products from the iso-butyl alcohol degradation that is accumulated inside the bubble. Such volatile products decrease the temperature inside the bubble, which, in turn, slow the sonolytic reactions (Tauber et al., 1999b).

In the presence of iso-butyl alcohol at low concentrations, unexpectedly, the rate of color degradation was accelerated. At high iso-butyl alcohol concentrations, the degradation was effectively quenched, but not completely, by the addition of iso-butyl alcohol (Merouani et al., 2010b). In our study, since low 1-butanol concentrations was used throughout sonication.

It is expected that the sonolytic degradation of color would mainly occur by $OH^\bullet$ attack (Adewuyi, 2001). In order to investigate the dependence of the $OH^\bullet$ during the degradation of color by ultrasonic irradiation, the sonolytic degradation of color in the presence of iso-butyl alcohol, known as an effective $OH^\bullet$ scavenger, was performed. The H_2O_2 measurement during acoustic cavitation in the OMI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the color treatment by sonication in OMI ww decreases with increasing sonication time at 60^oC (Table 5.71). In deionized water samples the H_2O_2 was accumulated and its concentration was measured as 161.00 mg/l, whereas this level was 162.00 mg/l after 60 min sonication time in OMI ww. The H_2O_2 concentration was only 24.00 mg/l in OMI ww after 150 min sonication time in the samples containing 2.00 g/l C_4H_9OH (Table 5.71). The $OH^\bullet$ ion concentrations also increased from $67.00x10^{-63}$ to $41.00x10^{-11}$ mg/l after 150 min sonication time in OMI ww containing 2.00 g/l C_4H_9OH. This showed that hydroxylation is the main mechanism for the removal of color in OMI ww in the presence of 1-butanol. In other words, $OH^\bullet$ is the major process for complete degradation of color in OMI ww.

Table 5.71 Effect of 2.00 g/l C_4H_9OH on H_2O_2 production and $OH^\bullet$ ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	162.00	0.00
H_2O_2 concentration (mg/l) for color (60°C) after 30 min sonication	161.00	67.00×10^{-63}
H_2O_2 concentration (mg/l) for color (60°C) after 120 min sonication	79.00	45.10×10^{-41}
H_2O_2 concentration (mg/l) for color (60°C) after 150 min sonication	24.00	41.00×10^{-11}

In a study performed by Priego-Capote et al. (2006) it was found 73.00% color removal after 110 min of sonication time at a power of 400 W and a frequency of 50 kHz at 60°C with 3.00 g/l C_4H_9OH concentration. In this study, 89.78% color yield was observed at 60°C after 150 min sonication time in 2.00 g/l C_4H_9OH. In the present study, the color removal is higher than the yield obtained by Priego-Capote et al. (2006) at 60°C as mentioned above.

5.10.12.2 Effect of C_4H_9OH Concentrations on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

81.65%, 84.74% and 87.19% total phenol removals were observed in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.72). 22.25%, 25.34% and 27.79% increase in total phenol removals were obtained in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=59.40% total phenol at pH=7.0 and at 30°C). A significant linear correlation between total phenol yields and 1-butanol concentration was observed (R^2=0.79, F=14.09, p=0.001) (Table 5.72).

Table 5.72 Effect of increasing C_4H_9OH concentrations on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
C_4H_9OH=0.10 g/l	43.93	75.45	81.65	47.68	81.04	85.48
C_4H_9OH=0.50 g/l	49.17	78.07	84.74	50.05	85.30	87.97
C_4H_9OH=2.00 g/l	51.88	80.73	87.19	53.33	86.32	90.47

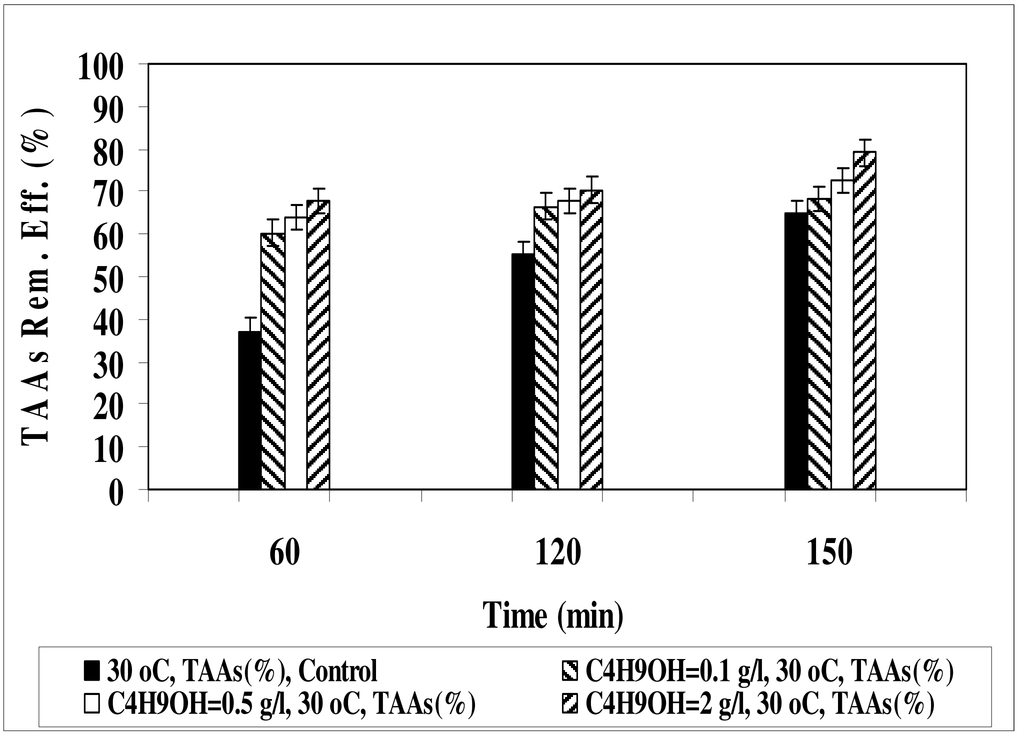
85.48%, 87.97% and 90.47% total phenol yields were found forn 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.72). The contribution of C_4H_9OH concentrations on total phenol removals were 24.24%, 26.73% and 29.23% in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=61.24% total phenol at pH=7.0 and at 60°C). The maximum total phenol removal efficiency was 90.47% in C_4H_9OH=2.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between total phenol yields and increasing 1-butanol concentrations was observed (R^2=0.76, F=14.38, p=0.001) (Table 5.72).

In a study performed by Vassilakis et al. (2004) it was observed that the phenol yield was 82.00% after 100 min sonication time at a power of 350 W and a frequency of 25 kHz at 60°C with 1.00 g/l C_4H_9OH concentration. In this study, 90.47% total phenol yield was observed at 60°C after 150 min sonication time in 2.00 g/l C_4H_9OH. It can be concluded that, in the present study, the total phenol removal is higher than the yield obtained by Vassilakis et al. (2004) at 60°C.

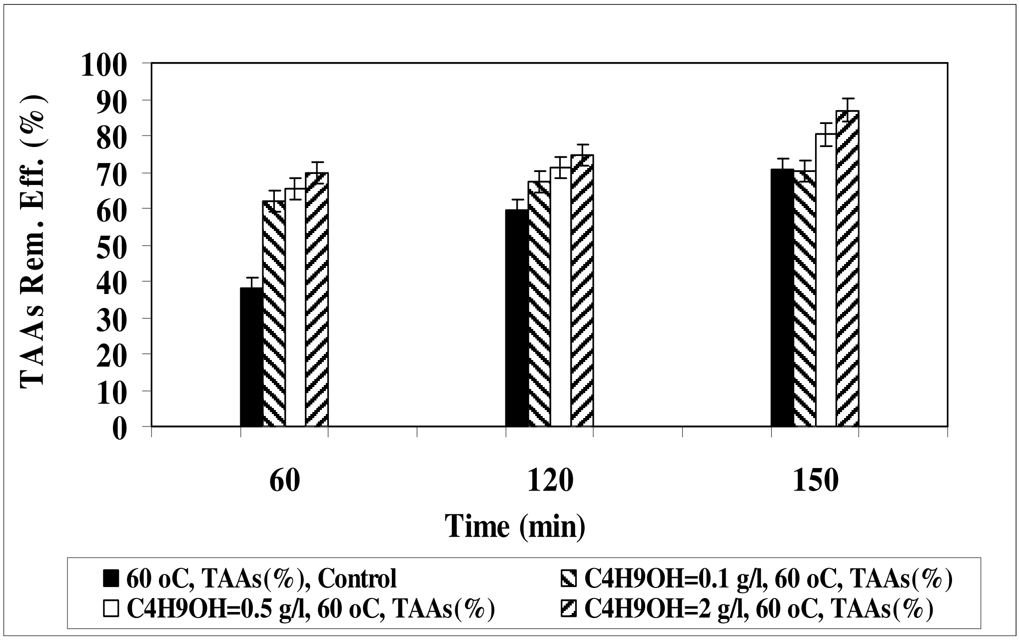
5.10.12.3 Effect of C_4H_9OH Concentration on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

68.31%, 72.53% and 79.20% TAAs removals were observed in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.71a). 3.33%, 7.55% and 14.22% increase in TAAs removals were obtained in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=64.98% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing 1-butanol concentrations was not observed (R^2=0.44, F=3.76, p=0.001) (Figure 5.71a).

70.21%, 80.27% and 87.01% TAAs yields were found in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.71b). The contribution of C_4H_9OH concentrations on TAAs removals were 9.75% and 16.49% in 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=70.52% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 87.01% in C_4H_9OH=2.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing 1-butanol concentrations was not observed (R^2=0.38, F=3.39, p=0.001) (Figure 5.71b).



(a)



(b)

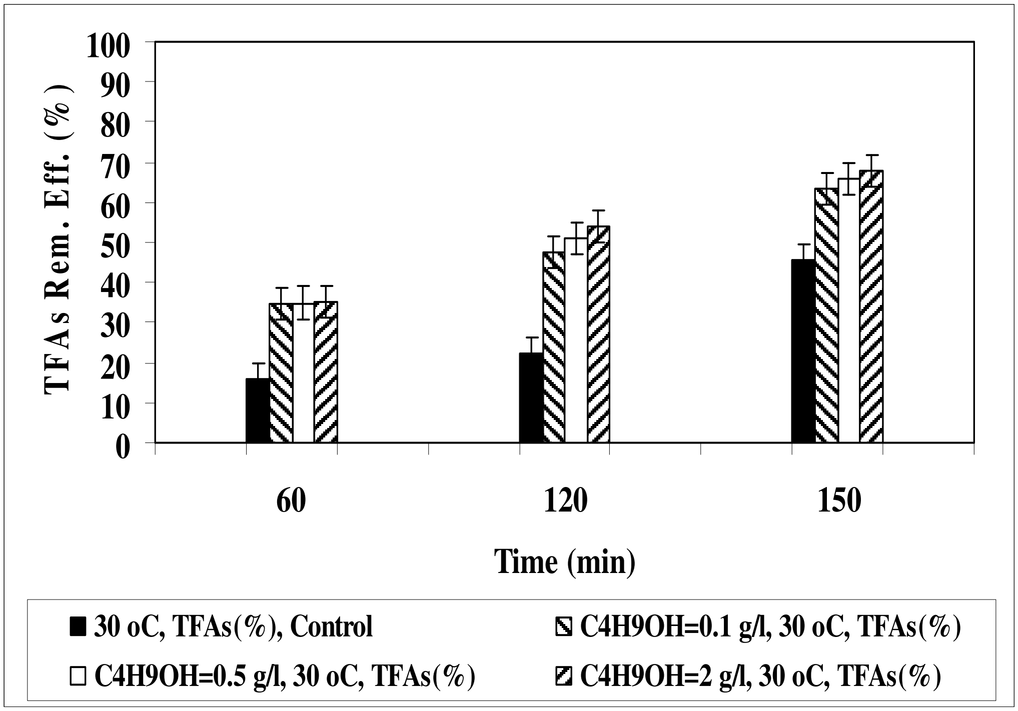
Figure 5.71 Effect of increasing C_4H_9OH concentrations on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

Alcohols are commonly used to quench the $OH^{\bullet}$. The retarding effect of iso-butanol on the sono-degradation of TAAs can be explained by $OH^{\bullet}$ competitive reactions with aromatic amines (Behnajady et al., 2008b; Mokhtar et al., 2010). However, in this study the inhibition effect of 1-butanol to the TAA removal was not observed the contribution of the 1-butanol to the TAAs yields was found to insignificant (R^2=0.29, F=2.56, p=0.01).

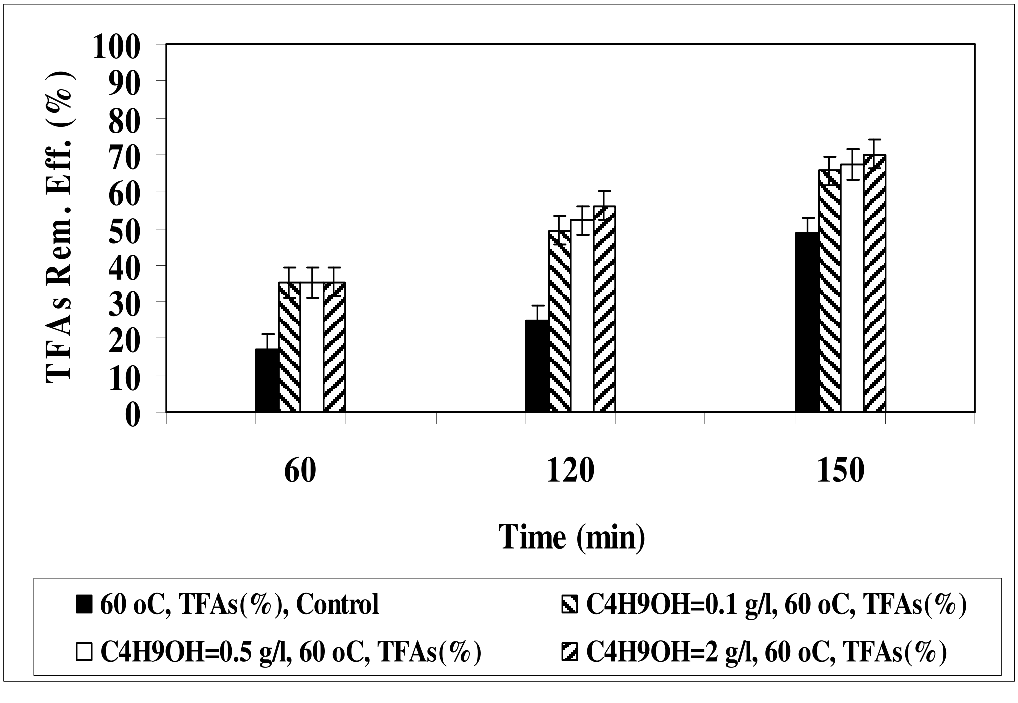
5.10.12.4 Effect of C_4H_9OH Concentration on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

63.34%, 65.80% and 67.72% TFAs removals were observed in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.72a). 17.68%, 20.14% and 22.06% increase in TFAs removals were obtained in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=45.66% TFAs at pH=7.0 and at 30°C). A significant linear correlation between TFAs yields and increasing 1-butanol concentrations was observed (R^2=0.79, F=13.89, p=0.001) (Figure 5.72a).

65.62%, 67.47% and 70.16% TFAs yields were found in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.72b). The contribution of C_4H_9OH concentrations on TFAs removals were 16.78%, 18.62% and 21.32% in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=48.84% TFAs at pH=7.0 and at 60°C). The maximum TFAs removal efficiency was 70.16% in C_4H_9OH=2.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TFAs yields and increasing 1-butanol concentrations was observed (R^2=083, F=17.29, p=0.001) (Figure 5.72b).



(a)



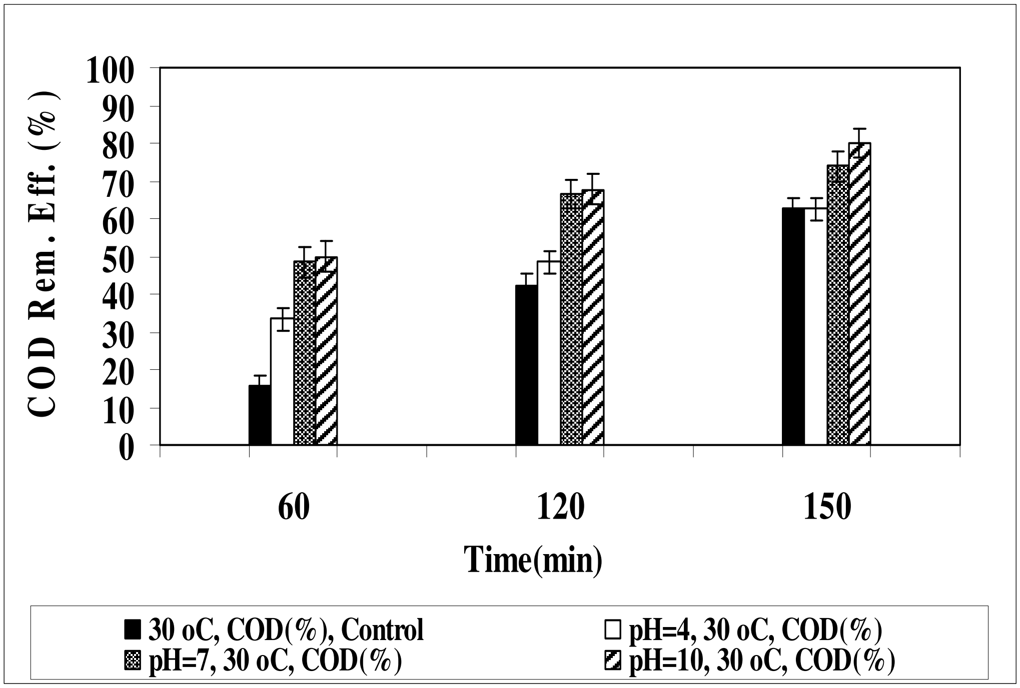
(b)

Figure 5.72 Effect of increasing C_4H_9OH concentrations on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

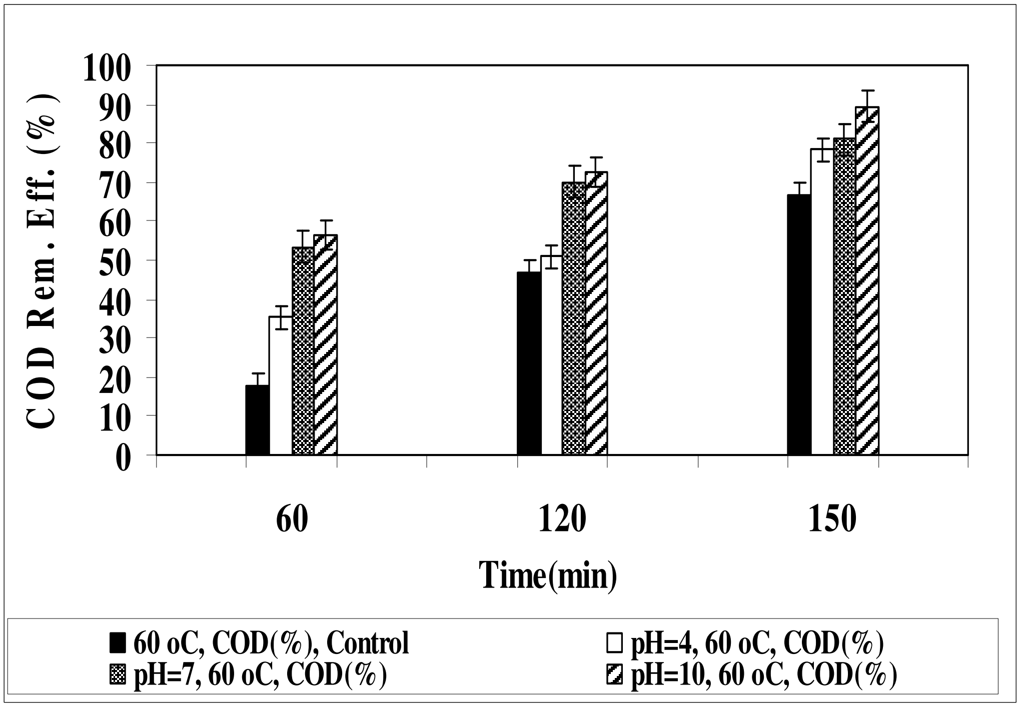
5.10.13 Effect of pH Values on the Removals of COD_{dis} in OMI ww

Increasing pH values (4.0 – 7.0 and 10.0) were adjusted in the OMI ww before sonication process. 62.59%, 73.99% and 80.04% COD_{dis} removals were observed at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C (Figure 5.73a). 0.02%, 11.42% and 17.47% increase in COD_{dis} removals were obtained at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C, compared to the control (E=62.57% COD_{dis} at pH=6.98 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing pH values was not observed (R^2=0.44, F=5.29, p=0.001) (Figure 5.73a).

78.23%, 81.11% and 89.31% COD_{dis} yields were found at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C (Figure 5.73b). The contribution of pH values on COD_{dis} removals were 11.40%, 14.28% and 22.48% at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C, compared to the control (E=66.83% COD_{dis} at pH=6.98 and at 60°C). The maximum COD_{dis} removal efficiency was 89.31% at pH=10.0 after 150 min sonication time at 60°C. A significant linear correlation between COD_{dis} yields and increasing pH levels was observed (R^2=0.82, F=17.88, p=0.001). In this study the maximum COD_{dis} yields were obtained under alkaline condition after 150 min sonication time at 60°C (Figure 5.73b).



(a)



(b)

Figure 5.73 Effect of increasing pH values on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

Decomposition of H_2O_2 is a complicated reaction and is influenced by a considerable number of variables, such as temperature, pH, time, quality of water, and some catalysts. The decomposition rate increases with temperature, pH and NaOH concentration as reported by Lewin (1983). According to Lewin (1983) a homogeneous decomposition of H_2O_2 takes place (with OH^{-1} catalysis) under alkaline conditions, as given in Eq. (5.81):

$$H_2O_2 + OH^{-1} \Leftrightarrow O_2H^{-1} + H_2O \tag{5.81}$$

In alkaline conditions at temperatures about 55 - 60°C a next reaction takes place, as given in Eq. (5.82):

$$H_2O_2 + O_2H^{-1} \Leftrightarrow OH^{\bullet} + H_2O + {}^{\bullet}O_2^{-1} \tag{5.82}$$

The oxidizing $OH^{\bullet}$ and the reducing ${}^{\bullet}O_2^{-1}$ may interact according to the reaction given in Eq. (5.83):

$${}^{\bullet}OH_2 + {}^{\bullet}O_2^{-1} \rightarrow OH^{-1} + O_2 \tag{5.83}$$

with this reaction O_2 was produced or it may react with other pollutants through sonication.

Since the recent lieratures concerning the effects of pH on the sonication of OMI was limited only with the effect of pH on the electrocoagulation of OMI ww, the COD yields in the present study was discussed with the study mentioned above. Electrocoagulation process has a removal capacity of 76.00% COD after 75 min sonication time at pHs ranges varying between 4.0 and 6.0 and at an optimum current density of 75 mA/cm^2 (Adhoum & Monser, 2004). This COD yield decreased to 56.00% at pH > 9.0. In this study, 89.31% COD_{dis} removal was measured at pH=10.0 at 60°C after 150 min sonication time. In this study, the maximum COD_{dis} yield is higher than the yield observed by Adhoum & Monser (2004) at alkaline pH while the maximum yields was found at acidic pH through electrocoagulation of OMI ww.

5.10.13.1 Effect of pH Values on the Color Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

83.77%, 85.87% and 87.07% color removals were observed at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C in OMI ww (Table 5.73). 9.32%, 11.42% and 12.62% increase in the color removals were obtained for pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C, compared to the control (E=74.45% color at pH=6.98 and at 30°C). A significant linear correlation between color yields and increasing pH levels was not observed (R^2=0.42, F=4.88, p=0.001) (Table 5.73).

Table 5.73 Effect of increasing pH values on the color removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
pH=4.0	61.32	74.15	83.77	64.03	74.95	89.28
pH=7.0	62.42	77.76	85.87	65.53	76.75	90.18
pH=10.0	74.95	79.66	87.07	69.94	78.46	92.38

89.28%, 90.18% and 92.38% color yields were found at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C (Table 5.73). The contributions of pH values on color removals were 5.51%, 6.41% and 8.61% at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication at 60°C, compared to the control (E=83.77% color at pH=6.98 and at 60°C). The maximum color removal efficiency was 92.38% at pH=10.0 after 150 min sonication time at 60°C. A significant linear correlation between color yields and increasing pH values was not observed (R^2=0.39, F=3.79, p=0.001) (Table 5.73).

In a study performed by Svitelska et al. (2004) it was found that the decolorization rate increased with the decreasing pH and reached the highest at a pH=2.0 in OMI ww by decomposition of H_2O_2 at low pH values. In this study, decolorization rate increased with the increasing of pH values and the highest color removal observed at pH=10.0 and at 60°C. The study performed by Svitelska et al. (2004) showed that the condensed tannins in OMI ww treated by ultrasound at 20 kHz frequency, in alkaline conditions (pH > 10.0), at 60°C and are sono-degraded according to Eqs. (5.84) and (5.85):

$$H_2O_2 + OH^{-1} \quad \Leftrightarrow \quad HOO^{-1} + H_2O \tag{5.84}$$

$$H_2O_2 + OOH^{-1} \quad \Leftrightarrow \quad OH^{\bullet} + H_2O + {}^{\bullet}O_2^{-1} \tag{5.85}$$

In a study performed by Svitelska et al. (2004) 60.00% color removal was obtained at higher pH values more radicals are formed. In this study, 92.38% color removal was observed at pH=10.0 at 60°C after 150 min sonication time. The color yield found in this study is higher than the yield obtained by Svitelska et al. (2004) at 60°C as mentioned above.

Adhoum & Monser (2004) investigated to effect of pH on the removal of color with electrocoagulation process in OMI ww. A removal capacity of 93.00% of color found after 75 min at pH=4.0 and an optimum current density of 75 mA/cm^2. In this study, 92.38% color removal was measured at pH=10.0 at 60°C after 150 min sonication time. The color yield found in this study by sonication exhibited similarities with the removal observed by Adhoum & Monser (2004) at 60°C by electrocoagulation process. In a study performed by Guzman-Duque et al. (2011) no significant differences in color removal was obtained at pH=3.5, pH=7.0 and pH=9.0, at 80 W power, at 800 kHz frequency and at 60°C.

5.10.13.2 Effect of pH Values on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

76.18%, 79.28% and 82.07% total phenol removals were observed at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C (Table 5.74). 16.78%, 19.28% and 22.67% increase in total phenol removals were obtained at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C, compared to the control (E=59.40% total phenol at pH=6.98 and at 30°C). A significant linear correlation between total phenol yields and increasing pH values was not observed (R^2=0.51, F=6.45, p=0.001) (Table 5.74).

Table 5.74 Effect of increasing pH values on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
pH=4.0	43.74	70.76	76.18	44.89	74.75	80.02
pH=7.0	44.41	71.37	79.28	45.41	75.31	83.60
pH=10.0	44.83	71.43	82.07	46.15	76.01	85.51

80.02%, 83.60% and 85.51% total phenol yields were found at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C (Table 5.74). The contribution of pH values on total phenol removals were 18.78%, 22.36% and 24.27% at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C, compared to the control (E=61.24% total phenol at pH=6.98 and at 60°C). The maximum total phenol removal efficiency was 85.51% at pH=10.0 after 150 min sonication time at 60°C. A significant linear correlation between total phenol yields and increasing pH values was not observed (R^2=0.54, F=6.79, p=0.001) (Table 5.74).

In OMI ww the degree of ionization of phenol from molecular state to the phenolate ion increases as the pH is raised, and at pH > pK_a (acid dissociation constant) (=10.0) (Petrier et al., 1994). The phenolate ion is the major species, where the uncombined $OH^{\bullet}$ concentration is at a maximum level in the bubble–liquid interface (Petrier et al., 1994). As pH is lowered and the fraction of molecular phenol increases, the probability of solutes approaching the interfacial area also increase, resulting in enhanced rates of phenol removal. In this study, it was found that the phenol removal was not dependent to the pH while no significant differences between total phenol yields and increasing pH values was obtained as mentioned above.

The initial rate of H_2O_2 formation associated to the total phenol treatment by sonication in OMI ww decreases with increasing sonication time at 60°C (Table 5.75). In the deionized water samples the H_2O_2 was accumulated and its concentration was measured as 170.00 mg/l, whereas this level was 171.00 mg/l after 60 min sonication time in OMI ww. The H_2O_2 concentration was only 10.00 mg/l in OMI ww after 150 min sonication time in the samples containing pH=10.0 (Table 5.75). The $OH^{\bullet}$ ion concentrations also increased from $56.00x10^{-61}$ to $8.00x10^{-7}$ mg/l after 150 min sonication time in OMI ww containing pH=10.0. This showed that hydroxylation is the main mechanism for the removal of total phenol in OMI ww. In other words, $OH^{\bullet}$ is the major process for complete degradation of total phenol in OMI ww.

Since the sonooxidation of total phenol comprised 0.90%, 0.93% and 0.99% of the total sonodegradation process, $OH^{\bullet}$ is the major process for complete degradation of the total phenol in the samples containing pH=10.0 (Table 5.75).

Table 5.75 Effect of pH=10.0 on H_2O_2 production and $OH^\bullet$ ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	170.00	0.00
H_2O_2 concentration (mg/l) for total phenol (60°C) after 30 min sonication	171.00	$56.00\text{x}10^{-61}$
H_2O_2 concentration (mg/l) for total phenol (60°C) after 120 min sonication	64.00	$32.00\text{x}10^{-42}$
H_2O_2 concentration (mg/l) for total phenol (60°C) after 150 min sonication	10.00	$8.00\text{x}10^{-7}$

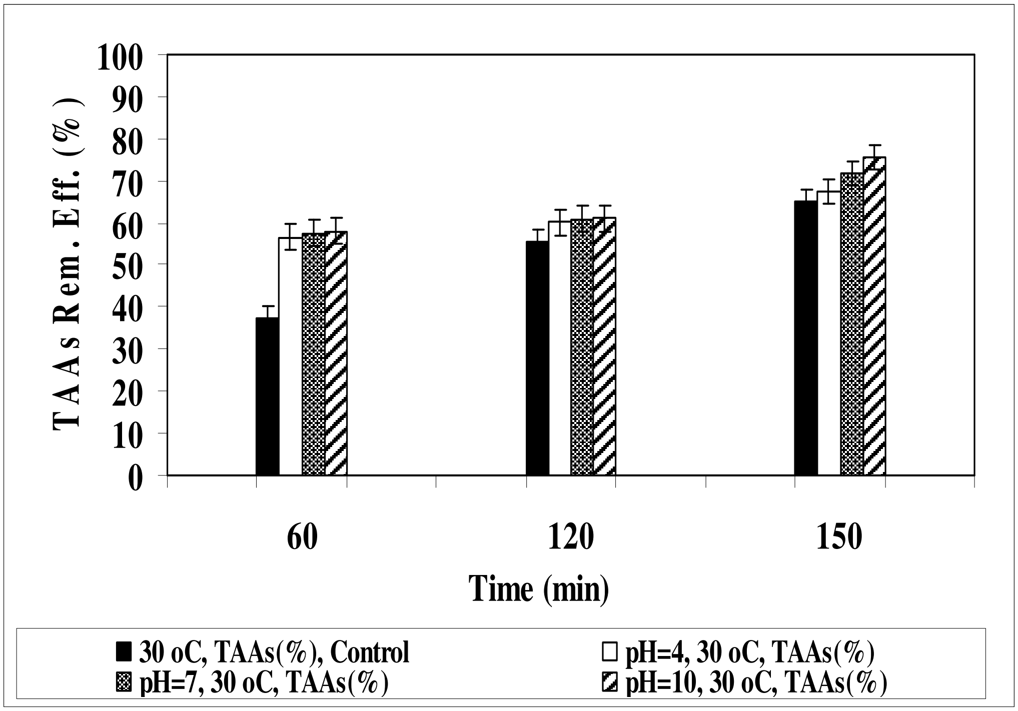
The study performed by Kidak & Ince (2007) showed that 60.00% phenol removal could be achieved at acidic pH with sonication at a frequency of 30 kHz after 90 min sonication time. In this study, 85.51% total phenol removal was observed for pH=10.0 at 60°C after 150 min sonication time. The total phenol yield, in the present study, is higher than the yield obtained by Kidak & Ince (2007) at 60°C. This could be attributed to the frequency and to sonication time and to properties of OMI ww used in this study.

Application of electrocoagulation procedure permitted high removal efficiencies of pollutants in OMI ww. Electrocoagulation process produces a removal capacity of 91.00% of polyphenols, after 85 min at pH=4.0-6.0, at an optimum current density of 75 mA/cm^2 (Adhoum & Monser, 2004). In this study, 85.51% total phenol removal was found for pH=10.0 at 60°C after 150 min sonication time. In the present study, the total phenol yield is lower than the yield obtained by Adhoum & Monser (2004) at 60°C as mentioned above. The study performed by Svitelska et al. (2004) showed that the condensed tannins in OMI ww were treated with 56.00% yields at pH values higher than 10.0 by ultrasound at a frequency of 20 kHz. Under these conditions mostly molecular H_2O_2 molecules were in alkaline conditions at a temperature around 60^{o}C. Therefore, at higher pH values more radicals are formed. In this study, 85.51% total phenol removal efficiency was obtained at pH=10.0 in OMI ww at 60^{o}C after 150 min sonication time. The total phenol yield is higher than the yield obtained by Svitelska et al. (2004) at 60^{o}C as mentioned above.

5.10.13.3 Effect of pH Values on the TAAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

67.53%, 71.75% and 75.56% TAAs removals were observed at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30^{o}C (Figure 5.74a). 2.55%, 6.77% and 10.58% increase in TAAs removals were obtained at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30^{o}C, compared to the control (E=64.98% TAAs at pH=6.98 and at 30^{o}C). A significant linear correlation between TAAs yields and increasing pH levels was not observed (R^2=0.42, F=3.88, p=0.001) (Figure 5.74a).

76.09%, 80.97% and 86.25% TAAs yields were found at pH=4.0, pH=7.0 and pH=10.0 respectively, after 150 min sonication time at 60^{o}C (Figure 5.74b). The contribution of pH values on TAAs removals were 5.57%, 10.45% and 15.73% at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60^{o}C, compared to the control (E=70.52% TAAs at pH=6.98 and at 60^{o}C). The maximum TAAs removal efficiency was 86.25% at pH=10.0 after 150 min sonication time at 60^{o}C. A significant linear correlation between TAAs yields and increasing pH levels was not observed (R^2=0.47, F=5.25, p=0.001) (Figure 5.74b).



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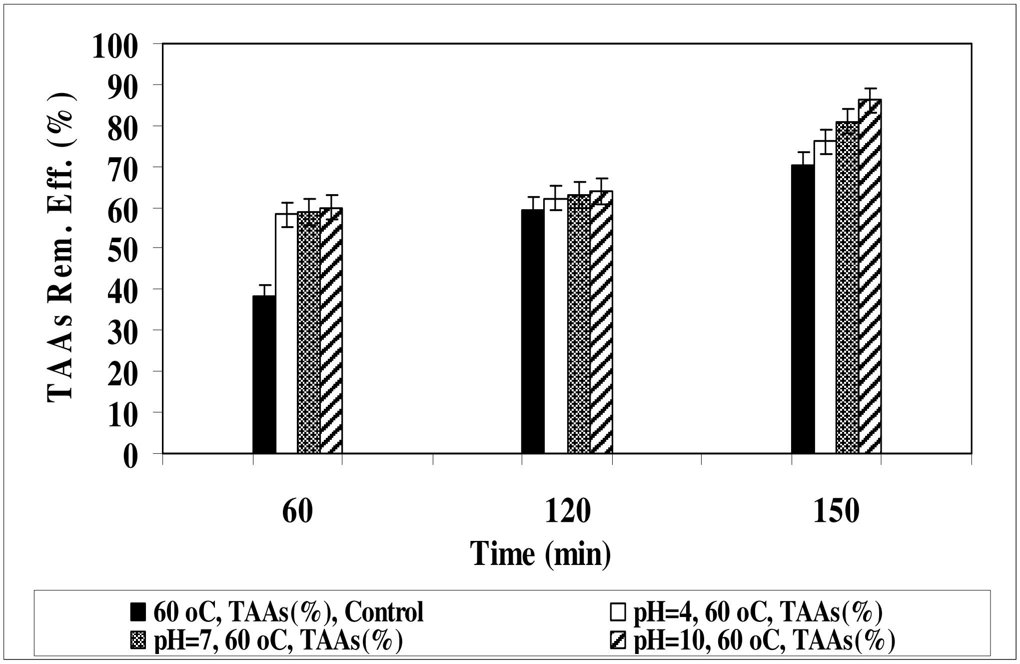


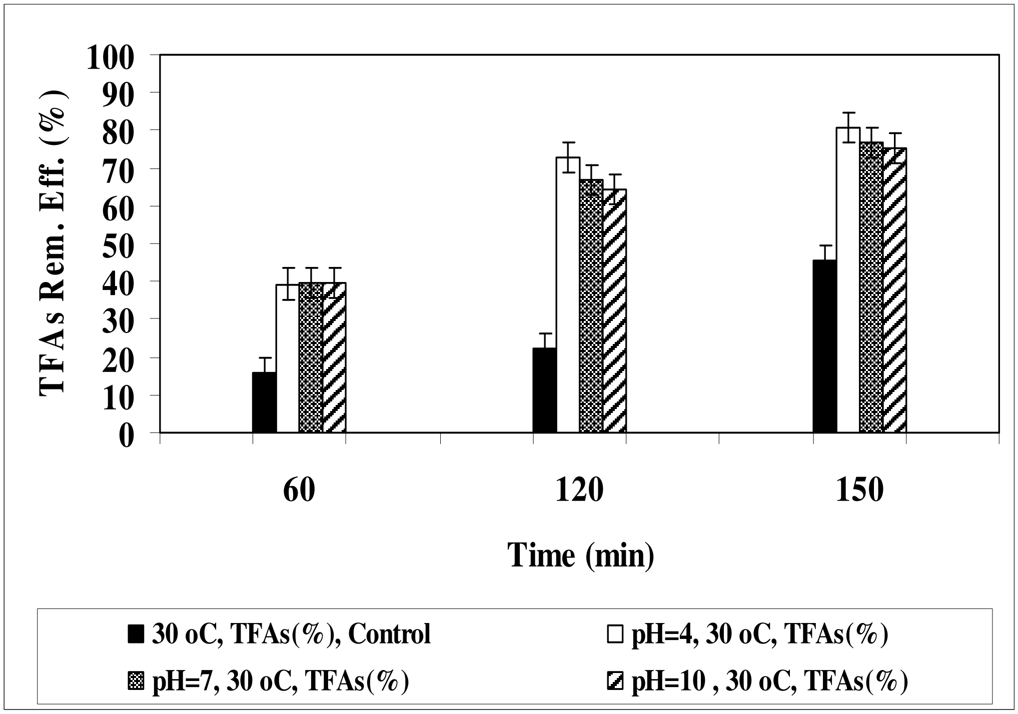
(b)

Figure 5.74 Effect of increasing pH values on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

5.10.13.4 Effect of pH Values on the TFAs Removal Efficiencies at Increasing Sonication Times and Temperatures

80.89%, 76.74% and 75.10% TFAs removals were observed at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C (Figure 5.75a). 35.23%, 31.08% and 29.44% increase in TFAs removals were obtained at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C, compared to the control (E=45.66% TFAs at pH=6.98 and at 30°C). A significant linear correlation between TFAs yields and increasing pH values was not observed (R^2=0.42, F=3.09, p=0.001) (Figure 5.75a).

82.39%, 78.87% and 78.06% TFAs yields were found at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C (Figure 5.75b). The contribution of pH values on TFAs removals were 35.21 %, 30.03% and 29.22% at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C, compared to the control (E=48.84% TFAs at pH=6.98 and at 60°C). The maximum TFAs removal efficiency was 78.87% at pH=7.0 after 150 min sonication time at 60°C. A significant linear correlation between TFAs yields and increasing pH values was not observed (R^2=0.38, F=3.26, p=0.001) (Figure 5.75b).



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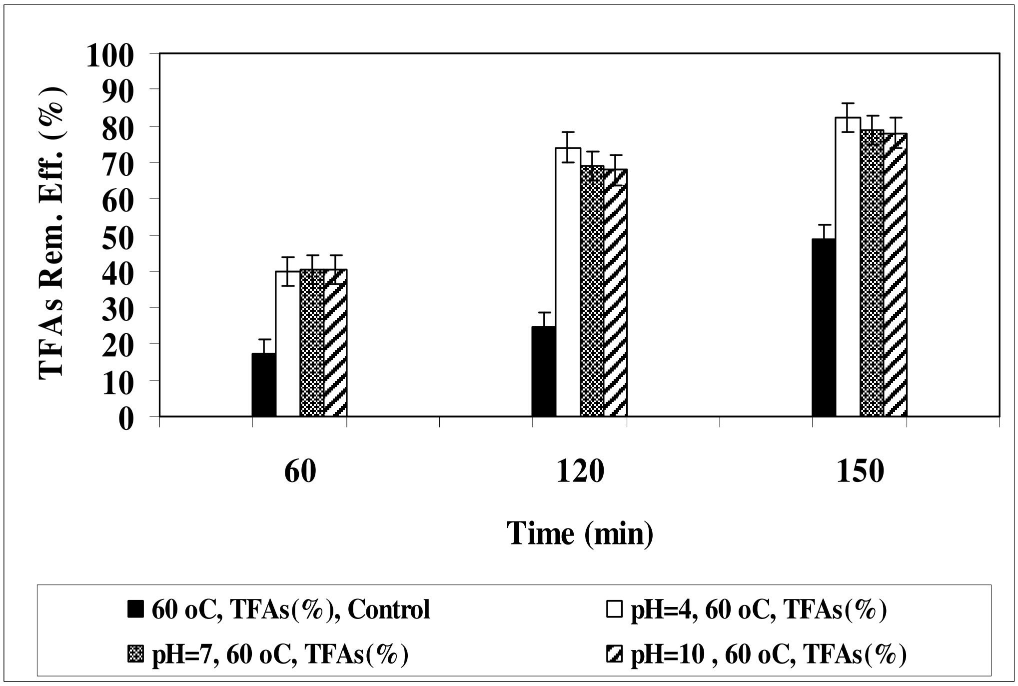


(b)

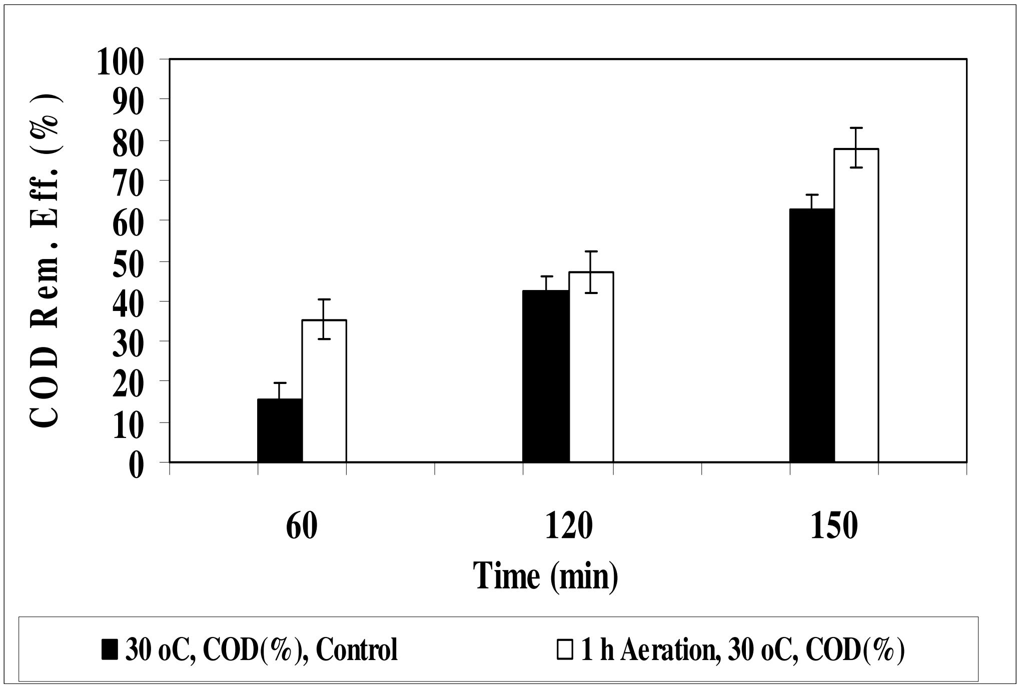
Figure 5.75 Effect of increasing pH values on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

The results of this study showed that the maximum TFAs yield was obtained under acidic conditions after 120 and 150 min sonication times. Free fatty acids produced by hydrolysis can undergo auto-oxidation. Oxidation primarily occurs with unsaturated fats by free radical-mediated processes at low pH (Richardson & Montgomery, 2005).

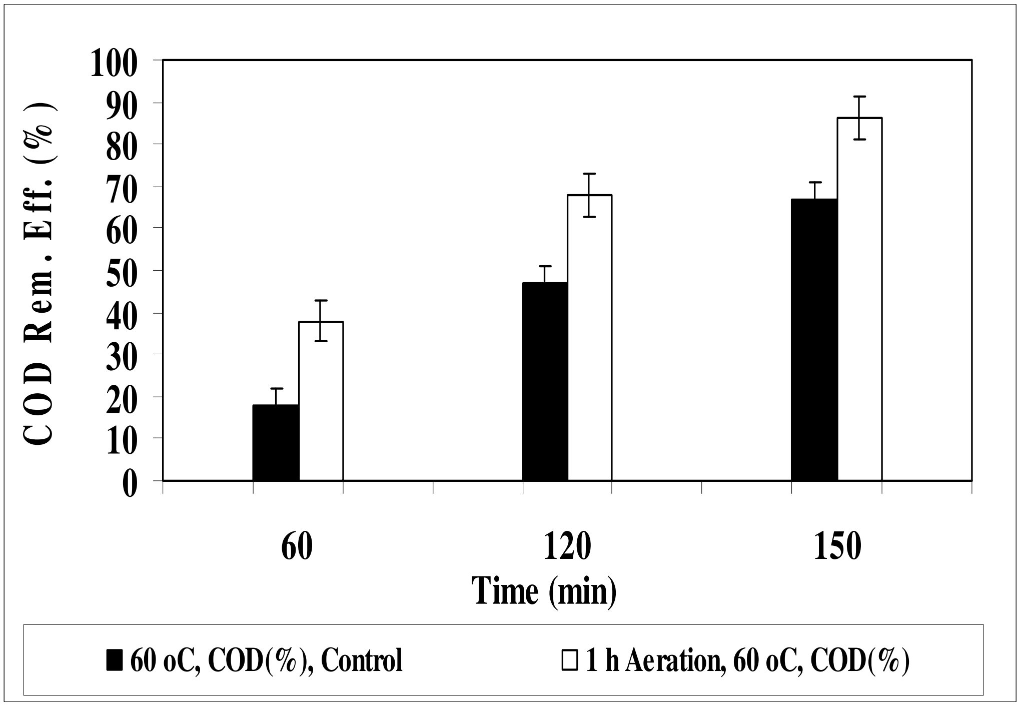
The study performed by Hachicha, R. et al. (2009) gives idea about the sonodegradation of mixture of OMI ww sludge and paltree manure. The TFAs fraction of OMI sludge containing oleic acid, palmitic and linoleic acid were degraded with yields varying between 55.40% and 56.00% at a pH of 7.0. In this study, the maximum TFAs yield (82.39%) was observed in acidic conditions (at pH=4.0) and at 60°C after 150 min sonication time. The TFAs yield observed in this study is higher than the yield obtained by Hachicha, R. et al. (2009) at a pH=7.0 and at 60°C as mentioned above.

5.10.14 Effect of Aeration on the Removals of COD_{dis} in OMI ww

OMI ww samples were aerated under 1 h with an air pump before the sonication experiments. 77.82% COD_{dis} removal was observed under 1 h aeration, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.76a). An increase of 15.25% in COD_{dis} removal was obtained under 1 h aeration after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without aeration while E=62.57% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and aeration was observed (R^2=0.70, F=15.63, p=0.001) (Figure 5.76a).



(a)



(b)

Figure 5.76 Effect of aeration on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

86.32% COD_{dis} yield was found under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.76b). The contribution of aeration on COD_{dis} removal was 19.49% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=66.83% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 86.32% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and aeration was observed (R^2=0.75, F=14.83, p=0.001) (Figure 5.76b).

If a continuous aeration is provided, the overall intensity of cavitation events may increase resulting in an increase in the extent of COD_{dis} degradation (Gogate & Pandit, 2004). Experiments with aeration (at constant rate of 1.02 cm^3/s using a multipoint sintered sparger) indicated that the extent of degradation increased by about 30.00% over entire 30 min of sonication. It should be also noted that more work is indeed for understanding the detailed effect of aeration in terms of parameters such as flow rate of air, using separate sparging of air followed by ultrasonic irradiation (simultaneous operation results in a decrease in the extent of dissolved air due to degassing effect) and experiments with different dissolved gases such as argon (Ar), Ar/air mixture, O_3 etc. (Gogate & Pandit, 2004).

In a study carried out Lafi et al. (2009) 28.90% COD_t removal efficiency was obtained with UV/O_3 process in OMI ww (UV time: 150 min ve O_3 dose: 35 l/h). Aerobic biodegradation followed by ozonation provided 80.00% COD_t removal in OMI ww at 50°C. In this study, 86.32% COD_{dis} yield was observed at 60°C after 150 min sonication time. In the present study, the COD_{dis} removals found by sonication are higher than the yields obtained by Lafi et al. (2009) by UV/O_3 combination at 50°C as mentioned above.

5.10.14.1 Effect of Aeration on the Color Removal Efficiencies in OMI ww at Increasing Sonication Time and Temperature

81.86% color removal was observed under 1 h aeration, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.76). An increase of 7.41% in color removal was obtained under 1 h aeration after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=74.45% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and aeration was not observed (R^2=0.39, F=4.22, p=0.001) (Table 5.76).

Table 5.76 Effect of aeration on the color removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial Color concentration=99.80 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	38.68	52.61	74.45	44.59	69.74	83.77
1 h aeration	67.54	78.16	81.86	71.44	85.37	88.48

88.48% color yield was found under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C (Table 5.76). The contribution of aeration on removal was 4.71% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=83.77% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 88.48% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and aeration was not observed (R^2=0.37, F=4.03, p=0.001) (Table 5.76).

The results of this study showed that the introduction of air would enhance the decolorization of OMI ww. Air is an important factor that affects aqueous sonochemical processes and it acts as nucleation sites for cavitation (Nanzai et al., 2008). This improved the color removal from OMI ww in combination with ultrasonic irradiation. The efficiency of acoustic cavitation increased in the presence of air since it is strongly consumed inside the bubble when the bubble temperature at the bubble collapse is higher such as 60^oC after 150 min sonication time (Nanzai et al., 2008). Dissolved gas is an important factor affecting the aqueous sonochemical processes and it acts as nucleation sites for cavitation. This may improve color removal by in combination with ultrasonic irradiation (Mahamuni & Pandit, 2006). However, the presence of air achieved less decolorization efficiency than that of DO (Mahamuni & Pandit, 2006). Thermal conductivities ($\gamma = C_p/C_v$) of the dissolved gases have been inversely correlated to the sonochemistry field. The organic compounds given the color in OMI ww was strongly consumed inside a bubble by oxidizing air when the bubble temperature at the bubble collapse is higher (Mahamuni & Pandit, 2006).

The H_2O_2 measurement during acoustic cavitation in the OMI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the color treatment by sonication in OMI ww decreases with increasing sonication time at 60^oC (Table 5.77). In the deionized water samples the H_2O_2 was accumulated and its concentration was measured as 173.00 mg/l, whereas this level was 174.00 mg/l after 60 min sonication time in OMI ww. The H_2O_2 concentration was only 17.00 mg/l in OMI ww after 150 min sonication time in the samples containing 1 h aeration (Table 5.77). The $OH^\bullet$ ion concentrations also increased from $61.00x10^{-61}$ to $12.00x10^{-8}$ mg/l after 150 min sonication time in OMI ww containing 1 h aeration. This showed that hydroxylation is the main mechanism for the removal of color in OMI ww. In other words, $OH^\bullet$ is the major process for complete degradation of color in OMI ww.

Table 5.77 Effect of 1 h aeration on H_2O_2 production and $OH^\bullet$ ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m^{-1}, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	173.00	0.00
H_2O_2 concentration (mg/l) for color (60°C) after 30 min sonication	174.00	$61.00\text{x}10^{-61}$
H_2O_2 concentration (mg/l) for color (60°C) after 120 min sonication	68.00	$43.00\text{x}10^{-43}$
H_2O_2 concentration (mg/l) for color (60°C) after 150 min sonication	17.00	$12.00\text{x}10^{-8}$

In this study, 93.79% and 88.48% color removal efficiencies were observed under DO=10.00 mg/l and 1 h aeration, respectively, after 150 min sonication time at 60°C. The color removal obtained with the addition of pure DO is higher than the color yield observed by 1 h aeration after 150 min sonication time at 60°C.

5.10.14.2 Effect of Aeration on the Total Phenol Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

70.91% total phenol removal was observed under 1 h aeration, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.78). An increase of 11.51% in total phenol removal was obtained under 1 h aeration after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=59.40% total phenol at pH=7.0 and at 30°C). A significant linear correlation between total phenol yields and aeration was not observed (R^2=0.34, F=2.99, p=0.001) (Table 5.78).

72.69% total phenol yield was found under 1 h aeration after 150 min sonication time at 60°C (Table 5.78). The contribution of aeration on total phenol removal was 11.45% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=61.24% total phenol at pH=7.0 and at 60°C). The maximum total phenol removal efficiency was 72.69% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between total phenol yields and aeration was not observed (R^2=0.44, F=5.02, p=0.001) (Table 5.78).

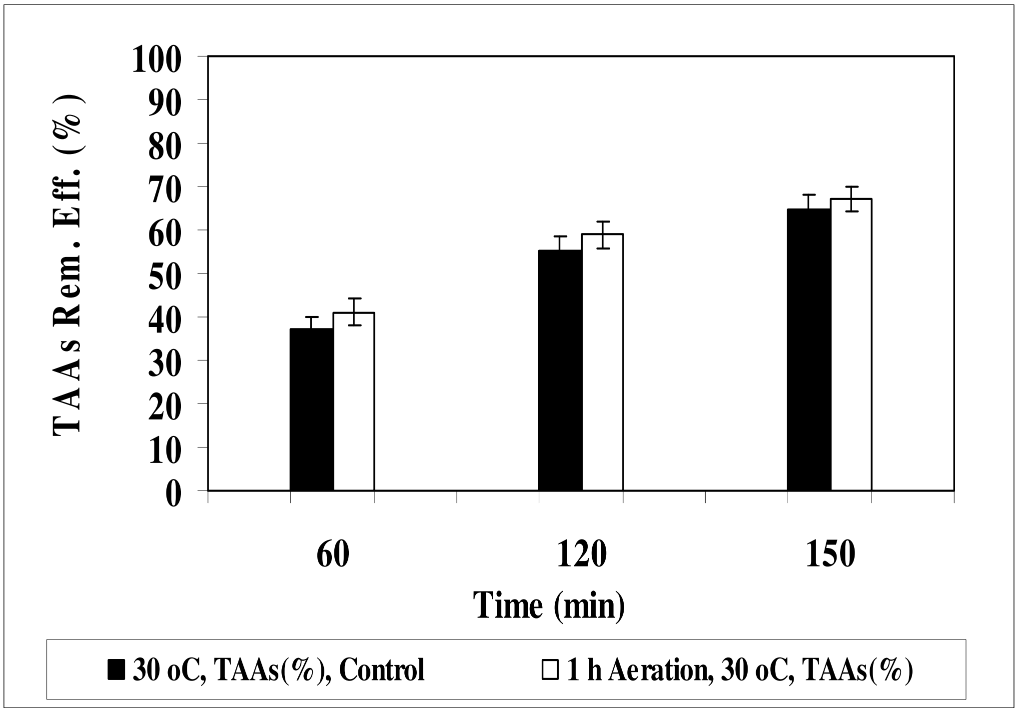
Table 5.78 Effect of aeration on the total phenol removal efficiencies in OMI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values).

Parameters	**Total Phenol Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	28.26	56.00	59.40	30.20	57.94	61.24
1 h aeration	44.52	69.82	70.91	45.13	70.39	72.69

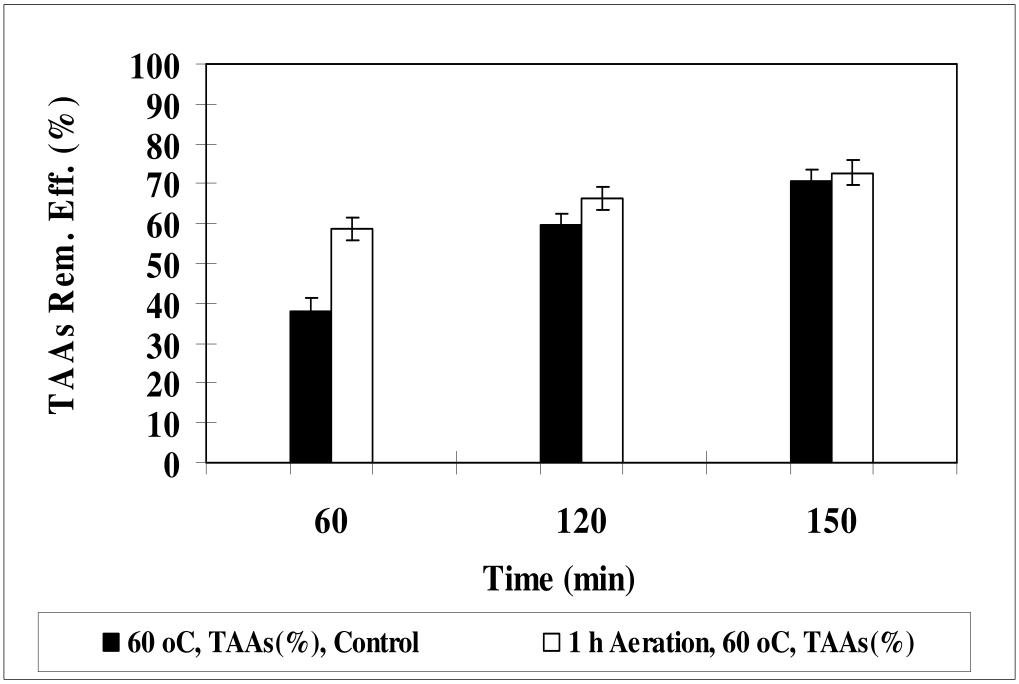
A number of studies have shown that ultrasonic treatment can result in successful sonodegradation of phenolic compounds (Entezari et al., 2003; Kotronarou et al., 1991; Okouchi et al., 1992; Pétrier & Francony, 1997; Serpone et al., 1992, 1994). In the presence of air the total phenol were removed due to their interaction with $OH^{\bullet}$, produced during thermal base catalysed decomposition of H_2O_2. This decomposition was more extended at higher temperatures such as 60°C.

5.10.14.3 Effect of Aeration on the TAAs Removal Efficiencies at Increasing Sonication Times and Temperatures

67.12% TAAs removal was observed under 1 h aeration, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.77a). An increase of 2.14% in TAAs removal was obtained under 1 h aeration after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=64.98% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and aeration was not observed (R^2=0.37, F=4.78, p=0.001) (Figure 5.77a).



(a)



(b)

Figure 5.77 Effect of aeration on the TAAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values).

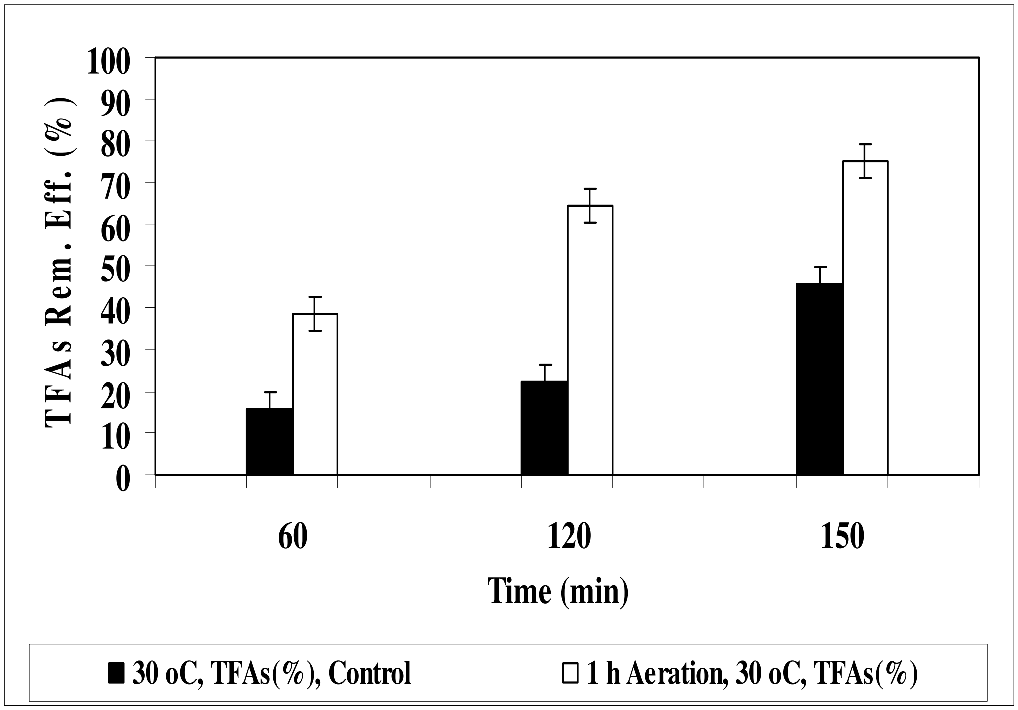
72.83% TAAs yield was found under 1 h aeration after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.77b). The contribution of aeration on TAAs removal was only 2.31% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=70.52% TAAs at pH=7.0 and at 60^{o}C). The maximum TAAs removal efficiency was 72.83% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between TAAs yields and aeration was not observed (R^2=0.32, F=4.03, p=0.001) (Figure 5.77b).

Dungan (2005) 27.00% TAAs (benzene, toluene, xylene, ethylbenzene, 1,3,5–trimethylbenzene, 1,2,4–trimethylbenzene) yields was obtained under aerated conditions after 60 min sonication time at 30^{o}C. This TAAs removal obtained by Dungan (2005) is lower than the present study (41.06%) at 30^{o}C after 60 min sonication.

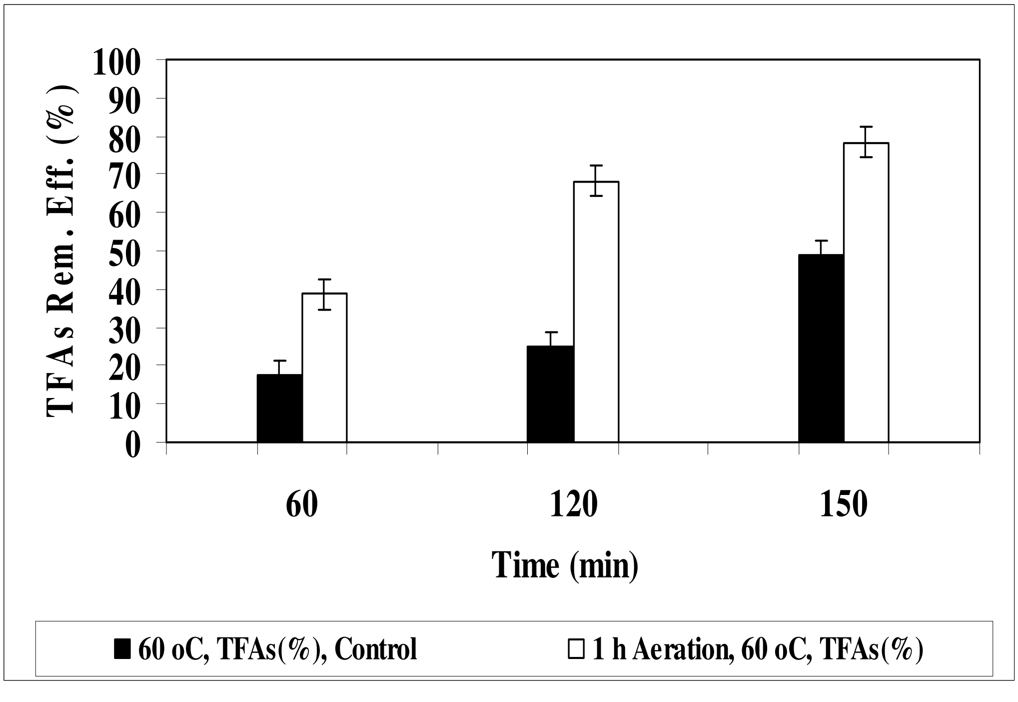
5.10.14.4 Effect of Aeration on the TFAs Removal Efficiencies in OMI ww at Increasing Sonication Times and Temperatures

75.07% TFAs removal was observed under 1 h aeration, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.78a). An increase of 29.41% in TFAs removal was obtained under 1 h aeration after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (45.66% TFAs yield at pH=7.0 and at 30^{o}C). A significant linear correlation between TFA**s** yields and aeration was observed (R^2=0.78, F=14.22, p=0.001) (Figure 5.78a).

78.33% TFAs yield was found under 1 h aeration after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.78b). The contribution of aeration on TFAs removal was 29.49% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=48.84% TFAs at pH=7.0 and at 60^{o}C). The maximum TFAs removal efficiency was 78.33% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between TFAs yields and aeration was observed (R^2=0.79, F=13.96, p=0.001) (Figure 5.78b).



(a)



(b)

Figure 5.78 Effect of aeration on the TFAs removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values).

In a study performed by Jimenez et al. (2007) 40.00%, 27.00% and 53.00% TFAs removals were found in OMI ww in three different sonicators with horn probe, cleaning bath and conventional thermal treatment, respectively, at a power of 150 W at a frequency of 25 kHz, in presence of 100 l/h air, for 20 min sonication time at temperatures varying between 28^{o}C and 30^{o}C. In the present study, high TFAs removals were measured (78.33%) compared to the TFAs removals obtained by Jimenez et al. (2007).

5.11 Sonication of TI ww

The TI ww used in this study contains color (> 70.90 m^{-1}), TAAs (> 1296 mg benzidine/l), COD (> 770 mg/l) and high BOD_5 (> 251 mg/l) concentrations with a BOD_5/COD ratio of 0.33. The characterization of TI ww was shown in Table 5.79 for minimum, medium and maximum values. All measurements were carried out three times and the results are given as the means of the triplicate samplings with standard deviation (SD) values.

Table 5.79 Characterization values of TI ww (n=3, mean values ± SD).

Parameters	**Values**		
	Minimum	**Medium**	**Maximum**
pH	5.00 ± 0.18	5.27 ± 0.19	6.00 ± 0.21
DO (mg/l)	1.30 ± 0.05	1.40 ± 0.05	1.50 ± 0.05
ORP (mV)	85.00 ± 2.98	106.00 ± 3.71	128.00 ± 4.48
TSS (mg/l)	285.00 ± 9.98	356.00 ± 12.46	430.00 ± 15.05
TVSS (mg/l)	192.00 ± 6.72	240.00 ± 8.40	290.00 ± 10.15
COD_{total} (mg/l)	931.70 ± 32.61	1164.60 ± 40.76	1409.20 ± 49.32
$COD_{dissolved}$ (mg/l)	770.40 ± 26.96	962.99 ± 33.71	1165.22 ± 40.78
TOC (mg/l)	462.40 ± 16.18	578.00 ± 20.23	700.00 ± 24.50
BOD_5 (mg/l)	251.50 ± 8.80	314.36 ± 11.00	380.38 ± 13.31
BOD_5/COD_{dis}	0.26 ± 0.01	0.33 ± 0.012	0.40 ± 0.014
Total N (mg/l)	24.80 ± 0.87	31.00 ± 1.09	37.51 ± 1.31
NH_4-N (mg/l)	1.76 ± 0.06	2.20 ± 0.08	2.66 ± 0.09
NO_3-N (mg/l)	8.00 ± 0.28	10.00 ± 0.35	12.10 ± 0.42
NO_2-N (mg/l)	0.13 ± 0.05	0.16 ± 0.06	0.19 ± 0.07
Total P (mg/l)	8.80 ± 0.31	11.00 ± 0.39	13.30 ± 0.47
PO_4-P (mg/l)	6.40 ± 0.22	8.00 ± 0.28	9.68 ± 0.34
Total phenol (mg/l)	29.60 ± 1.04	37.00 ± 1.30	44.80 ± 1.57
SO_4^{-2} (mg/l)	1248.00 ± 43.70	1560.00 ± 54.60	1888.00 ± 66.10
Color (m^{-1})	70.90 ± 2.48	88.56 ± 3.10	107.20 ± 3.75
TAAs (mg benzidine /l)	1296.00 ± 45.36	1620.00 ± 56.70	1960.00 ± 68.60

5.11.1 Effect of Increasing Sonication Time on the Removals of COD$_{dis}$ and TOC in TI ww at 25^{o}C Ambient Conditions

TI ww were sonicated at 60 min, 120 and 150 min sonication times. 30.43%, 53.69% and 74.27% COD$_{\text{dis}}$ removals were observed at 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25$^{\text{o}}$C (Figure 5.79). The maximum COD$_{\text{dis}}$ removal efficiency was 74.27% after 150 min sonication time at pH=7.0 and at 25$^{\text{o}}$C. As the sonication time was increased the COD$_{\text{dis}}$ removal efficiency in TI ww was enhanced. A significant linear correlation between COD$_{\text{dis}}$ yields and increasing sonication time was observed (R^2=0.81, F=16.12, p=0.01) (Figure 5.79).

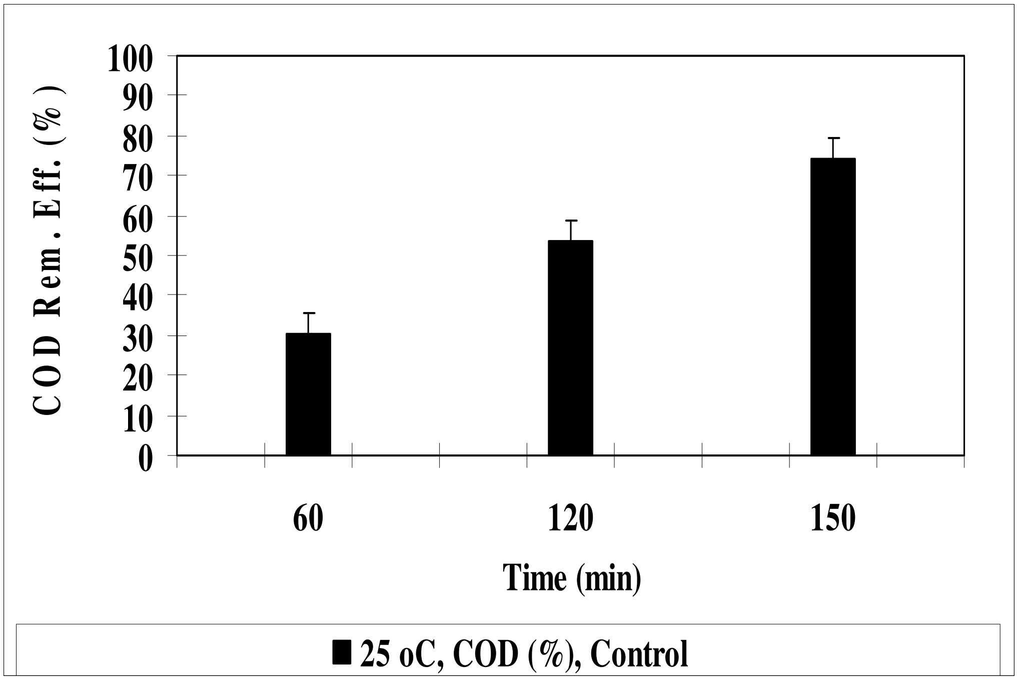


Figure 5.79 Effect of increasing sonication time on the COD$_{\text{dis}}$ removal efficiencies in TI ww at 25$^{\text{o}}$C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial COD$_{\text{dis}}$ concentration=962.99 mg/l, n=3, mean values).

31.64%, 51.42% and 72.95% TOC removals were observed after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25$^{\text{o}}$C (Figure 5.80). The maximum TOC removal efficiency was 72.95% after 150 min sonication time at pH=7.0 and at 25°C. A significant linear correlation between TOC yields and increasing sonication time was observed (R^2=0.83, F=15.77, p=0.01) (Figure 5.80).

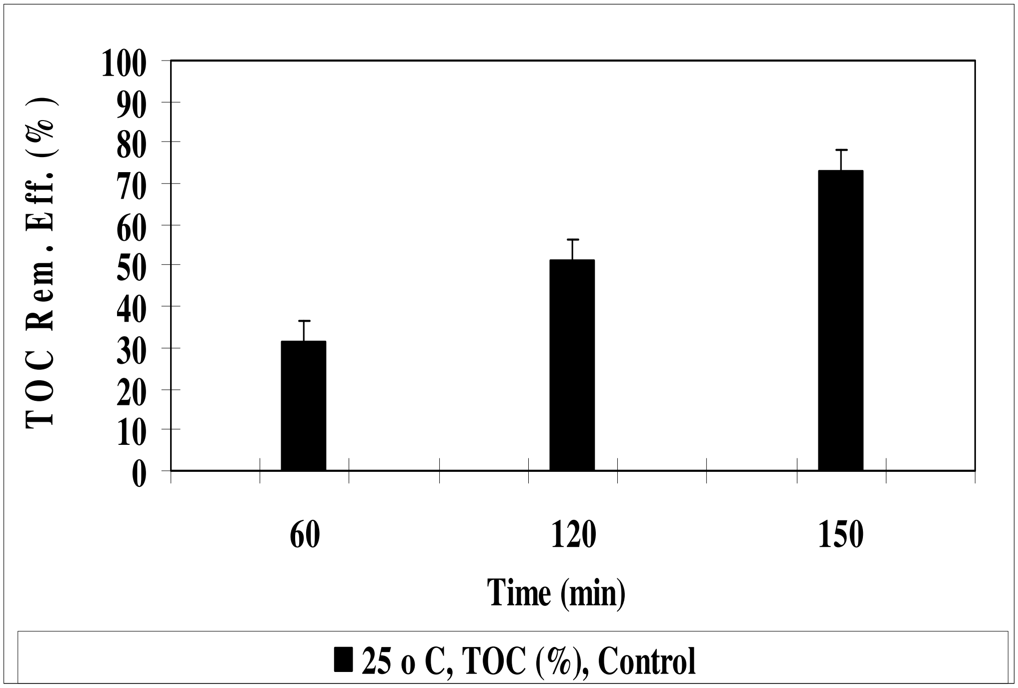


Figure 5.80 Effect of increasing sonication time on the TOC removal efficiencies in TI ww at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial TOC concentration=587.84 mg/l, n=3, mean values).

The sonochemical activity arises mainly from acoustic cavitation in liquid media. The acoustic cavitation occurring near a solid surface will generate microjets which will facilitate the liquid to move with a higher velocity resulting in increased diffusion of solute inside the pores of the TI ww (Gogate et al., 2004a, 2004b). In the case of sonication, localized temperature raise and swelling effects due to ultrasound may also improve the diffusion. The stable cavitation bubbles oscillate which is responsible for the enhanced molecular motion and stirring effect of ultrasound. In case of cotton dyeing TI ww, the effects produced due to stable cavitation may be realized at the interface of fabric and colored solution. Mass transport intensification using a conventional approach such as very high elevated temperatures (> 500°C), is not always feasible, due to undesired side-effects such as fabric damage. About 87.00% and 81.00% COD_{dis} yields was achieved using 40 and 50 min ultrasounds while compared to only 48.00% and 28.90% COD_{dis} removals in the absence of ultrasound in TI ww at 25°C (Vankar & Shanker, 2008).

Behnajady et al. (2008a) 67.00% COD_{dis} removal was achieved in a TI ww containing 10.00 mg/l Rhodamine B concentration at an initial COD_{dis} concentration of 12.00 mg/l at 35 kHz frequency, at 170 W power and at a power density of 0.163 W/ml after 180 min sonication time at 25°C. In this study, 74.27% COD_{dis} removal was observed after 150 min sonication time at 25°C. The COD_{dis} yield found in the present study is higher than the yield obtained by Behnajady et al. (2008a) at 25°C. This could be attributed to the differences between sonication power and sonication frequency applied to the TI wws.

Destaillats et al. (2000b) achieved 50.00% TOC removal in a TI ww containing 16.00 mg/l Methyl Orange at 500 kHz frequency, at 50 W power and $2 W/cm^2$ power intensity after 60 min sonication time at 25°C. In this study, 72.95% TOC removal was measured after 150 min sonication time at 25°C. The TOC yield measured in the present study is higher than the yield observed by Destaillats et al. (2000b) at 25°C as mentioned above.

Yachmenev et al. (2004) found 88.00% COD removal in a TI ww containing 20.00 mg/l Reactive Blue 9, at 20 kHz frequency, after 60 min sonication time at 25°C and at pH=8.0. In this study, 74.27% COD_{dis} removal was observed after 150 min sonication time at 25°C. The COD_{dis} yield found in this study is lower than the yield obtained by Yachmenev et al. (2004) at 25°C.

5.11.2 Effect of Increasing Sonication Time on the Removals of Color and TAAs in TI ww at 25^{o}C Ambient Conditions

Table 5.80 summarizes the removals of Color and TAAs removal efficiencies at increasing sonication times at pH=7.0 and at 25^{o}C ambient conditions in TI ww.

Table 5.80 Effect of increasing sonication time on color and TAAs removals in TI ww before and after sonication experiments at 25^{o}C ambient conditions at pH=7.0 (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values ± SD).

Parameters	**Initial Conc.**	**Removal Efficiencies (%)**		
		25^{o}C		
		60. min	**120. min**	**150. min**
Color	88.56 ± 3.10 m^{-1}	12.37	53.47	57.09
TAAs	1620 ± 56.70 mg/l	16.73	20.15	26.98

5.11.2.1 Effect of Increasing Sonication Time on the Color Removal Efficiencies in TI ww at 25^{o}C Ambient Conditions

12.37%, 53.47% and 57.09% color removals were found after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25^{o}C. The maximum color removal efficiency was 57.09% after 150 min sonication time at pH=7.0 and at 25^{o}C (Table 5.80). A significant linear correlation between color yields and increasing sonication time was not observed (R^2=0.41, F=4.90, p=0.01).

The textile industries use enormous amount of H_2O and chemicals for the Wet processing of textiles and also use various types of dyes to impart attractive colors of commercial importance. The wastewater let out by the textile industries generally contain about 10.00% of dyes used for the textile coloration (Easton, 1995). These dye stuff include various types like acidic, basic, azo, reactive, anthroquinone-based compounds and among these azo dyes are widely used by the industries. Further, azo dyes contribute about 60.00–70.00% of the total dyestuff produced (Garcia-Montano et al., 2007).

The main reaction pathway for TI ww containing azo dye solutions is the oxidation by $OH^{\bullet}$ attack in the bulk liquid via sonication in Eq. (5.86), while thermal reactions may occur at the bubble–liquid interface for some dye molecules to approach gaseous bubble surfaces as reported by Ince & Tezcanli-Guyer (2004) in Eq. (5.87):

$$OH^{\bullet} + Dye \;\rightarrow\; [Dye - OH\ adduct]^{\bullet} \;\rightarrow\; Oxidized\ dye + CO_2 + H_2O \qquad (5.86)$$

$$Dye \;\xrightarrow{)))}\; Organic\ radicals + Dissociated\ dye\ fragments + C_2H_4 \qquad (5.87)$$

The H_2O_2 measurement during acoustic cavitation, in absence and in the presence of TI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the color treatment by sonication in TI ww decreases with increasing sonication time at 25°C (Table 5.81). In the absence of TI ww (in deionized water) the H_2O_2 was accumulated and its concentration was measured as 156.00 mg/l while the H_2O_2 concentration increased to 86.00 and 122.00 mg/l after 30 and 120 min sonication times, whereas the H_2O_2 level was only 10.00 mg/l in TI ww after 150 min sonication time in samples (Table 5.81). The $OH^{\bullet}$ ion concentrations also increased from $11.20\text{x}10^{-60}$ to $4.63\text{x}10^{-9}$ mg/l after 150 min sonication time in TI ww. This showed that oxidation and pyrolysis are main degradation mechanisms for decolorization with ultrasound. In other words, $OH^{\bullet}$ is the major process for complete degradation of color. In this study, in TI ww the most sonogenerated $OH^{\bullet}$ reacted with 57.09% maximum color removal and radical recombination to produce H_2O_2.

Table 5.81 Effect of increasing sonication time on H_2O_2 and $OH^\bullet$ ion concentrations in TI ww at 25°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (25°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (25°C)	156.00	0.00
H_2O_2 concentration (mg/l) in TI ww (25°C) after 30 min sonication	86.00	11.20×10^{-60}
H_2O_2 concentration (mg/l) in TI ww (25°C) after 120 min sonication	122.00	2.56×10^{-50}
H_2O_2 cncentration (mg/l) in TI ww (25°C) after 150 min sonication	10.00	4.63×10^{-9}

Fung et al. (1999) observed 86.00% C.I. Reactive Red 20 decolorization at a 320 kHz frequency, at a 66 W power after 90 min sonication time at 25°C in TI ww. In this study, 57.09% color removal was measured after 180 min sonication at 60°C. The color yield found in this study is lower than the yield obtained by Fung et al. (1999) at 25°C as mentioned above. Fung et al. (2000a) 80.00% C.I. Reactive Red 20 removal was achieved at 320 kHz frequency, at 66 W power after 100 min sonication time at 25°C in TI ww. In this study, 57.09% color removal was observed after 150 min sonication time at 25°C. The color yield in this study is lower than the yield obtained by Fung et al. (2000a) at 25°C as mentioned above. The low color yields in this study could be attributed to the low temperature and to the the low sonication times applied to the TI wws. Furthermore the physicochemical properties of color given organics and dyestuffs affect the sonodegradation efficiencies of the TI wws.

The color yields obtained in this study are lower than the decolorization efficiencies obtained by Destaillats et al. (2000a) (80.00%) and Sun et al. (2007) (89.00%) in TI wws containing 10.00 mg/l Methyl Orange and 10.00 mg/l Acidic Black-1 at 500 kHz frequency, at 50 W power and at 2W/cm^2 power intensity after 60 min sonication time at 45°C. This could be attributed to the differences in dyestuff properties, to the dyestuff concentrations in TI ww and to the some operational conditions such as sonication at high frequency.

In a study performed by Singla et al. (2009) 80.00% color removal was obtained in a TI ww containing 15.00 mg/l Martius Yellow dye at 355 kHz frequency, at 30 W power, at power densities varying between 0.049 and 1.16 W/l, after 240 min sonication time at 25^{o}C. In this study, 57.09% color removal was observed after 150 min sonication time at 30^{o}C. The color yield found in this study is lower than the yield obtained by Singla et al. (2009) at 30^{o}C. This could be attributed to the low ambient temperature and to the high frequency used throughout sonication and to the high dye concentrations.

5.11.2.2 Effect of Increasing Sonication Time on the TAAs Removal Efficiencies in TI ww at 25^{o}C Ambient Conditions

16.73%, 20.15% and 26.98% TAAs removals were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25^{o}C(Table 5.80; Figure 5.81). The maximum TAAs removal efficiency was 26.98% after 150 min sonication time at pH=7.0 and at 25^{o}C. A significant linear correlation between TAAs yields and increasing sonication time was not observed (R^2=0.39, F=4.21, p=0.01) (Table 5.80; Figure 5.81).

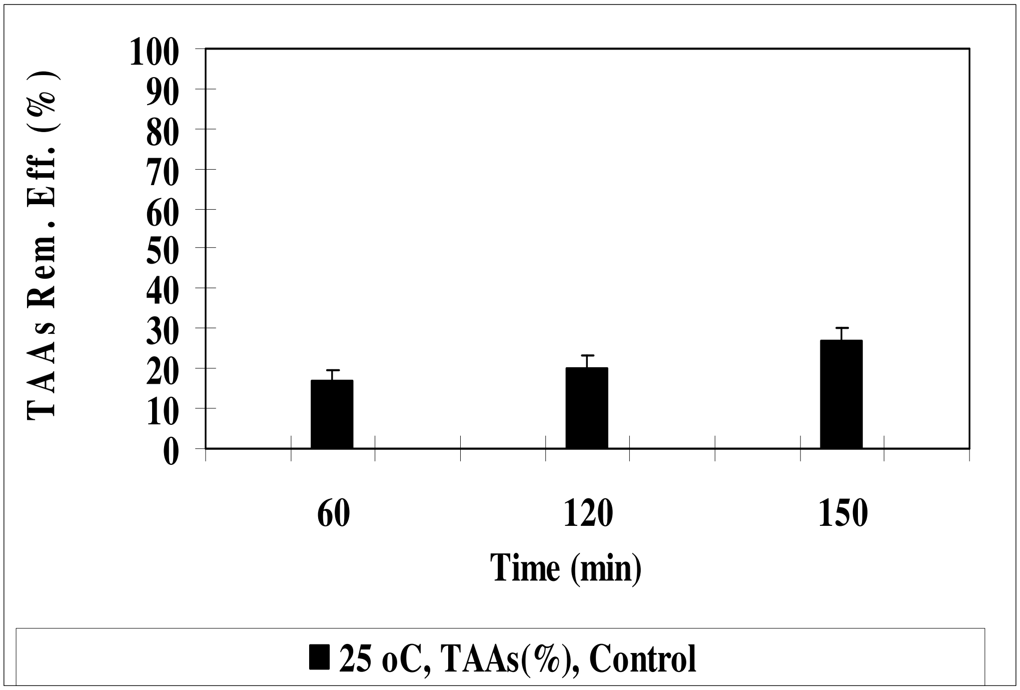


Figure 5.81 Effect of increasing sonication time on the TAAs removal efficiencies in TI ww at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

Azo dyes, which constitute the largest group of colorants used in industry (Zollinger, H. 1998), leave municipal wastewater plants highly diluted but nearly unchanged because they resist aerobic and short-term anaerobic treatment (Shaul et al., 1991; Walker, 1970). Only small amounts can be precipitated or adsorbed, while under anaerobic conditions azo dyes are cleaved by microorganisms, forming potentially carcinogenic aromatic amines (Chung & Cerniglia, 1992). This can occur in river sediments. The fragments of azo bond cleavage can undergo autoxidation under aerobic conditions, forming colorful products, as in case of Acid Orange 52, where fragments form “aniline black” by polymerization (Christen & Vogtle, 1989). Azo dyes forming “forbidden aromatic amines” are not allowed to be produced in Germany (Tauber et al., 2005). Among forbidden aromatic amines (TAAs in TI ww) are some alkylated derivatives of aniline, such as 2,4,5–trimethylaniline, *o*–toluidine, naphthylamine derivatives, such as 2–naphthylamine and benzidine derivatives. They are toxic and, as has been proven, potential carcinogens (Chung & Cerniglia, 1992). It is possible that toxic metabolites (for example, cytochrome P450) are formed after hydroxylation or oxidation of forbidden aromatic amines (Sterner, 1999). This creates an urgent demand for the development of multistep treatment concepts which guarantee not only irreversible decolorization but also mineralization of azo dyes. Hydrolysis and pyrolysis are main degradation mechanisms for AAs with ultrasound in TI ww (Gogate et al., 2004; Rehorek et al., 2004). The attack of non-volatile compounds in the ‘‘bulk’’ water by $OH^{\bullet}$ that destroy the chromophoric system through azo bond cleavage. Joseph et al. (2000) assumes that $OH^{\bullet}$ attack leads to hydroxyl amines followed by subsequent oxidation forming aromatic nitroso and nitro compounds. Other researchers postulate the attack at the carbon atom adjacent to the azo bond, leading to phenyl derivative radicals (for example, aminobiphenyls) (Rasanu et al., 2000). Further degradation pathways are difficult to predict since the fate of the fragments depends on their physical and chemical properties. Further reactions may occur inside the cavity (pyrolysis), in the hypercritical water layer or in the ‘‘bulk’’ water (Rehorek et al., 2004). As the reaction proceeds the degradation rate decreases independently on the initial dye concentration. The enrichment of low molecular weight species like $C_4/C_3/C_2$ is responsible for that observation as these species are harder to degrade and act as quencher (Stock et al., 2000). The attack of non-volatile compounds in the ‘‘bulk’’ water by $OH^{\bullet}$ destroy the chromophoric system through azo bond cleavage (azobenzene, diazene, azobisizobutylonitrile, 2,4,5–trimethylaniline, *o*–toluidine, naphthylamine, etc.) (Rehorek et al., 2004).

The TAAs in suspension (a homogeneous fluid containing solid particles that are sufficiently large for sedimentation) and some intermediates of reactive azo dyes (Methylene Blue) were used in textile and dye processing industries (Cardoso et al., 2010). The oxidation of the aromatic components performed with $OH^{\bullet}$, H_2O_2, $O_2H^{\bullet}$ and $^{\bullet}O_2$ which they are products of H_2O sonolysis througout sono-degradation as proposed in Eq. (5.86) (See in Eq. (5.86) at 5.11.2.1 Section) by Ince & Tezcanli-Guyer (2004).

The studies performed by Sivakumar & Pandit (2001) and Yuan et al. (2009) exhibited 76.00% and 35.00% TAAs removals in TI ww containing 10.00 mg/l Rhodamine B and 12.00 mg/l Methylene Blue at 30 kHz frequency and at 100 W power, after 90 min sonication time at 60^oC. The TAAs yield found in this study at 25^oC is lower than the yield obtained by the studies mentioned above. This could be attributed to the low ambient temperature (at 25^oC).

5.11.3 Effect of Increasing Temperature on the Removals of COD$_{dis}$ and TOC versus Sonication Times in TI ww

5.11.3.1 Effect of Increasing Sonication Time on the Removals of COD$_{dis}$ in TI ww

At the beginning of the studies the TI ww were sonicated at 30°C and 60°C at a pH=7.0 at increasing sonication times from 5 min up to 60 min to determine the lowest sonication times for the maximum COD$_{dis}$ removal efficiencies (Table 5.82). The lowest sonication time was determined as 60 min for the maximum COD$_{dis}$ removals.

Table 5.82 Effect of increasing sonication times (5–10–15–20–25–30–35–40–45–50–55 and 60 min) on TI ww at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD$_{dis}$ concentration=962.99 mg/l, n=3, mean values ± SD).

Time (min)	**30°C**		**60°C**	
	COD$_{dis}$ (mg/l)	**Rem. Eff. (%)**	**COD$_{dis}$ (mg/l)**	**Rem. Eff. (%)**
0	962.99 ± 33.71	0.00	962.99 ± 33.71	0.00
5	929.97 ± 33.70	3.43	924.40 ± 32.35	4.01
10	893.86 ± 31.29	7.18	885.79 ± 31.00	8.02
15	857.89 ± 30.03	10.91	847.09 ± 29.65	12.04
20	822.90 ± 28.80	14.55	807.59 ± 28.27	16.14
25	791.75 ± 27.71	17.78	768.69 ± 26.90	20.18
30	757.87 ± 26.53	21.30	730.39 ± 25.56	24.16
35	724.59 ± 25.36	24.76	691.79 ± 24.21	28.16
40	690.83 ± 24.18	28.26	652.19 ± 22.83	32.28
45	655.61 ± 22.95	31.92	615.68 ± 21.55	36.07
50	621.77 ± 21.76	35.44	575.39 ± 20.14	40.25
55	587.24 ± 20.55	39.02	537.29 ± 18.81	44.21
60	554.79 ± 19.42	42.39	499.94 ± 17.50	48.08

42.39%, 67.34% and 81.53% COD_{dis} removals were observed after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Figure 5.82). 11.96%, 13.65% and 7.26% increase in COD_{dis} removals were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control (E=74.27% COD_{dis} after 150 min sonication time at pH=7.0 and at 25°C). A significant linear correlation between COD_{dis} yields and temperature was not observed (R^2=0.33, F=2.88, p=0.01) (Figure 5.82).

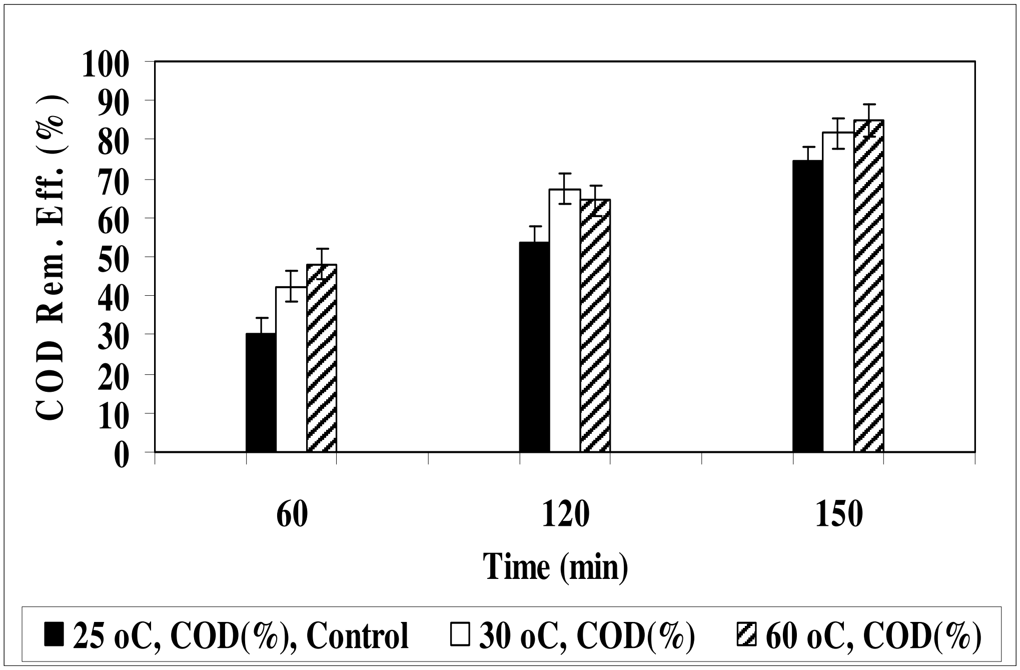


Figure 5.82 Effect of increasing temperature on the COD_{dis} removal efficiencies in TI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

48.08%, 64.48% and 84.92% COD_{dis} yields were found after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.82). The contribution of temperature on COD_{dis} removals were 17.65%, 10.79% and 10.65% after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 25°C. Sonication alone provided 74.27% COD_{dis} yield after 150 min sonication time at pH=7.0 and at 25°C. The maximum COD_{dis} removal efficiency was 84.92% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD$_{dis}$ yields and temperature was observed (R^2=0.71, F=13.92, p=0.01) (Figure 5.82).

40.57%, 66.96% and 80.79% TOC removals were observed after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Figure 5.83). 8.93%, 15.54% and 7.84% increase in TOC removals were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 25°C. Control provided 72.95% TOC yield after 150 min sonication time at pH=7.0 and at 25°C. A significant linear correlation between TOC yields and temperature was not observed (R^2=0.40, F=3.53, p=0.01) (Figure 5.83).

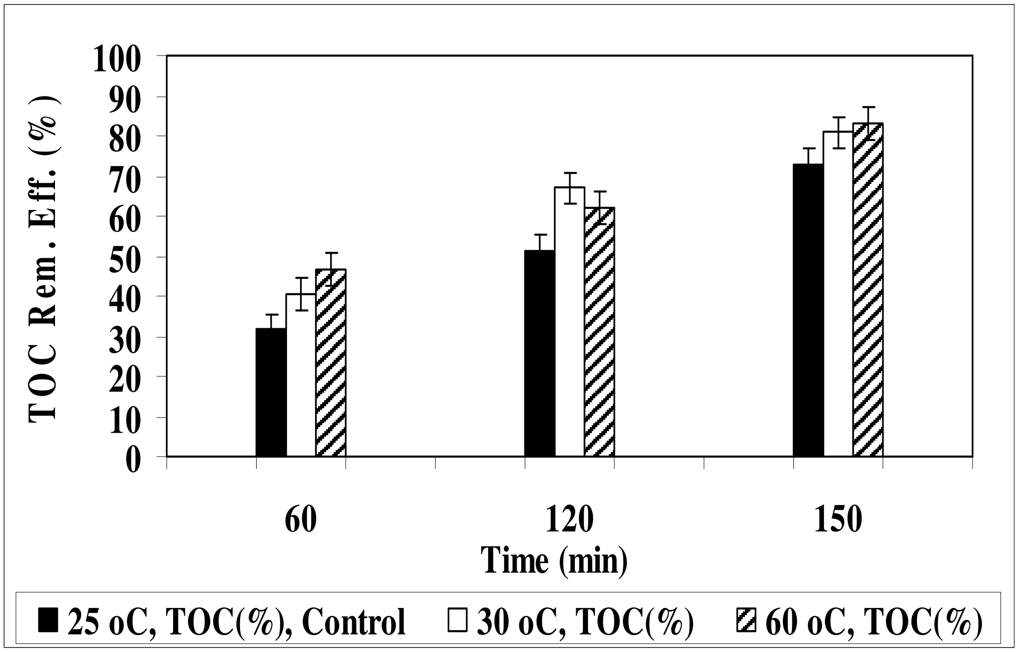


Figure 5.83 Effect of increasing temperature on the TOC removal efficiencies in TI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TOC concentration=587.84 mg/l, n=3, mean values).

46.56%, 62.17% and 83.22% TOC yields were found after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.83). 14.92%, 10.75% and 10.27% increase in TOC removals were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 60°C. Control provided 72.95% TOC yield after 150 min sonication time at pH=7.0 and at 25^oC. The maximum TOC removal efficiency was 83.22% after 150 min sonication time at pH=7.0 and at 60^oC. Although, the TOC yields increased as the sonication times and temperatures were increased a significant linear correlation between TOC yields and temperature was not observed (R^2=0.33, F=2.95, p=0.01) (Figure 5.83).

The optimum time to reach equilibrium and the faster rate of removal in the presence of ultrasound was attributed to the higher mass transfer and higher surface area produced by the cavitation process (Sivakumar & Pandit, 2001). The phenomenon responsible for removals of COD_{dis} and TOC is the formation of $OH^\bullet$ during sonication of aqueous solution by the cavitation process. This process consists of the formation, growth and collapse by violent implosions to release extreme temperatures and pressures at local hot spots in the liquid (Suslick, 1986). Under these critical conditions, the entrapped molecules of H_2O in the bubble dissociate into very reactive $OH^\bullet$ and $H^\bullet$ (Entezari & Sharif Al-Hoseini, 2007).

With an increase in the temperature, the initial sono-degradation rate was increased in TI ww. This could be explained by the hydrophilic property of the pollutant which is mostly degraded outside the cavitation process by the $OH^\bullet$ produced by ultrasound in TI ww (Moore & Ausley, 2004). Therefore, reactions in the bulk are facilitated by increasing the temperature due to the higher mass transfer of different species at higher temperatures and this leads to an enhancement of the reaction rate of radicals with COD or TOC molecules (Ghodbane & Hamdaoui, 2009a). On the other hand, any increase in temperature will raise the vapor pressure of a medium and so lead to easier cavitation (Behnajady et al., 2008a).

The H_2O_2 measurement during acoustic cavitation, in absence and in the presence of TI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the COD_{dis} treatment by sonication in TI ww decreases with increasing sonication time at 60^oC (Table 5.83). In the absence of TI ww (in deionized water) the H_2O_2 was accumulated and its concentration was measured as 177.00 mg/l while the H_2O_2

concentration increased to 92.00 and 158.00 mg/l after 30 and 120 min sonication times, whereas the H_2O_2 level was only 13.00 mg/l in TI ww after 150 min sonication time in samples at 60°C (Table 5.83). The $OH^\bullet$ ion concentrations also increased from 2.35×10^{-58} to 6.87×10^{-8} mg/l after 150 min sonication time in TI ww. This showed that hydroxylation is main degradation mechanism of the removal of COD_{dis}. In other words, $OH^\bullet$ is the major process for complete degradation of COD_{dis}. In this study, in TI ww the most sonogenerated $OH^\bullet$ reacted with 84.92% maximum COD_{dis} removal and radical recombination to produce H_2O_2.

Table 5.83 Effect of increasing sonication temperature on H_2O_2 and $OH^\bullet$ ion concentrations in TI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (25°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	177.00	0.00
H_2O_2 concentration (mg/l) in TI ww (60°C) after 30 min sonication	92.00	2.35×10^{-58}
H_2O_2 concentration (mg/l) in TI ww (60°C) after 120 min sonication	58.00	12.11×10^{-45}
H_2O_2 concentration (mg/l) in TI ww (60°C) after 150 min sonication	13.00	6.87×10^{-8}

In a study performed by Arslan et al. (2000) 80.00% COD removal was achieved at 30 kHz frequency, at 640 W power, 22 W/m^2 power intensity after 80 min sonication time at 30°C in TI ww. In this study, 81.53% COD_{dis} removal was observed after 150 min sonication time at 30°C. The COD_{dis} yield found in the present study is higher than the yield obtained by Arslan et al. (2000) at 30°C as mentioned above.

Yavuz et al. (2009) accomplished 98.30% COD removal in a TI ww containing 20.00 mg/l Basic Red 29 at 40 kHz frequency, at 25 W power and at 0.25 W/ml power density after 30 min sonication time at 40°C. In this study, 84.92% COD_{dis} removal was observed after 150 min sonication time at 60°C. The COD_{dis} yield in the present study is lower than the yield obtained by Yavuz et al. (2009) at 40°C as mentioned above. This could be attributed to the differentiations in the organic content of the TI ww studied.

5.11.3.2 Effect of Increasing Temperature on the Color Removal Efficiencies in TI ww at Increasing Sonication Time

52.29%, 76.38% and 78.26% color removals were observed after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Table 5.84). 39.92%, 22.91% and 21.17% increase in the color removals were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control (E=12.37%, E=53.47% and E=57.09% color after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25°C). A significant linear correlation between color yields and temperature was not observed (R^2=0.46, F=4.51, p=0.01) (Table 5.84).

Table 5.84 Effect of increasing temperature on color and TAAs removals in TI ww before and after sonication experiments at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

Parameters	**Removal Efficiencies (%)**								
	25°C (control)			**30°C**			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Color (m^{-1})	12.37	53.47	57.09	52.29	76.38	78.26	79.32	83.20	87.66
TAAs (mg benzidine/l)	16.73	20.15	26.98	20.09	27.28	33.89	20.70	30.00	40.62

79.32%, 83.20% and 87.66% color yields were found after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Table 5.84). The contribution of temperatures on color removals were 66.95%, 29.73% and 30.57% after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control (E=12.37%, E=53.47% and E=57.09% color after 60 min, 120 and 150 min sonication times, respecvtively, at pH=7.0 and at 25°C). The maximum color removal efficiency was 87.66% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and temperature was not observed (R^2=0.51, F=3.09, p=0.01) (Table 5.84).

Vankar & Shanker (2008) found that the ultrasonic waves can reduce the concentration of Methylene Blue up to 10.00% in 30 min sonication time at 30°C. In this study, 78.26% color removal was observed after 150 min sonication time at 30°C. The color yield in the present study is higher than the yield obtained by Vankar & Shanker (2008) at 30°C.

Sayan (2006) reported 80.62% color removal in a TI ww containing 1.00 g/l Rifacion Yellow HE4R with ultrasound and combined ultrasound/activated carbon at 850 kHz frequency, 140 W power, after 120 min sonication at 30°C. In this study, 78.26% color removal was observed after 150 min sonication at 30°C. In this study, similar yields were observed with the yields obtained by Sayan (2006) at 30°C as mentioned above.

Zhang & Zheng (2009) achieved 96.30% color yield in a TI ww containing 79.50 mg/l C.I. Acid Green 20, at 40 kHz frequency, at 250 W power and at 1.08 W/l power density after 150 min sonication time at 60°C. In this study, 87.66% color removal was observed after 150 min sonication time at 60°C. The color yield in the present study is lower than the yield obtained by Zhang & Zheng (2009) at 60°C. This could be attributed to the different dyestuff properties of the TI ww studied and to the different operational conditions used in the sonication such as frequency and sonication power.

In a study performed by Entezari & Sharif Al-Hoseini (2007) 98.00% color removal was accomplished in a TI ww containing 50.00 mg/l Methylene Blue, at 20 kHz frequency, at 120 W power, after 30 min sonication time at 30°C with 700 rpm agitation. In this study, 78.26% color removal was observed after 150 min sonication time at 30°C at not agitated conditions. The color yield in the present study is lower than the yield obtained by Entezari & Sharif Al-Hoseini (2007) at 30°C as mentioned above. This could be attributed to the differentiations in dyes present in TI to the operational conditions such as sonication duration, sonication frequency and to non stirred conditions of sonicated wastewater.

Entezari et al. (2008) obtained 91.50% color yield in a TI ww containing 250 mg/l Reactive Black 5, at 500 kHz frequency, at 1 W/cm^2 power intensity, after 240 min sonication time at 30°C and at pH=5.5 with 700 rpm agitation. In this study, 78.26% color removal was observed after 150 min sonication time at pH=7.0 and at 30°C. The color yield in the present study is lower than the yield observed by Entezari et al. (2008) at 30°C as mentioned above. This could be attributed to the different pH values studied throughout sonication period.

5.11.3.3 Effect of Increasing Temperature on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times

20.09%, 27.28% and 33.89% TAAs removals were observed after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Table 5.84; Figure 5.84). 3.36%, 7.13% and 6.91% increase in TAAs removals were obtained after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 25°C. Control provided 26.98% TAAs yield after 150 min sonication time at pH=6.98 and at 25°C. A significant linear correlation between TAAs yields and temperature was not observed (R^2=0.34, F=4.47, p=0.01) (Table 5.84; Figure 5.84).

20.70%, 30.00% and 40.62% TAAs yields were found after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Table 5.84; Figure 5.84). The contribution of temperatures on TAAs removals were 3.97%, 9.85% and 13.64%

after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 25°C. Control provided 16.73%, 20.15% and 26.98% TAAs yield after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 25°C. The maximum TAAs removal efficiency was 40.62% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and Temperature was not observed ($R^2=0.33$, F=4.06, p=0.01) (Table 5.84; Figure 5.84).

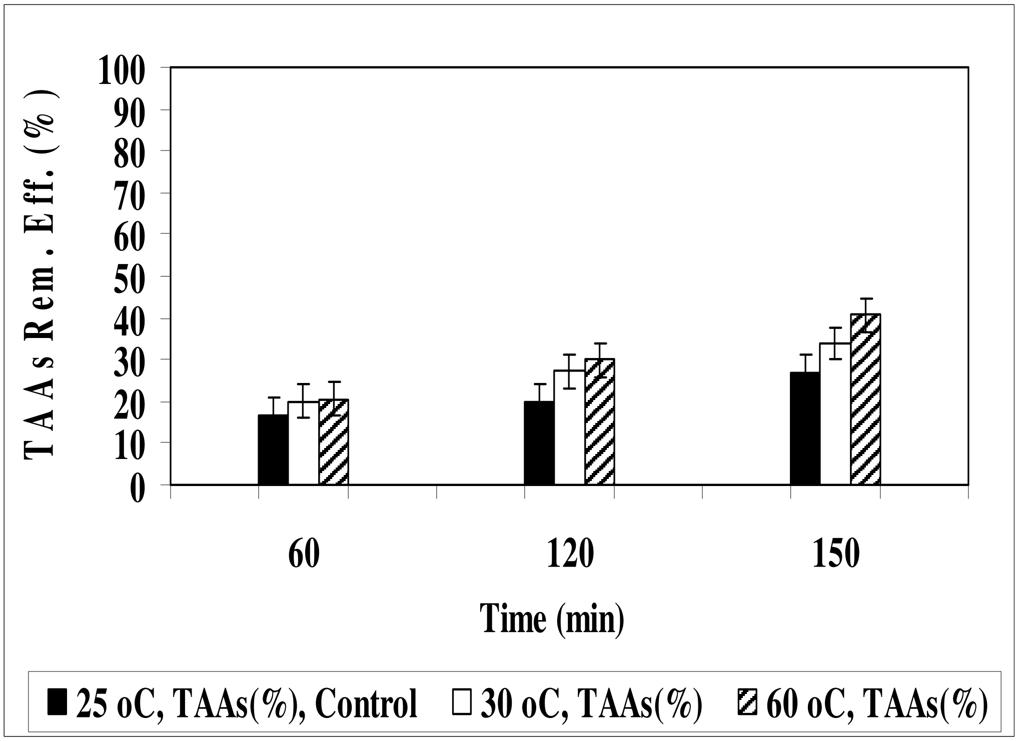
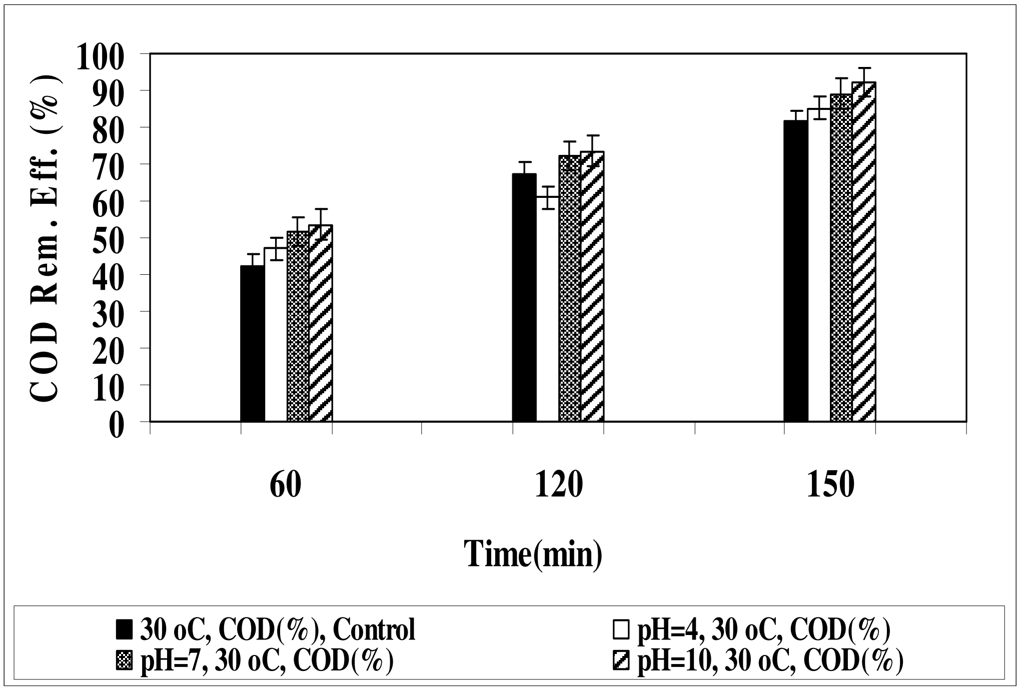


Figure 5.84 Effect of increasing sonication time on the TAAs removal efficiencies in TI ww at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

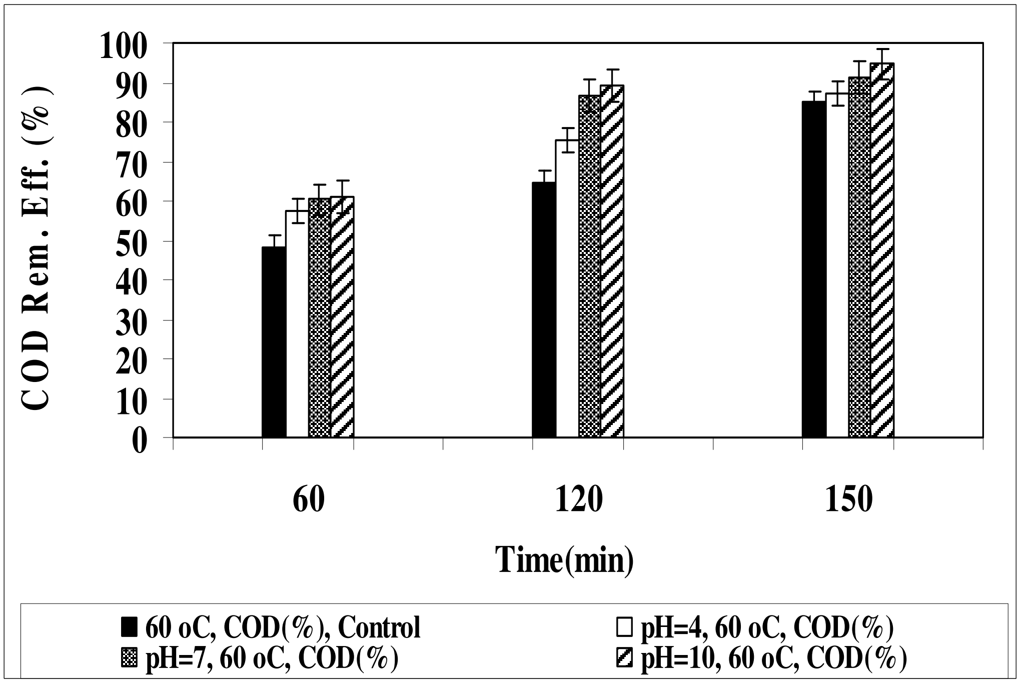
5.11.4 Effect of pH Values on the Removals of COD_{dis} in TI ww

85.10%, 89.11% and 92.21% COD_{dis} removals were observed at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C (Figure 5.85a). 3.57%, 7.58% and 10.68% increase in COD_{dis} removals were obtained at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C, compared to the control (81.53% COD_{dis} yield at pH=6.98 and at 30°C). Although, the COD_{dis} yields increased as the sonication times and pH values increased no significant contribution of pH on COD_{dis} yields was observed. A significant linear correlation between COD_{dis} yields and increasing pH values was not observed (R^2=0.41, F=0.30, p=0.01) (Figure 5.85a).

87.10%, 91.14% and 94.70% COD_{dis} yields were found at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C (Figure 5.85b). The contribution of pH values on COD_{dis} removals were 2.18%, 6.22% and 9.78% at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C, compared to the control (E=84.92% COD_{dis} at pH=6.98 and at 60°C). The maximum COD_{dis} removal efficiency was 94.70% at pH=10.0 after 150 min sonication time at 60°C. A significant linear correlation between COD_{dis} yields and increasing pH values was not observed (R^2=0.44, F=4.81, p=0.01) (Figure 5.85b).



(a)



(b)

Figure 5.85 Effect of increasing pH values on the COD_{dis} removal efficiencies in TI ww at (a) 30^{o}C and (b) 60^{o}C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

If ultrasound power is effectively used, sonication temperature, sonication time and initial pH are important process parameters affecting the COD reduction throughout sonication. High pH values are more effective for degradation of dyestuff. Because, COD_{dis} removal to increases with the increasing degradation rate constant, the increasing sonication temperature and the increasing $OH^{\bullet}$ production during cavitation process (Sayan, 2006). Under extreme alkaline conditions, $OH^{\bullet}$ scavenging effects become more significant (Vajnhandl et al., 2007). The enhancement of degradation rate at basic conditions may be caused by the change of hydrophobic property of dye. The hydrophilic property of the dye which is mostly degraded outside the cavitation process by the $OH^{\bullet}$ produced by ultrasound (Ghodbane & Hamdaoui, 2009b).

In a study performed by Guzman-Duque et al. (2011) it was reported 90.00% COD_{dis} removal in a TI ww containing 150 mg/l Crystal Violet after 180 min sonication time at 800 kHz frequency, at 80 W power, at pH=5.5 and at a temperature of 30°C. In this study, 92.21% COD_{dis} removal was observed at pH=10.0 after 150 min sonication time at 30°C. The COD_{dis} yield found in this study is higher than the yield obtained by Guzman-Duque et al. (2011) at 30°C as mentioned above. This could be attributed to the acidic pH levels which are found to be more effective in the sono-degradation of COD_{dis} compared to the alkaline conditions.

In a study performed by Sayan (2006) it was reported that 85.22% COD removal in a TI ww containing 1.00 g/l Rifacion Yellow HE4R VIA combined ultrasound/activated carbon at 850 kHz frequency, at 140 W power after 120 min sonication time at pH=2.0-12.0 and at 60°C. In this study, 94.70% COD_{dis} removal was observed after 150 min sonication time at 60°C. The COD_{dis} yield in this study is higher than the yield obtained by Sayan (2006) at 60°C. This could be attributed to the enhancing of the COD_{dis} yields with the increase of the sonication time from 120 to 150 min.

He et al. (2008) 70.00% COD removal found in a TI ww containing 20.00 mg/l C.I. Reactive Blue 19, at 20 kHz frequency, at 176 W power, at 176 W/l energy density, after 30 min sonication time at 60^{o}C and at pH=8.0. In this study, 94.70% COD$_{dis}$ removal was observed after 150 min sonication time at 60^{o}C. The COD$_{dis}$ yield in the present study is higher than the yield obtained by He et al. (2008) at 60^{o}C and at a pH of 8.0.

In a study performed by Madhavan et al. (2010) 82.00% COD removal was accomplished in a TI ww containing 90.00 mg/l Orange-G, at 213 kHz frequency, at 450 W power, after 75 min sonication time at 30^{o}C and at pH=5.8. In this study, 92.21% COD$_{dis}$ removal was measured after 150 min sonication time at 30^{o}C. The COD$_{dis}$ yield in present is higher than the yield observed by Madhavan et al. (2010) at 30^{o}C at a pH of 5.8. The sonolytic degradation of Orange-G was relatively higher at pH=5.8 than that at pH=12.0.

5.11.4.1 Effect of pH Values on the Color Removal Efficiencies in TI ww at Increasing Sonication Time and Temperature

87.43%, 88.84% and 89.07% color removals were observed at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30^{o}C (Table 5.85). 9.17%, 10.58% and 10.81% increase in color removals were obtained at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30^{o}C, compared to the control (at pH=6.98 while E=78.26% color at 30^{o}C). Color removal was increased with increasing sonication temperature, increasing sonication time and decreasing pH values. A significant linear correlation between color yields and increasing pH values was not observed (R^2=0.39, F=4.72, p=0.01) (Table 5.85).

94.01%, 93.77% and 95.06% color yields were found at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60^{o}C (Table 5.85). The contribution of pH values on the color removals were 6.35%, 6.11% and 7.40% at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60^{o}C, compared to the control (E=87.66% color at pH=6.98 and at 60^{o}C). The maximum color removal efficiency was 95.06% at pH=10.0 after 150 min sonication time at 60^{o}C. Although, as the color yields increased as the pH, temperature and sonication time were increased a significant linear correlation between color yields and increasing pH values was not observed (R^2=0.41, F=3.88, p=0.01) (Table 5.85).

Table 5.85 Effect of increasing pH values on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
pH=4.0	76.15	84.14	87.43	87.54	91.07	94.01
pH=7.0	78.61	86.25	88.84	89.54	91.54	93.77
pH=10.0	81.20	86.96	89.07	89.89	91.77	95.06

The pH of the medium is an important parameter for the degradation of chemical pollutants with hydrodynamic cavitation combined with H_2O_2 (Wang, X. et al., 2009). The reason may be that the oxidization potentials of $OH^\bullet$ and H_2O_2 are higher in acidic medium than that in basic. So the removal ratio of dyestuff is increased with decreasing the medium pH. On the other hand, a high pH value may create more free radical scavengers (i.e., CO_3^{-2}, HCO_3^{-1}) and results in the decrease in the concentration of $OH^\bullet$. This may be another reason for the decrease of removal ratio of dyestuff at higher pH value. Five different pH values were operated in this study. A pH value of 3.0 was selected as the optimal operational pH value for maximum removal of Acid Red B in TI ww (Wang, X. et al., 2009).

Ghodbane & Hamdaoui (2009a) showed that the initial decolorization rate is a function of the initial pH in TI ww. The initial bleaching rates in acidic solutions (pH=1.0–3.0) are higher, especially at pH=1.0, and decrease from pH=1.0 to pH=5.0, and there is almost no change in the pH range of 5.0–8.0. Higher decolorization rates are observed in basic media (9.3–11.8). Acid Blue 25 is a nonvolatile compound and the region of decolorization would be at the exterior of the cavitation bubbles. The change the solution pH in TI ww results in the change of hydrophobic property of the Acid Blue 25 dye, which affects the ultrasonic decolorization. The acceleration of decolorization in acidic conditions is probably associated with the effect of protonation of negatively charged SO_3^{-1} group (in Acid Blue 25) in acidic medium and, obviously, the hydrophobic character of the resulting molecule enhances its reactivity under ultrasound treatment because Acid Blue 25 is accumulated in the interface of the cavitation bubbles. In acidic conditions (pH=1.0–3.0), the recombination of $OH^\bullet$ reaction is less effective before react against Acid Blue 25 concentrated in the interface. In the pH range 5.0–8.0, Acid Blue 25 reaches the ionized state, and its hydrophilicity and solubility are enhanced, and thus the decolorization is carried out in the bulk of the solution where there is a lower concentration of $OH^\bullet$ because only about 10.00% of the $OH^\bullet$ generated in the bubble can diffuse into the bulk solution (Goel et al., 2004). Additionally, the bleaching rates decrease at pH=5.0 and pH=8.0 due to the fact that a higher number of $OH^\bullet$ species recombine to H_2O_2. The enhancement of decolorization rate at basic conditions may be caused by the change of hydrophobic property of the dye (Ghodbane & Hamdaoui, 2009a, 2009b). The same results were obtained for the decolorization of reactive Brilliant Red by 20 kHz ultrasonic irradiation (Wang, X. et al., 2008). In present study, COD_{dis} removal increased with increasing pH values (from 4.0 to 10.0). Both increasing pH values (from 4.0 to 10.0) and increasing temperature (from 25°C to 60°C) was increased the COD_{dis} yields after sonication process.

Under extreme alkaline conditions, $OH^\bullet$ scavenging effects become more significant (Vajnhandl et al., 2007). The enhancement of degradation rate at basic conditions may be caused by the change of hydrophobic property of dye. The hydrophilic property of the dye which is mostly degraded outside the cavitation process by the $OH^\bullet$ produced by ultrasound (Ghodbane & Hamdaoui, 2009b).

Minero et al. (2008) observed 99.00% decolorization in a TI ww containing 50.00 mg/l Acid Blue 40 at 35 W power, at 354.5 kHz frequency, at 176 W/l power density after 20 min sonication timeat 60°C at pH=11.0. In this study, 95.06% color removal was observed at pH=10.0 after 150 min sonication time at 60°C. The Color yield in the present study is lower than the yield obtained by Minero et al. (2008) at 60°C as mentioned above. This could be attributed to the different dyestuff properties studied.

Sayan (2006) reported that 99.90% color removal in in a TI ww containing 1.00 g/l Reactive Dye Rifacion Yellow HE4R was accomplished with combined ultrasound/activated carbon at 850 kHz frequency, at 140 W power after 120 min sonication time, at pH=2.0-12.0 and at 30°C. In this study, 89.07% color removal was observed at pH=10.0 after 150 min sonication time at 30°C. The color yield in the present study is lower than the yield obtained by Sayan (2006) at 30°C as mentioned above. This could be attributed to the different dyestuff properties studied.

In a study performed by He et al. (2007) 93.00% decolorization in a TI ww containing 500 mg/l C.I. Reactive Yellow 84 was achieved at a 20 kHz frequency, at 176 W/l power density after 60 min sonication time at 60°C and a pH=10.0. In this study, 95.06% color removal was observed at pH=10.0 after 150 min sonication time at 60°C. The color yield in the present study is higher than the yield observed by He et al. (2007) at 60°C as mentioned above.

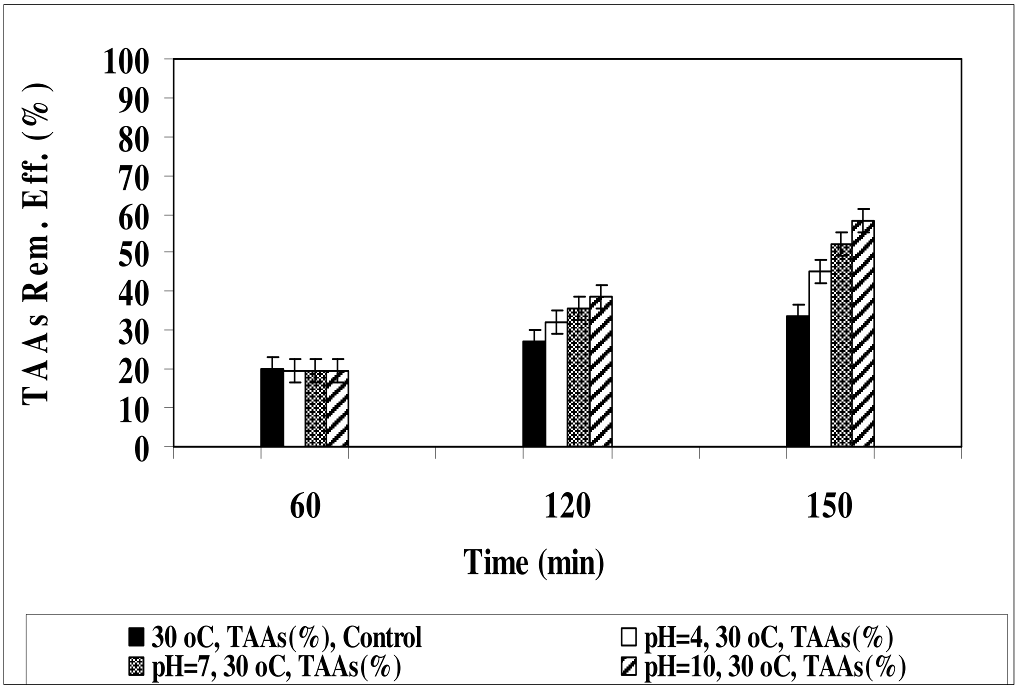
Madhavan et al. (2010) observed 85.00% color removal in a TI ww containing 90.00 mg/l Orange-G, at 213 kHz frequency, at 450 W power, after 75 min sonication time at 30°C and at pH=12.0. In this study, 89.07% color removal was measured at pH=10.0 after 150 min sonication time at 30°C. The color yield in the present study is higher than the yield obtained by Madhavan et al. (2010) at 30°C as mentioned above.

In a study performed by Küncek & Sener (2010) 95.00% color removal was achieved in a TI ww containing 80.00 mg/l Methylene Blue, at 20 kHz frequency, at 750 W power, after 90 min sonication time at 60°C and at pH=8.3 with 400 rpm agitation. In this study, 95.06% color removal was measured at pH=10.0 after 150 min sonication time at 60°C. In this study, similar yields were observed with the study performed by Küncek & Sener (2010) at 60°C.

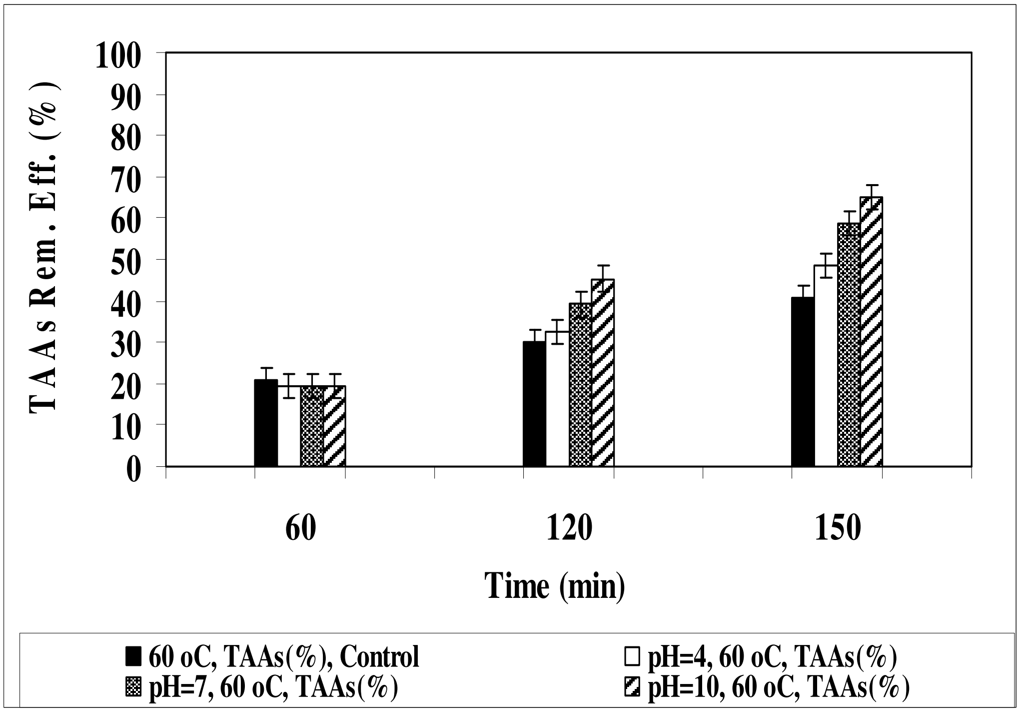
5.11.4.2 Effect of pH Values on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Time and Temperature

45.39%, 52.05% and 58.39% TAAs removals were observed at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C (Figure 5.86a). 11.50%, 18.16% and 24.50% increase in TAAs removals were obtained at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 30°C, compared to the control (33.89% TAAs yield at pH=6.98 and at 30°C). A significant linear correlation between TAAs yields and increasing pH values was not observed (R^2=0.43, F=5.01, p=0.01) (Figure 5.86a).

48.57%, 58.61% and 64.89% TAAs yields were found at pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C (Figure 5.86b). The contribution of pH values on TAAs removals were 7.95%, 17.99% and 24.27% for pH=4.0, pH=7.0 and pH=10.0, respectively, after 150 min sonication time at 60°C, compared to the control (E=40.62% TAAs at pH=6.98 and at 60°C). In this study, it was found that as the pH, sonication time and temperatures were increased the TAAs yields increased. The maximum TAAs removal efficiency was 64.89% at pH=10.0 after 150 min sonication time at 60°C. A significant linear correlation between TAAs yields and increasing pH values was observed (R^2=0.83, F=13.95, p=0.01) (Figure 5.86b).



(a)



(b)

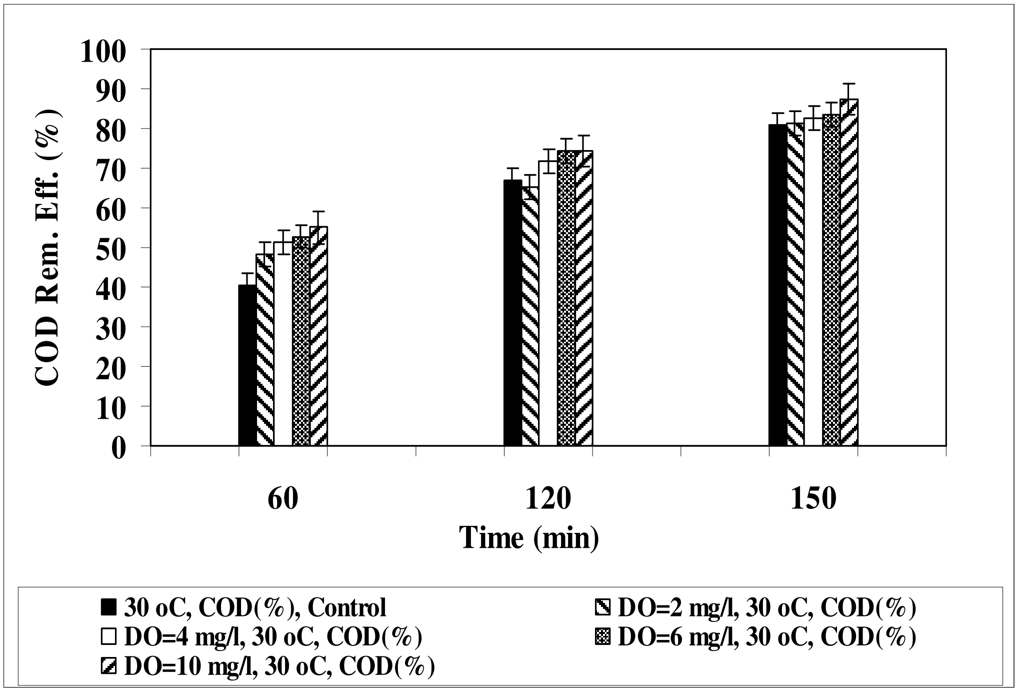
Figure 5.86 Effect of increasing pH values on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

Zhang, H. et al. (2006) found 82.80% TAAs removal at combined US/O_3 systems in a TI ww containing 400 mg/l Methyl Orange, at 20 kHz frequency, at 250 W power, after 120 min sonication time at 60°C and at pH=9.70. In this study, 64.89% TAAs removal was observed at pH=10.0 after 150 min sonication time at 60°C. The TAAs yield in present study is lower than the yield obtained by Zhang, H. et al. (2006) at 60°C. This could be attributed to the more $OH^\bullet$ ion concentrations generation in both O_3 and sonication processes.

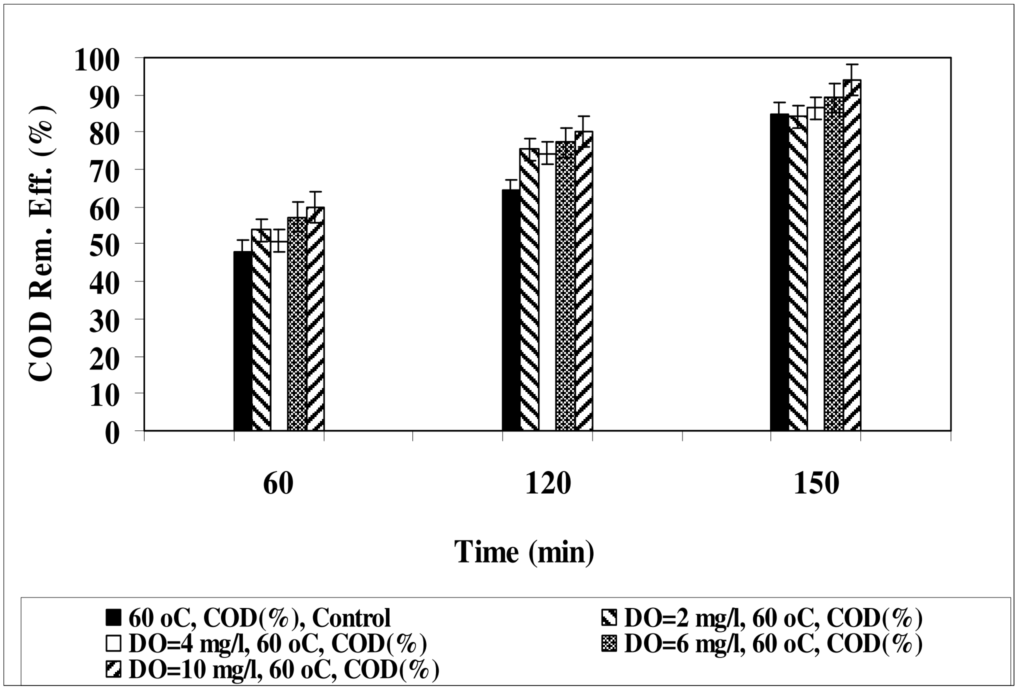
In a study performed by Wang, X. et al. (2009) 90.00% TAAs removal was accomplished in a TI ww containing 10.00 mg/l Acid Red B, at 40 kHz frequency, at 50 W power, after 100 min sonication time at 60°C and at pH=7.0. In this study, 64.89% TAAs removal was measured at pH=10.0 after 150 min sonication time at 60°C. The TAAs yield in the present study is lower than the yield observed by Wang, X. et al. (2009) at 60°C as mentioned above. This could be attributed to high $OH^\bullet$ ion concentration at neutral pH compared to the alkaline conditions ending with hydroxylation reaction for TAAs removal.

5.11.5 Effect of DO Concentrations on the Removals of COD_{dis} in TI ww

81.21%, 82.44%, 83.41% and 87.30% COD_{dis} removals were observed in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.87a). 0.91%, 1.88% and 5.77% increase in COD_{dis} removals were obtained in 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=81.53% COD_{dis} at DO=0.00 mg/l, at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing DO concentrations was not observed (R^2=0.27, F=3.31, p=0.01) (Figure 5.87a).



(a)



(b)

Figure 5.87 Effect of increasing DO concentrations on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

84.27%, 86.59%, 89.31% and 94.07% COD_{dis} yields were found in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.87b). The contribution of DO concentrations on COD_{dis} removals were 1.67%, 4.39% and 9.15% in 4 mg/l, 6 and 10 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=84.92% COD_{dis} at DO=0.00 mg/l, at pH=7.0 at 60^{o}C). The maximum COD_{dis} removal efficiency was 94.07% at DO=10.00 mg/l after 150 min sonication time at pH=7.0 and at 60^{o}C. Although, the COD_{dis} yields increased as the sonication time and DO concentration were increased a significant linear correlation between COD_{dis} yields and increasing DO concentrations was not observed (R^2=0.30, F=3.26, p=0.01) (Figure 5.87b).

The H_2O_2 measurement during acoustic cavitation, in absence and in the presence of TI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the COD_{dis} treatment by sonication in TI ww decreases with increasing sonication time at 60^{o}C (Table 5.86). In the absence of TI ww (in deionized water) the H_2O_2 was accumulated and its concentration was measured as 190.00 mg/l while the H_2O_2 concentration increased to 95.00 and 166.00 mg/l after 30 and 120 min sonication times, whereas the H_2O_2 level was only 17.00 mg/l in TI ww after 150 min sonication time in samples containing 10.00 mg/l DO (Table 5.86). The $OH^\bullet$ ion concentrations also increased from 6.54x10^{-59} to 3.21x10^{-7} mg/l after 150 min sonication time in TI ww. This showed that hydroxylation is main degradation mechanism of the removal of COD_{dis}. In other words, $OH^\bullet$ is the major process for complete degradation of COD_{dis}. In this study, in TI ww the most sonogenerated $OH^\bullet$ reacted with 94.07% maximum COD_{dis} removal and radical recombination to produce H_2O_2.

Table 5.86 Effect of DO=10.00 mg/l concentration on H_2O_2 and $OH^{\bullet}$ ion concentrations in TI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (25°C)**	**$OH^{\bullet}$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	190.00	0.00
H_2O_2 concentration (mg/l) in TI ww (60°C) after 30 min sonication	95.00	$6.54x10^{-59}$
H_2O_2 concentration (mg/l) in TI ww (60°C) after 120 min sonication	166.00	$7.50x10^{-42}$
H_2O_2 concentration (mg/l) in TI ww (60°C) after 150 min sonication	17.00	$3.21x10^{-7}$

Ge & Qu (2003) obtained 48.12% COD removal in a TI ww containing 100 mg/l Acid Red B, at 50 kHz frequency, at 150 W power, after 240 min sonication time at 60°C with stirring at 150 rpm under DO=4.00 mg/l. In this study, 94.07% COD_{dis} removal was found in DO=10.00 mg/l after 150 min sonication time at 60°C. The COD_{dis} yield in the present study is higher than the yield observed by Ge & Qu (2003) at 60°C as mentioned above.

In a study performed by Kritikos et al. (2007) 75.00% COD removal was achieved in a TI ww containing 120 mg/l Reactive Black 5, at 80 kHz frequency, at 135 W power, DO=7.00 mg/l, after 60 min sonication time at 30°C and at pH=5.8. In this study, 87.30% COD_{dis} removal was measured in DO=10.00 mg/l after 150 min sonication time at 30°C. The COD_{dis} yield in the present study is higher than the yield obtained by Kritikos et al. (2007) at 30°C as mentioned above.

5.11.5.1 Effect of DO Concentrations on the Color Removal Efficiencies in TI ww at Increasing Sonication Time and Temperature

90.25%, 91.77%, 92.83% and 95.06% color removals were observed in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.87). 11.99%, 13.51%, 14.57% and 16.80% increase in the color removals were obtained in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (DO=0.00 mg/l while E=78.26% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing DO concentrations was observed (R^2=0.87, F=14.70, p=0.01) (Table 5.87).

Table 5.87 Effect of increasing DO concentrations on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
DO=2.00 mg/l	87.78	88.84	90.25	91.07	93.77	95.65
DO=4.00 mg/l	88.95	89.31	91.77	91.30	93.89	96.47
DO=6.00 mg/l	89.19	91.07	92.83	91.42	94.24	97.06
DO=10.00 mg/l	89.89	93.65	95.06	92.24	95.06	97.65

95.65%, 96.47%, 97.06% and 97.65% color yields were found in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.87). The contribution of DO concentrations on color removals were 7.99%, 8.81%, 9.40% and 9.99% in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=87.66% color at DO=0.00 mg/l, at pH=7.0 and at 60°C). The maximum color removal efficiency was 97.65% in DO=10.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing DO concentrations was observed (R^2=0.81, F=13.20, p=0.01) (Table 5.87).

Vinodgobal & Kamat (1998) reported the results of three $OH^\bullet$ mediated oxidation reactions (photocatalysis, g-radiolysis and sonolysis) for the degradation of reactive dye, Acid Orange 7 under the effect of saturation with O_2. They noted that the similarity of reaction pathways in all three processes and concluded that textile azo dyes are effectively destroyed by $OH^\bullet$ mediated reaction pathways under aerated conditions. In another study, Vinodgopal et al. (1998) investigated the ultrasonic mineralization of a textile dye, Remazol Black B at 640 kHz under a stream of O_2 gas. They reported that dye destruction starts with the rupture (degradation under pressure) of the azo-bond by $OH^\bullet$ attack at a DO concentration of 4.00 mg/l while the complete decolorization is accompanied by total mineralization.

Ge & Qu (2003) found 90.88% color removal in a TI ww containing 100 mg/l Acid Red B, at 50 kHz frequency, at 150 W power, in DO=6.00 mg/l, after 240 min sonication at 60°C with stirring at 150 rpm. In this study, 97.65% color removal was observed in DO=10.00 mg/l after 150 min sonication time at 60°C. The color yield found in the present study is higher than the yield obtained by Ge & Qu (2003) at 60°C.

In a study performed by Byun & Kwak (2005) 90.00% color removal was accomplished in a TI ww containing 40.00 mg/l Methylene Blue, at 20 kHz frequency, at 500 W power, after 30 min sonication time at 60°C and at pH=3.85 with DO=5.00 mg/l. In this study, 97.65% color removal was observed at DO=10.00 mg/l after 150 min sonication time at 60°C. The color yield in the present study is higher than the yield obtained by Byun & Kwak (2005) at 60°C as mentioned above.

In a study performed by Tangestaninejad et al. (2008) 82.00% and 86.00% color removals were accomplished in a TI ww containing 60.00 mg/l Coproxon Navy Blue R1 and 200 mg/l Nylosan Black 2-BI-Acid Black at 24 kHz frequency, at 400 W power under O_2=5.00 ml/min, after 20 min sonication time at 30^oC and at pH=4.3. In this study, 95.06% color removal was observed at DO=10.00 mg/l after 150 min sonication time at 30^oC. The color yield in the present study is higher than the yield obtained by Tangestaninejad et al. (2008) at 30^oC.

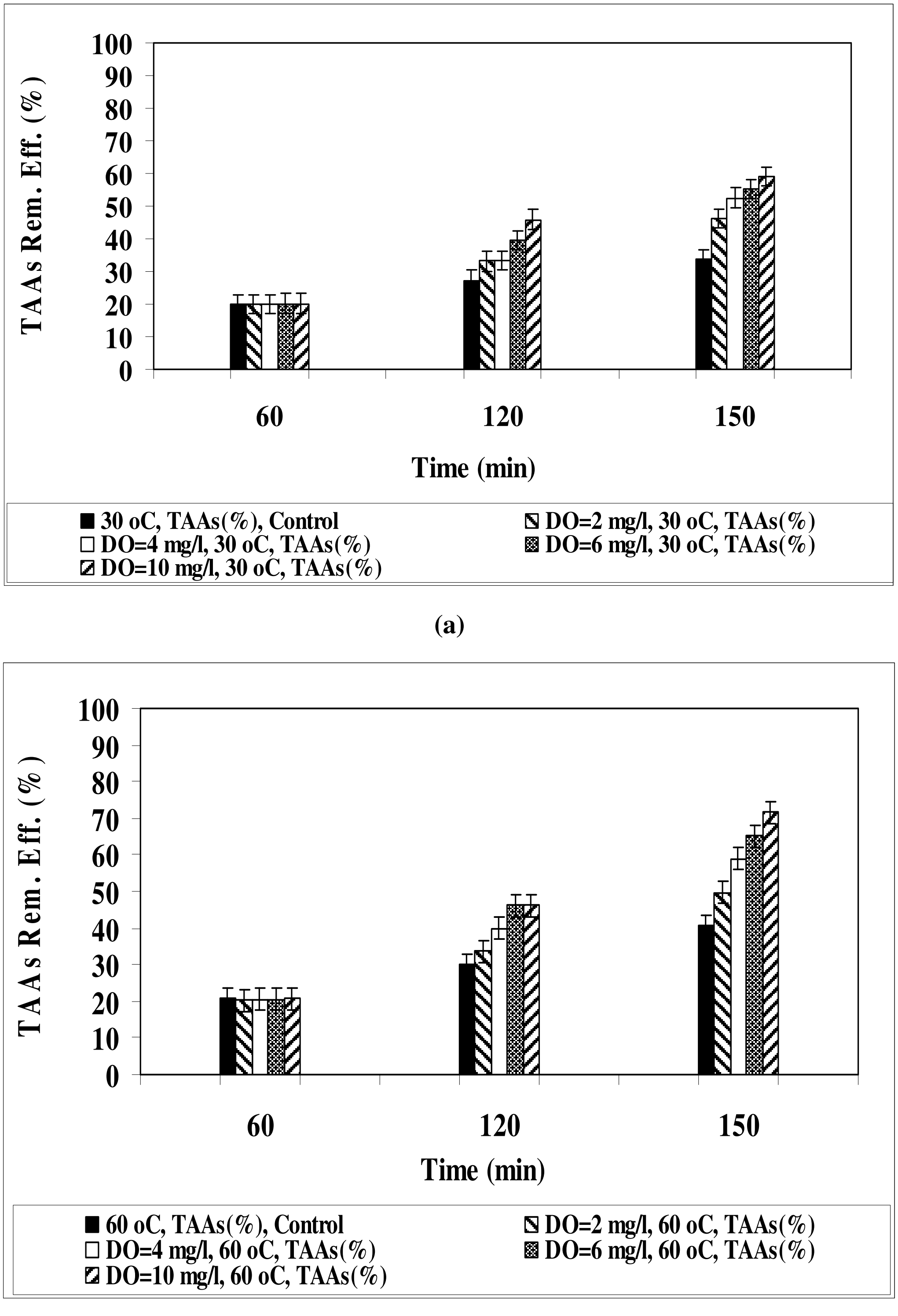
Tangestaninejad et al. (2008) found 75.00% and 78.00% color removals were obtained in a TI ww containing 20.00 mg/l Methyl Orange and 40 mg/l Congo Red, at 24 kHz frequency, at 400 W power and under O_2=5.00 ml/min, after 20 min sonication time at 30^oC and at pH=4.3. In this study, 95.06% color removal was observed at DO=10.00 mg/l after 150 min sonication time at 30^oC. The color yield in the present study is higher than the yield obtained by Tangestaninejad et al. (2008) at 30^oC as mentioned above.

In a study performed by Tangestaninejad et al. (2008) 79.00%, 85.00% and 80.00% color removals were achieved in a TI ww containing 40.00 mg/l Bromothymol Blue, 10.00 mg/l Methylene Blue and 30.00 mg/l Rhodamine B, respectively, at 24 kHz frequency, at 400 W power, under O_2=5.00 ml/min, after 30 min sonication time at 30^oC and at pH=4.3. In this study, 95.06% color removal was obtained in DO=10.00 mg/l after 150 min sonication time at 30^oC. The color yield in the present study is higher than the yield obtained by Tangestaninejad et al. (2008) at 30^oC as mentioned above.

5.11.5.2 Effect of DO Concentrations on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

46.27%, 52.55%, 55.26% and 59.05% TAAs removals were observed in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.88a). 12.38%, 18.66%, 21.37% and 25.16% increase in TAAs removals were obtained in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (DO=0.00 mg/l while E=33.89% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing DO concentrations was observed (R^2=0.78, F=14.73, p=0.01) (Figure 5.88a).

49.57%, 58.89%, 65.17% and 71.56% TAAs yields were found in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.88b). The contribution of DO concentrations on TAAs removals were 8.95%, 18.27%, 24.55% and 30.94% in 2.00 mg/l, 4.00 mg/l, 6.00 and 10.00 mg/l DO, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (DO=0.00 mg/l while E=40.62% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 71.56% in DO=10.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing DO concentrations was observed (R^2=0.89, F=15.25, p=0.01) (Figure 5.88b).



(a)

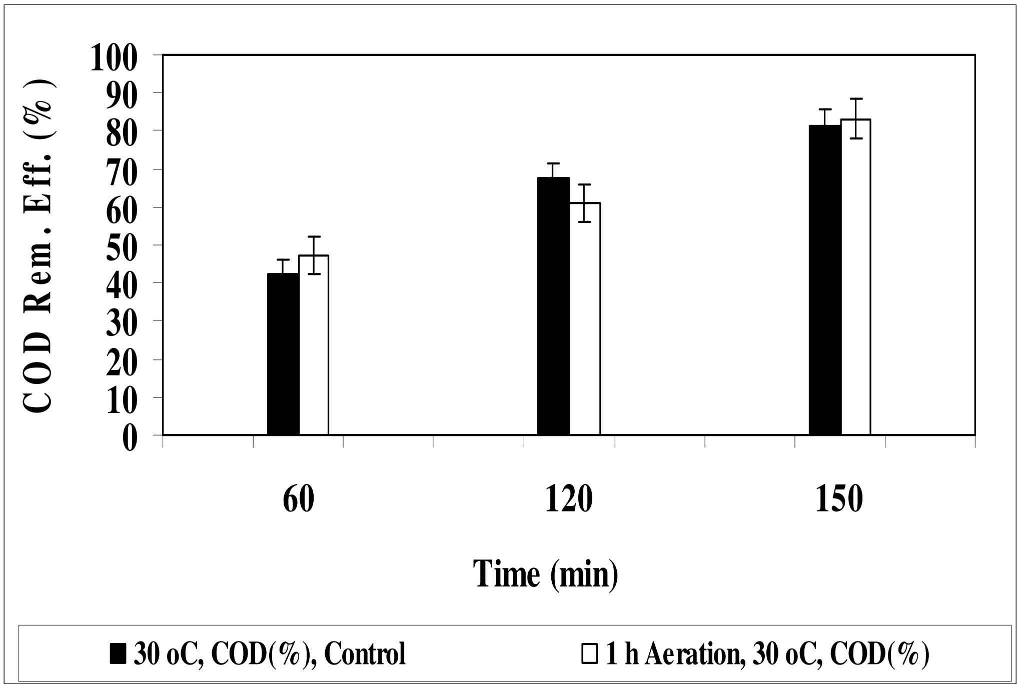
(b)

Figure 5.88 Effect of increasing DO concentrations on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing Sonication Times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

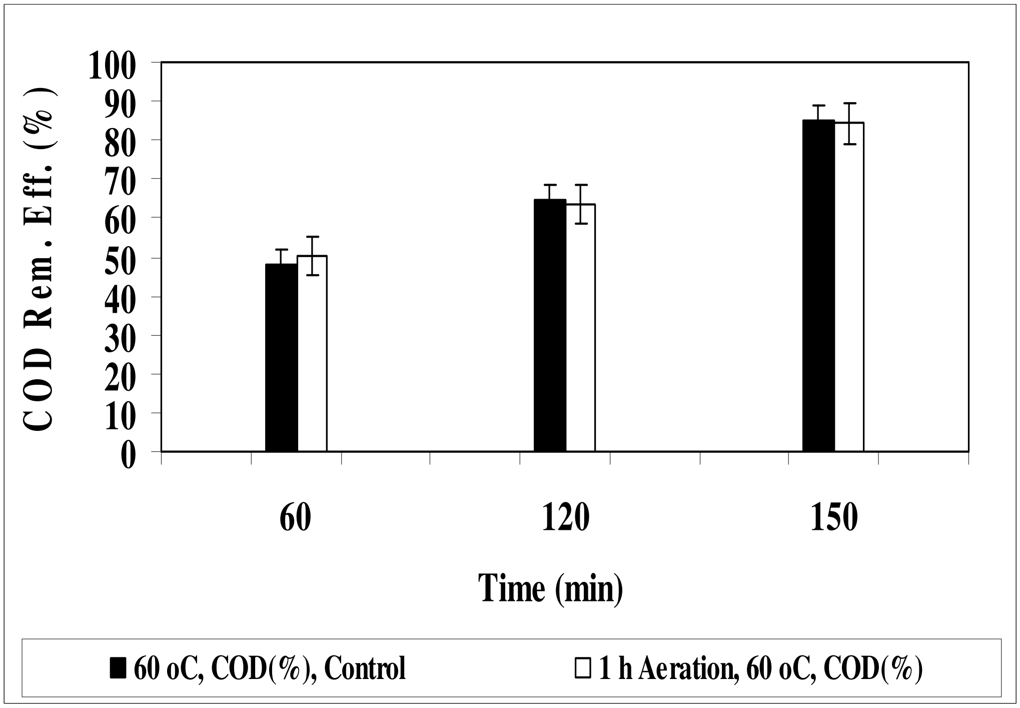
5.11.6 Effect of Aeration on the Removals of COD_{dis} in TI ww

47.45%, 60.79% and 83.21% COD_{dis} removals were observed under 1 h aeration, after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Figure 5.89a). 5.06% and 1.68% increase in COD_{dis} removals were obtained under 1 h aeration, after 60 and 150 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control (without aeration at pH=7.0 and at 30°C). Control provided 30.43%, 53.69% and 74.27% COD_{dis} removals after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C. A significant linear correlation between COD_{dis} yields and aeration was not observed (R^2=0.39, F=0.26, p=0.01) (Figure 5.89a).

50.26%, 63.30% and 84.28% COD_{dis} yields were found under 1 h aeration, after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.89b). The contribution of aeration on COD_{dis} removals were 2.18% after 60 min sonication time at pH=7.0 and at 60°C, compared to the control (at pH=7.0 and at 60°C). Sonication alone provided 48.08%, 64.48% and 84.92% COD_{dis} yields after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C. The maximum COD_{dis} removal efficiency was 84.28% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C. Although, the COD_{dis} removal efficiencies increased versus increasing sonication times the COD_{dis} removal efficiencies was not affected significantly by the aeration. Therefore it can be concluded that a significant linear correlation between COD_{dis} yields and aeration was not observed (R^2=0.33, F=2.21, p=0.01) (Figure 5.89b).



(a)



(b)

Figure 5.89 Effect of Aeration on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

If a continuous source of nuclei in the form of continuous aeration is provided, the overall intensity of cavitation events may increase resulting in an increase in the extent of degradation (Gogate et al, 2004a). In the studies performed by Gogate et al. (2004a) with aeration (at constant rate of 1.02 cm^3/s using a multipoint sintered sparger) indicated that the extent of degradation increased by about 30.00% over entire 30 min of operation. Factors affecting the effect of aeration on the COD_{dis} removals are flow rate of air, separate sparging of air followed by ultrasonic irradiation (simultaneous operation results in a decrease in the extent of dissolved air due to degassing effect) and experiments with different dissolved gases such as argon (Ar), Ar/air mixture, O_3 etc. (Gogate et al, 2004a). In this study, COD_{dis} removal efficiency increased with the flow rate of air (0.10 ml/min), increasing sonication temperature (from 25°C to 60°C), increasing sonication time (from 60 min to 150 min) and increasing pH values (from 4.0 to 10.0) during sonication process.

In a study performed by Ince & Tezcanli (2001) 76.00% COD removal was achieved in a TI ww containing 363 mg/l C.I. Reactive Black 5, at 520 kHz frequency, at 100 W power, 1.63 W/cm^2, after 240 min sonication time at 80°C and at pH=11.0 under 15 min aeration. In this study, 84.28% COD_{dis} removal was observed under 1 h aeration after 150 min sonication time at 60°C. The COD_{dis} yield in the present study at 60°C is higher than the yield obtained by Ince & Tezcanli (2001) at 80°C as mentioned above.

Gogate et al. (2004a) observed 25.00% COD removal in a TI ww containing 4.50 mg/l Rhodamine B, at 20+30+50 kHz frequencies, at 900 W power, at 0.025-0.1 W/l power density, after 30 min sonication time at 60°C under aeration. In this study, 84.28% COD_{dis} removal was measured under 1 h aeration after 150 min sonication time at 60°C. The COD_{dis} yield in the present study is higher than the yield observed by Gogate et al. (2004a) at 60°C as mentioned above.

5.11.6.1 Effect of Aeration on the Color Removal Efficiencies at Increasing Sonication Time and Temperature

53.35%, 77.91% and 80.61% color removals were observed under 1 h aeration, after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Table 5.88). 1.06%, 1.53% and 2.35% increase in the color removals were obtained under 1 h aeration, after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C, compared to the control (without aeration while E=52.29%, E=76.38% and E=78.26% color after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C). A significant linear correlation between color yields and aeration was not observed (R^2=0.49, F=4.99, p=0.01) (Table 5.88).

Table 5.88 Effect of increasing concentrations on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
1 h aeration	53.35	77.91	80.61	53.47	83.55	90.25

53.47%, 83.55% and 90.25% color yields were found under 1 h aeration after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Table 5.88). The contribution of aeration on color removals were 0.35% and 2.59% under 1 h aeration after 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control (E=79.32%, E=83.20% and E=87.66% color after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C). The maximum color removal efficiency was 90.25% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C. Although, the color removal efficiencies increased as the sonication times and temperatures were increased at 1 h Aeration. A significant linear correlation between color yields and Aeration was not observed (R^2=0.30, F=3.99, p=0.01) (Table 5.88).

In a study performed by Vinodgopal et al. (1998) it was reported that 60.00% mineralization was achieved in a TI ww containing 75.00 mg/l Remazol Black after 360 min irradiation under 500 kHz frequency and 100 W power under 120 min aeration. In this study, 90.25% color removal was observed underr 1 h aeration after 150 min sonication time at 60°C. The color yield in the present study is higher than the yield obtained by Vinodgopal et al. (1998) at 80°C as mentioned above.

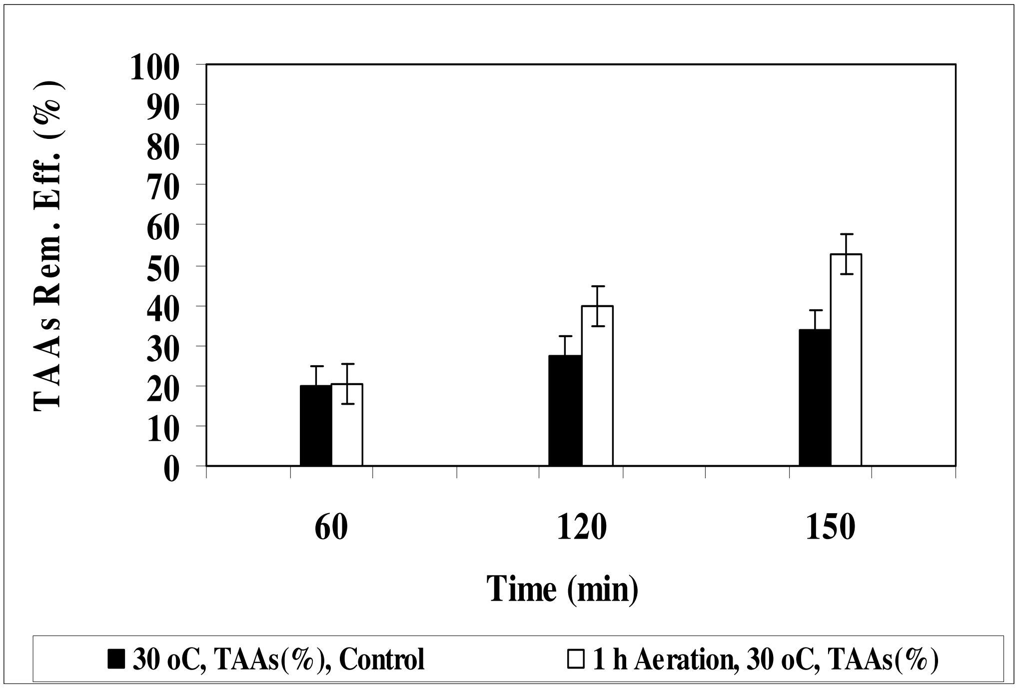
Jamalluddin & Abdullah (2010) found 96.00% color yield in a TI ww containing 70.00 mg/l Reactive Blue 4, at 35 kHz frequency, at 50 W power, under 4 μmol/min aeration, after 60 min sonication time at 60°C and at pH=4.0. In this study, 90.25% color removal was measured under 1 h aeration after 150 min sonication time at 60°C. The color yield in the present study is lower than the yield observed by Jamalluddin & Abdullah (2010) at 60°C as mentioned above.

Guzman-Duque et al. (2011) achieved 80.00% and 73.00% color yield in a TI ww containing 350 mg/l Crystal Violet and 120 mg/l Orange G under aeration (3.5 mg/l.min) after 180 min sonication time under 800 kHz frequency, 80 W power, at pH=3.0 and at 30°C. In this study, 80.61% color removal was found under 1 h aeration after 150 min sonication time at 30°C. The color yield in the present study is higher than the yield obtained by Guzman-Duque et al. (2011) at 30°C as mentioned above.

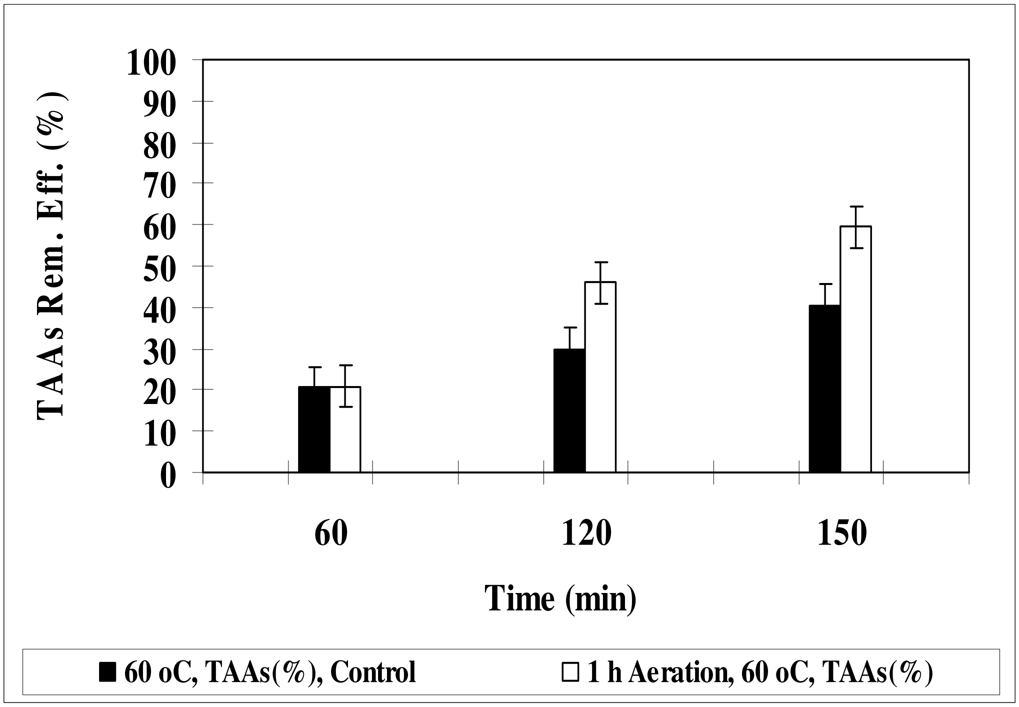
5.11.6.2 Effect of Aeration on the TAAs Removal Efficiencies at Increasing Sonication Times and Temperatures

20.48%, 39.87% and 52.82% TAAs removals were observed under 1 h aeration after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C (Figure 5.90a). 0.39%, 12.59% and 18.93% increase in TAAs removals were obtained under 1 h aeration after 60 min, 120 and 150 min sonication times at pH=7.0 and at 30°C, compared to the control (20.09%, 27.28% and 33.89% TAAs removals after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and aeration was not observed ($R^2=0.32$, F=2.98, p=0.01) (Figure 5.90a).

20.86%, 46.10% and 59.38% TAAs yields were found under 1 h aeration after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C (Figure 5.90b). The contribution of aeration on TAAs removals were 0.16%, 16.10% and 18.76% under 1 h aeration after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C, compared to the control (20.70%, 30.00% and 40.62% TAAs yields after 60 min, 120 and 150 min sonication times, respectively, at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 59.38% under 1 h aeration after 150 min sonication time at pH=7.0 and at 60°C. Although, the TAAs yields increased as the sonication temperatures and sonication times were increased under 1 h aeration. A significant linear correlation between TAAs yields and aeration was not observed ($R^2=0.42$, F=4.09, p=0.01) (Figure 5.90b).



(a)



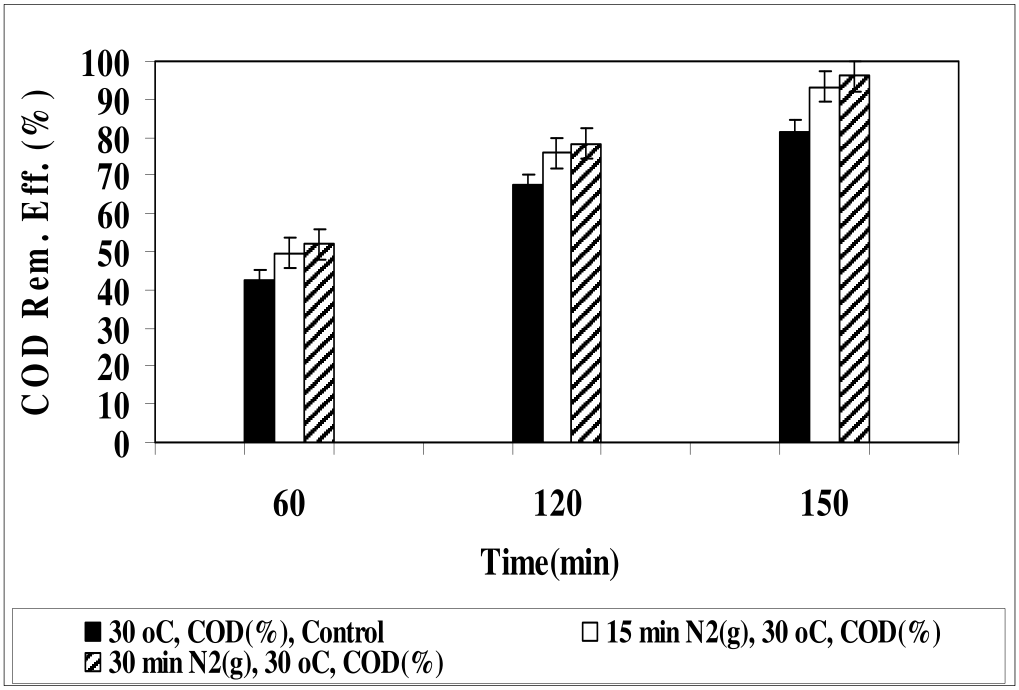
(b)

Figure 5.90 Effect of aeration on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

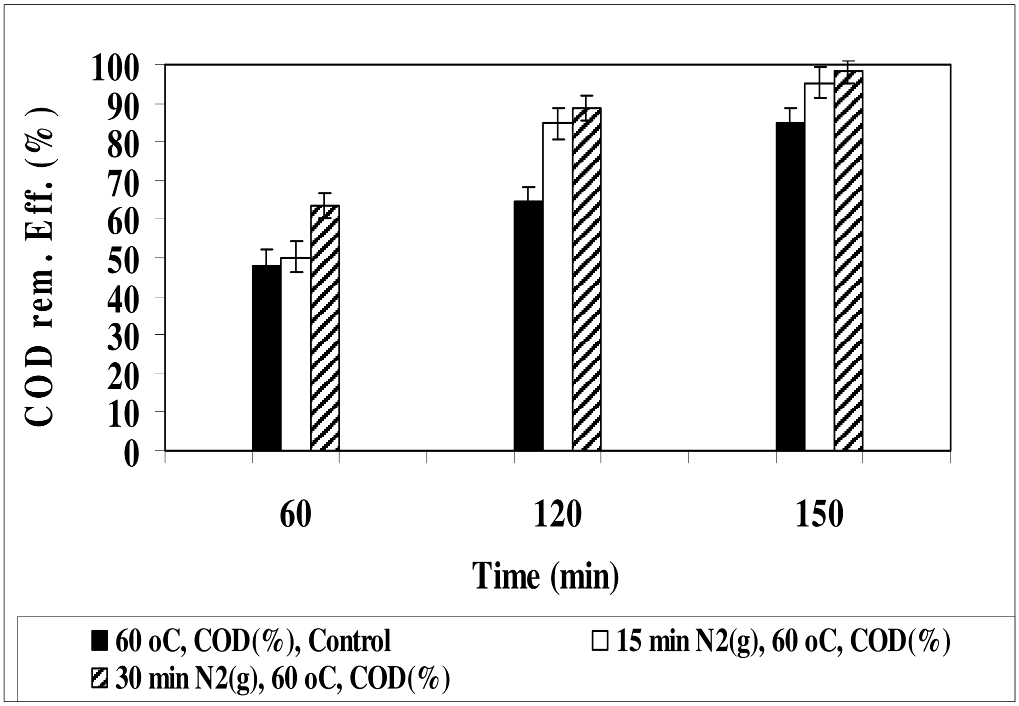
5.11.7 Effect of $N_2(g)$ on the Removals of COD_{dis} in TI ww

93.10% and 96.21% COD_{dis} removals were observed underr 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.91a). 11.53% and 14.68% increase in COD_{dis} removals were obtained under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without $N_2(g)$ sparging, E=74.27% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing $N_2(g)$ sparging was observed (R^2=0.91, F=18.11, p=0.01) (Figure 5.91a).

95.22% and 98.23% COD_{dis} yields were found under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.91b). The contribution of $N_2(g)$ sparging on COD_{dis} removals were 10.30% and 13.31% under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 at 60°C, compared to the control (E=84.92% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 98.23% at 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing $N_2(g)$ sparging was observed (R^2=0.92, F=18.12, p=0.01) (Figure 5.91b).



(a)



(b)

Figure 5.91 Effect of increasing N_2(g) sparging on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

In principle, N_2(g) sparging enhances sonochemical activity as gases act as nucleation sites for cavitation. There are three properties of gases that can affect sonochemical activity, namely: (i) The polytropic ratio since the maximum temperatures and pressures achieved upon bubble collapse increase with increasing polytropic ratio (Adewuyi, 2001; Thompson & Doraiswamy, 1999), (ii) gas thermal conductivity. Although, bubble collapse is modeled as adiabatic, there is always a small amount of heat dissipated upon collapse; therefore, gases with low thermal conductivities should reduce heat dissipation, thus favoring increased collapse temperatures and consequently increasing sonochemical activity, (iii) gas solubility. As solubility increases, more nucleation sites become available, thus facilitating cavitation. N_2(g) has a greater polytropic ratio (i.e. 1.67 against 1.4), lower thermal conductivity (17.90 against 26.30 mW/m.K at 27^{o}C) and is slightly more soluble (5.60 against 4.90 ml/100 ml H_2O) than O_2 and all these would explain the increased reactivity observed with N_2(g) (Kritikos et al., 2007).

In a study performed by Kritikos et al. (2007) 97.00% COD removal was accomplished in a TI ww containing 120 mg/l Reactive Black 5, at 80 kHz frequency, at 135 W power, under N_2=4.20 mg/l.min, after 90 min sonication time at 30^{o}C and at pH=5.8. In this study, 96.21% COD_{dis} removal was found underr 30 min N_2(g) (6.00 mg/l N_2) sparging after 150 min sonication time at 30^{o}C. In this sudy, similar result at COD_{dis} yield obtained by Kritikos et al. (2007) at 30^{o}C as mentioned above.

5.11.7.1 Effect of N_2(g) on the Color Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

86.02% and 90.48% color removals were observed under 15 and 30 min N_2(g) (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Table 5.89). 7.76% and 12.22% increase in the color removals were obtained under 15 and 30 min N_2(g) (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=78.26% color at pH=7.0 and at 30^{o}C). A significant linear correlation between color yields and increasing $N_2(g)$ sparging was observed ($R^2=0.79$, F=14.28, p=0.01) (Table 5.89).

Table 5.89 Effect of increasing $N_2(g)$ sparging on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
15 min $N_2(g)$ (3.00 mg/l N_2)	54.76	77.20	86.02	80.96	85.08	92.24
30 min $N_2(g)$ (6.00 mg/l N_2)	56.40	83.67	90.48	83.90	88.37	95.30

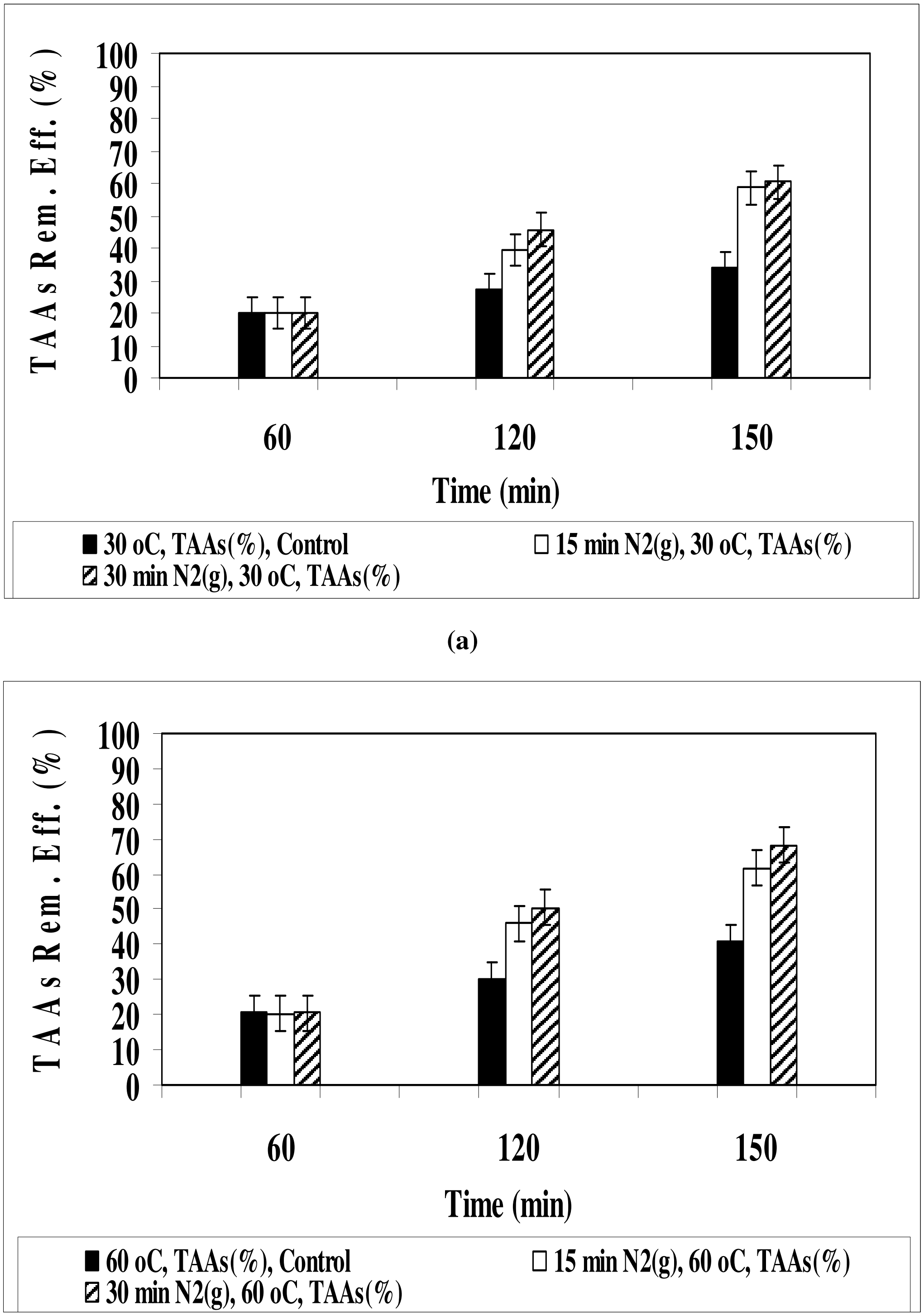
92.24% and 95.30% color yields were found under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.89). The contribution of $N_2(g)$ sparging on color removals were 4.58% and 7.64% for 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=87.66% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 95.30% at 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing $N_2(g)$ sparging was observed ($R^2=0.82$, F=17.06, p=0.01) (Table 5.89).

For decolorization under $N_2(g)$ sparging, reactions inside or in the vicinity of the bubble (where fast thermal decomposition and increased concentrations of radicals exist) are unlikely to occur to an appreciable extent and, therefore, its degradation will be driven by $OH^{\bullet}$-mediated secondary activity in the liquid bulk. This would explain discrepancies in reactivity of dyestuff between sonochemical since the latter involve the participation of a more diverse range of reactive species (i.e. radicals, holes and electrons) than the former. In addition to the physicochemical properties of the substrate in question that are likely to dictate the dominant reaction site(s) for sonochemical activity and, consequently, degradation efficiency, sonochemical reactions are also sensitive to several other operating parameters such as ultrasound frequency and intensity, reactor geometry, mode of ultrasound irradiation (i.e. continuous or pulsed), solution temperature and the water matrix. For instance, different ranges of ultrasound frequency are suitable for hydrophilic and hydrophobic organics, while increased reaction temperatures may cause a decrease in degradation (Adewuyi, 2001). In some cases, ultrasound irradiation in an ‘‘on-off’’ mode may be more beneficial than the continuous one leading to a more effective utilization of $OH^{\bullet}$ and a better temperature control (Velegraki et al., 2006).

Kritikos et al. (2007) found 80.00% decolorization in a TI ww containing 120 mg/l Reactive Black 5, at 80 kHz frequency, at 135 W power, N_2=4.20 mg/l.min, after 90 min sonication time at 30^{o}C and at pH=5.8. In this study, 90.48% color removal was measured under 30 min N_2 (g) (6.00 mg/l N_2) sparging after 150 min sonication time at 30^{o}C. The color yield in the present study is higher than the yield obtained by Kritikos et al. (2007) at 30^{o}C as mentioned above.

5.11.7.2 Effect of N_2(g) on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

58.56% and 60.41% TAAs removals were observed under 15 and 30 min N_2(g) (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.92a). 24.67% and 26.52% increase in TAAs removals were obtained under 15 and 30 min N_2(g) (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=33.89% TAAs at pH=7.0 and at 30^{o}C). A significant linear correlation between TAAs yields and increasing N_2(g) sparging was not observed (R^2=0.62, F=3.21, p=0.01) (Figure 5.92a).



(a)

(b)

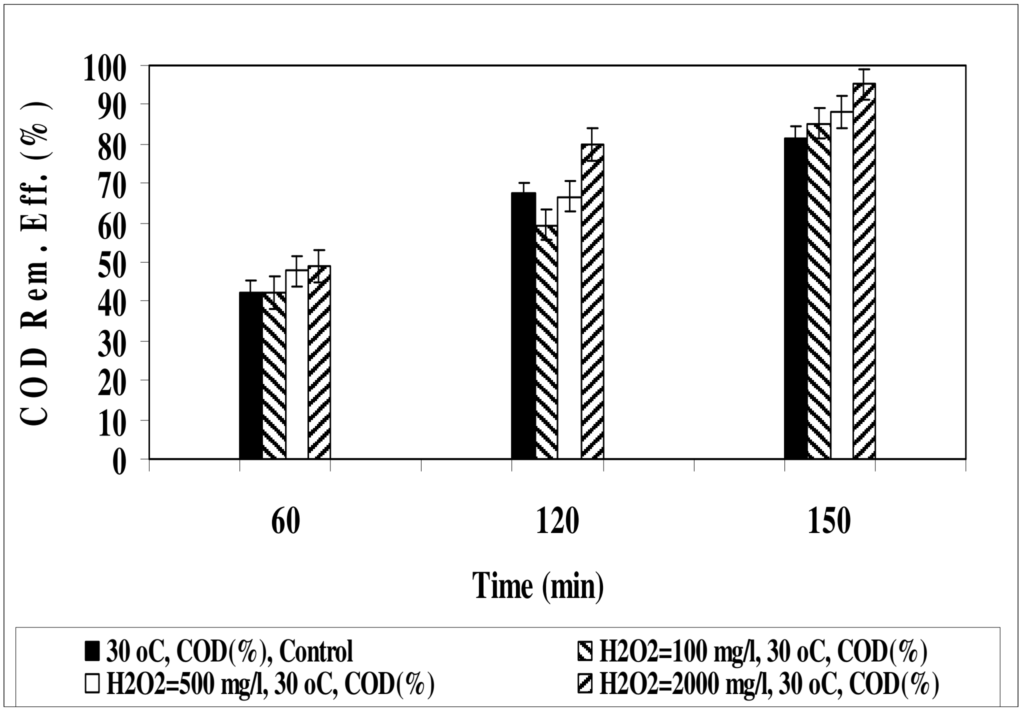
Figure 5.92 Effect of increasing $N_2(g)$ sparging on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

61.79% and 68.08% TAAs yields were found under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.92b). The contribution of $N_2(g)$ sparging on TAAs removals were 21.17% and 27.46% under 15 and 30 min $N_2(g)$ (3.00 and 6.00 mg/l N_2) sparging, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=40.62% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 68.08% at 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing $N_2(g)$ sparging was not observed (R^2=0.31, F=3.90, p=0.01) (Figure 5.92b).

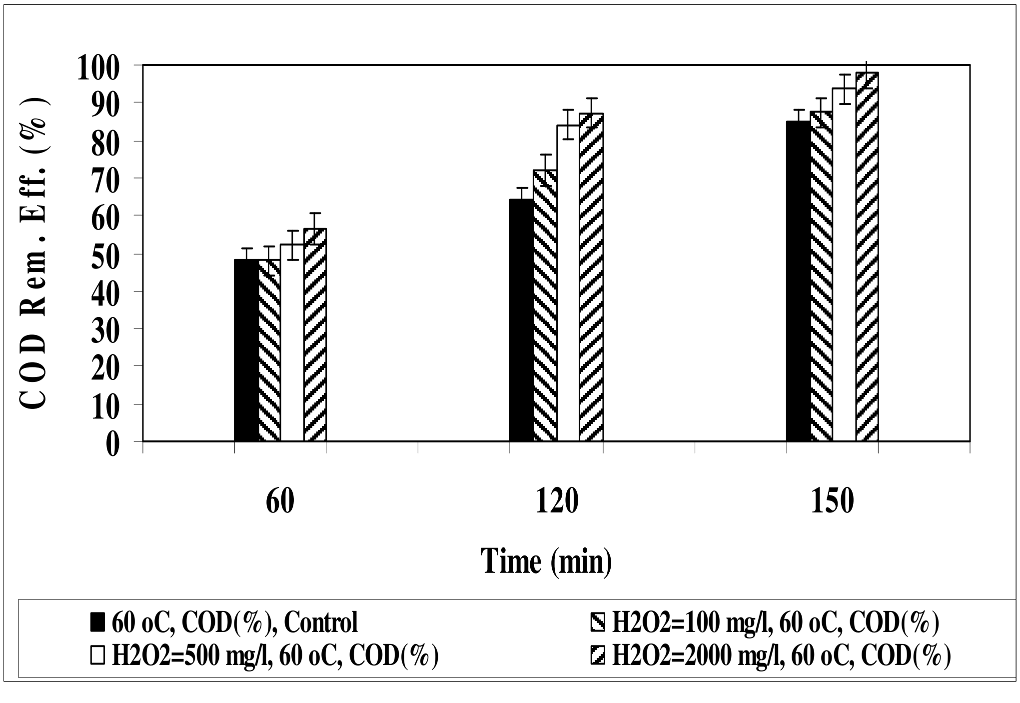
5.11.8 Effect of H_2O_2 Concentrations on the Removals of COD_{dis} in TI ww

85.22%, 88.12% and 95.10% COD_{dis} removals were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.93a). 3.69%, 6.59% and 13.57% increase in COD_{dis} removals were obtained in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without H_2O_2 while E=81.53% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing H_2O_2 concentrations was observed (R^2=0.88, F=18.02, p=0.01) (Figure 5.93a).

87.42%, 93.62% and 97.92% COD_{dis} yields were found in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.93b). The contribution of concentrations on COD_{dis} removals were 2.50%, 8.70% and 13.00% in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=84.92% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 97.92% at 30 min $N_2(g)$ sparging after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing H_2O_2 concentrations was observed (R^2=0.79, F=15.40, p=0.01) (Figure 5.93b).



(a)



(b)

Figure 5.93 Effect of increasing H_2O_2 concentrations on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

The enhancement of H_2O_2 for the degradation of dyestuff could be mainly due to contribution of additional $OH^{\bullet}$ produced from H_2O_2 dissociation. More $OH^{\bullet}$ would be produced and higher degradation ratios were observed at higher H_2O_2 concentration. H_2O_2 can also react with $OH^{\bullet}$ as following: Eq. (5.88) (Wang, J. et al., 2009).

$$H_2O_2 + OH^{\bullet} \quad \rightarrow \quad H_2O + O_2H^{\bullet} \tag{5.88}$$

The rate of this reaction increase with H_2O_2 concentration and it can be competitive for $OH^{\bullet}$ (Wang, J. et al., 2009). As the addition of H_2O_2 enhances the degradation rate of dyestuff due to additional free radicals generation, it can be concluded that the controlling mechanism of dyestuff degradation is the free radical attacks (Ghodbane & Hamdaoui, 2009b).

Balcioglu & Arslan (1999) achieved 60.00% COD yield in a TI ww containing 10.00 mg/l Rhodamine B in H_2O_2=340 mg/l, at a 30 kHz frequency, at a 20 W power after 90 min sonication time at 40°C. In this study, 97.92% COD_{dis} removal was observed in H_2O_2=2000 mg/l after 150 min sonication time at 60°C. The COD_{dis} yield in the present study is higher than the yield obtained by Balcioglu & Arslan (1999) at 60°C as mentioned above.

In a study performed by Arslan et al. (1999) 50.00% COD removal was obtained in a TI ww containing 12.00 mg/l Rhodamine B in H_2O_2=250 mg/l, at a 45 kHz frequency, at a 285 W power after 80 min sonication time at 30°C at pH=2.8-3.0. In this study, 95.10% COD_{dis} removal was measured in H_2O_2=2000 mg/l after 150 min sonication time at 30°C. The COD_{dis} yield in the present study is higher than the yield observed by Arslan et al. (1999) at 30°C as mentioned above.

Zhang, H. et al. (2009a) found 40.00% COD yield in a TI ww containing 79.50 mg/l C.I. Acid Orange 7, in H_2O_2=265 mg/l, at 20 kHz frequency, 250 W power, 10 W/cm^2 power intensity after 30 min sonication time at pH=10.0 at 30°C. In this study, 95.10% COD_{dis} removal was observed in H_2O_2=2000 mg/l after 150 min sonication time at 30^{o}C. The COD$_{dis}$ yield in the present study is higher than the yield obtained by Zhang, H. et al. (2009a) at 30^{o}C as mentioned above.

Mehrdad & Hashemzadeh (2010) accomplished 78.00% COD yield in a TI ww containing 60.00 mg/l Rhodamine B, at 24 kHz frequency, at 400 W power, in H_2O_2=198 mg/l, after 10000 min sonication time at 30^{o}C and at pH=5.0-8.0. In this study, 95.10% COD$_{dis}$ removal was found in H_2O_2=2000 mg/l after 150 min sonication time at 30^{o}C. The COD$_{dis}$ yield in the present study is higher than the yield observed by Mehrdad & Hashemzadeh (2010) at 30^{o}C as mentioned above.

In a study performed by Sundararaman et al. (2009) 82.00% COD removal was achieved with sono-fenton process in a TI ww containing 50.00 mg/l Reactive Yellow 16, at 34 kHz frequency, at 120 W power, in H_2O_2=900 mg/l, after 30 min sonication time at 60^{o}C and at pH > 8.00. In this study, 97.92% COD$_{dis}$ removal was measured in H_2O_2=2000 mg/l after 150 min sonication time at 60^{o}C. The COD$_{dis}$ yield in the present study is higher than the yield observed by Sundararaman et al. (2009) at 60^{o}C as mentioned above.

Zhang, H. et al. (2009b) 72.00% COD removal was found in a TI ww containing 79.50 mg/l C.I. Acid Orange 7, at 20 kHz frequency, at 250 W power, in H_2O_2=170 mg/l, after 30 min sonication time at 30^{o}C and at pH=3.0. In this study, 95.10% COD$_{dis}$ removal was observed in H_2O_2=2000 mg/l after 150 min sonication time at 30^{o}C. The COD$_{dis}$ yield in the present study is higher than the yield found by Zhang, H. et al. (2009b) at 30^{o}C as mentioned above.

5.11.8.1 Effect of H_2O_2 Concentrationson the Color Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

80.96%, 82.14% and 83.78% color removals were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.90). 2.70%, 3.88% and 5.52% increase in the color yields were obtained in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=78.26% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing H_2O_2 concentrations was not observed (R^2=0.36, F=3.24, p=0.01) (Table 5.90).

Table 5.90 Effect of increasing H_2O_2 concentrations on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
H_2O_2=100 mg/l	74.62	77.79	80.96	82.26	85.08	87.54
H_2O_2=500 mg/l	75.44	78.61	82.14	83.78	86.37	89.19
H_2O_2=2000 mg/l	77.67	80.73	83.78	87.31	91.07	95.06

87.54%, 89.19% and 95.06% color yields were found in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.90). The contribution of H_2O_2 concentrations on color removals were 1.53% and 7.40% in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=87.66% color at pH=7.0 and at 60°C). 95.06% maximum color removal efficiency was observed in 2000 mg/l H_2O_2 after 150 min sonication time at pH=7.0 and at 60°C. Although, the color yields increased as the H_2O_2 concentrations, sonication time and sonication temperature were increased. A significant linear correlation between color yields and increasing H_2O_2 concentrations was not observed (R^2=0.32, F=3.25, p=0.01) (Table 5.90).

In TI ww ultrasonic irradiation includes the formation of free radicals as a consequence of cavitation. The thermal decomposition of the water vapor and H_2O_2 in a cavitation bubble leads to the formation of $OH^\bullet$, $H^\bullet$and $O_2H^\bullet$ radicals (Wang, J. et al., 2009). Scavenging of radicals in the bubble or at the interface increases the concentration of the oxidizing radicals. The radicals may also reach the liquid bubble interface and may pass into bulk solution where they can react with solutes. Therefore, there would be an increase in degradation yield compared to the case where only H_2O_2 molecules were responsible for decolorization process. H_2O_2 played an important role in degradation efficiency of colorful organics throuhout sonication of TI wws.

In a study performed by Ghodbane &Hamdaoui (2009b) 85.00% color yield found in a TI ww containing 150 mg/l Acid Blue 25 with ultrasound/H_2O_2 process, at 1700 kHz frequency, at 14 W power, in H_2O_2=350 mg/l after 35 min sonication time at 60°C and at pH=5.7. In this study, 95.06% color removal was observed in H_2O_2=2000 mg/l after 150 min sonication time at 60°C. The color yield in the present study is higher than the yield observed by Ghodbane & Hamdaoui (2009b) at 60°C as mentioned above.

In a study performed by Balcioglu & Arslan (1999) and Arslan et al. (1999) 93.00% and 85.00% color removals were achieved in a TI ww containing 20.00 mg/l C.I. Acid Orange 7 and 30.00 mg/l C.I. Acid Blue in 340 and 250 mg/l H_2O_2, concentrations at 30 and 45 kHz frequencies, at 20 and 285 W powers after 90 and 80 min sonication times at 60°C at pH=2.8-3.0, respectively. In this study, 95.06% color removal was observed in H_2O_2=2000 mg/l after 150 min sonication time at 60°C. The color yield in the present study is higher than the yield observed by Balcioglu & Arslan (1999) and by Arslan et al. (1999) at 60°C as mentioned above.

In a study performed by Wang, X. et al. (2008) and Wang, J. et al. (2011) 60.00% and 97.20% color removal was accomplished in TI ww containing 10.00 mg/l Reactive Brilliant Red K-BP and 20.00 mg/l Reactive Brilliant Red K-2BP, at 20 kHz frequency, at 150 W power, in 680 and 300 mg/l H_2O_2 concentrations, after 240 and 120 min sonication times at 30°C and at 60°C and at pH=5.5, respectively. In this study, 95.06% color removal was observed in H_2O_2=2000 mg/l after 150 min sonication time at 60°C. The color yield is higher than the yield obtained by Wang, X. et al. (2008) at 30°C and by Wang, J. et al. (2011) at 60°C as mentioned above.

Mrowetz et al. (2003) and Zhang & Zheng (2009) achieved 45.00% and 90.00% color yields in TI ww containing 10.00 mg/l C.I. Acid Orange 8 and 20.00 mg/l C.I. Acid Orange 7, at 20 kHz frequency, at 250 W power, in 100 and 1700 mg/l H_2O_2 concentrations after 100 and 30 min sonication times at 35°C and at 60°C and at pH=3.0, respectively. In this study, 95.06% color removal was found in H_2O_2=2000 mg/l after 150 min sonication time at pH=7.0 and at 60°C. The color yield in the present study is higher than the yield observed by Mrowetz et al. (2003) at 35°C and by Zhang & Zheng (2009) at 60°C as mentioned above.

In a study performed by Ghodbane & Hamdaoui (2009b) and Sun et al. (2007) 93.00% and 92.39% color removals were achieved in TI ww containing 50 mg/l Acid Blue 25 and 90.00 mg/l Acid Black 1, at 1700 and 40 kHz frequencies, at 14 and 50 W powers, at a 50 W/l power density, in 386 and 150 H_2O_2 concentrations, after 30 min sonication time at 60°C and at 40°C and at pH=5.0-8.0, respectively. In this study, 95.06% color removal was observed in H_2O_2=2000 mg/l after 150 min sonication time at 60°C. The color yield in the present study is higher than the yield found by Ghodbane & Hamdaoui (2009b) at 60°C and by Sun et al. (2007) at 40°C as mentioned above.

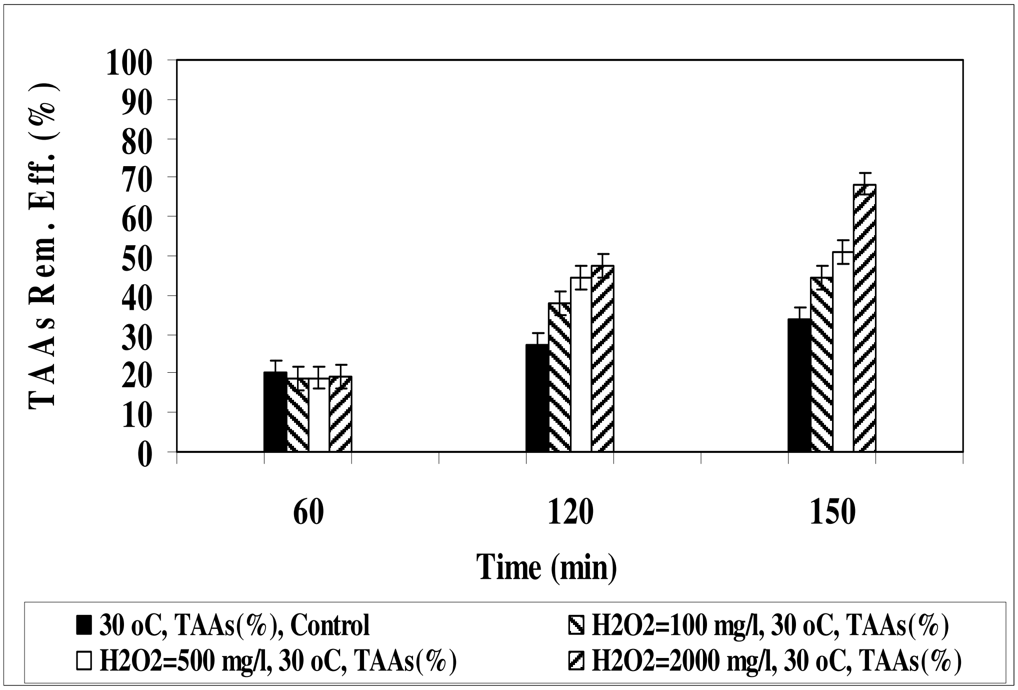
Sundararaman et al. (2009) accomplished 95.00% color removal with Sono-fenton process in a TI ww containing 50.00 mg/l Reactive Yellow 16, at 34 kHz frequency, at 120 W power, in H_2O_2=900 mg/l, after 30 min sonication time at 60°C and at pH > 8.00. In this study, 95.06% color removal was measured in H_2O_2=2000 mg/l after

150 min sonication time at 60°C. In this study, similar result observed by Sundararaman et al. (2009) at 60°C as mentioned above.

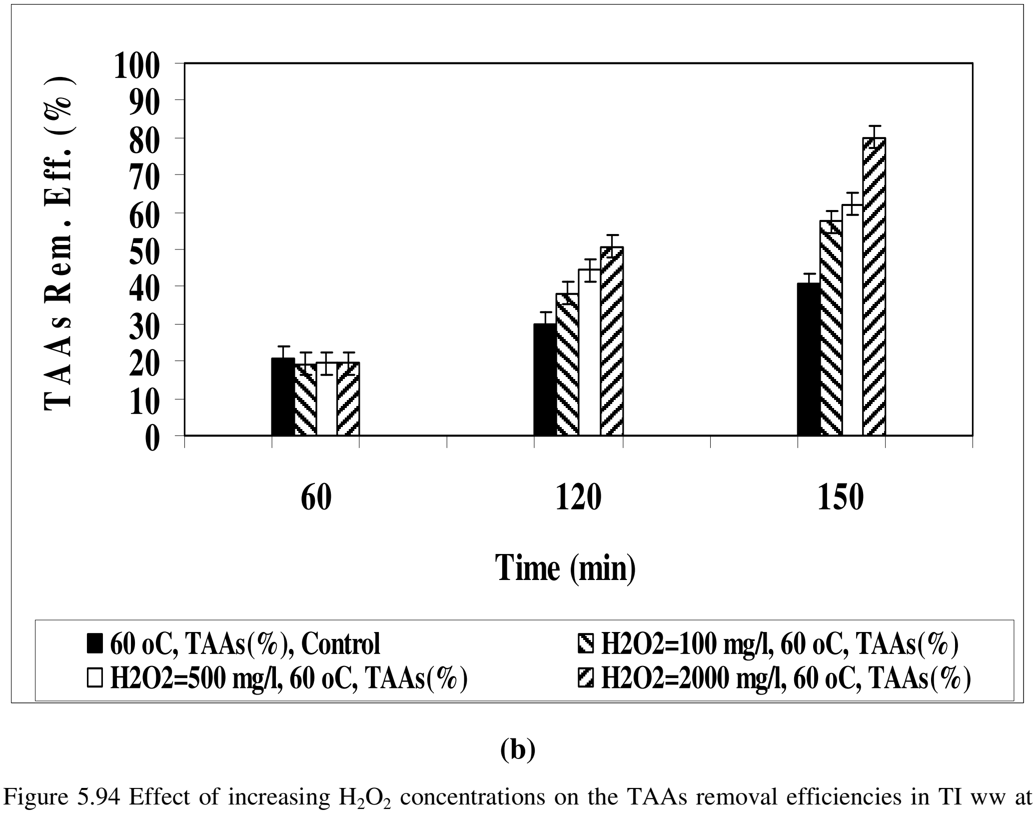
5.11.8.2 Effect of H_2O_2 Concentrations on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

44.62%, 51.07% and 68.40% TAAs removals were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.94a). 10.73%, 17.18% and 34.51% increase in TAAs removals were obtained in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=33.89% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing H_2O_2 concentrations was observed (R^2=0.85, F=13.35, p=0.01) (Figure 5.94a).

57.40%, 62.09% and 80.16% TAAs yields were found in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.94b). The contribution of H_2O_2 concentrations on TAAs removals were 16.78%, 21.47% and 39.54% in 100 mg/l, 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=40.62% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 80.16% at 30 min N_2(g) sparging after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing H_2O_2 concentrations was observed (R^2=0.76, F=13.54, p=0.01) (Figure 5.94b).



(a)



(b)

Figure 5.94 Effect of increasing H_2O_2 concentrations on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

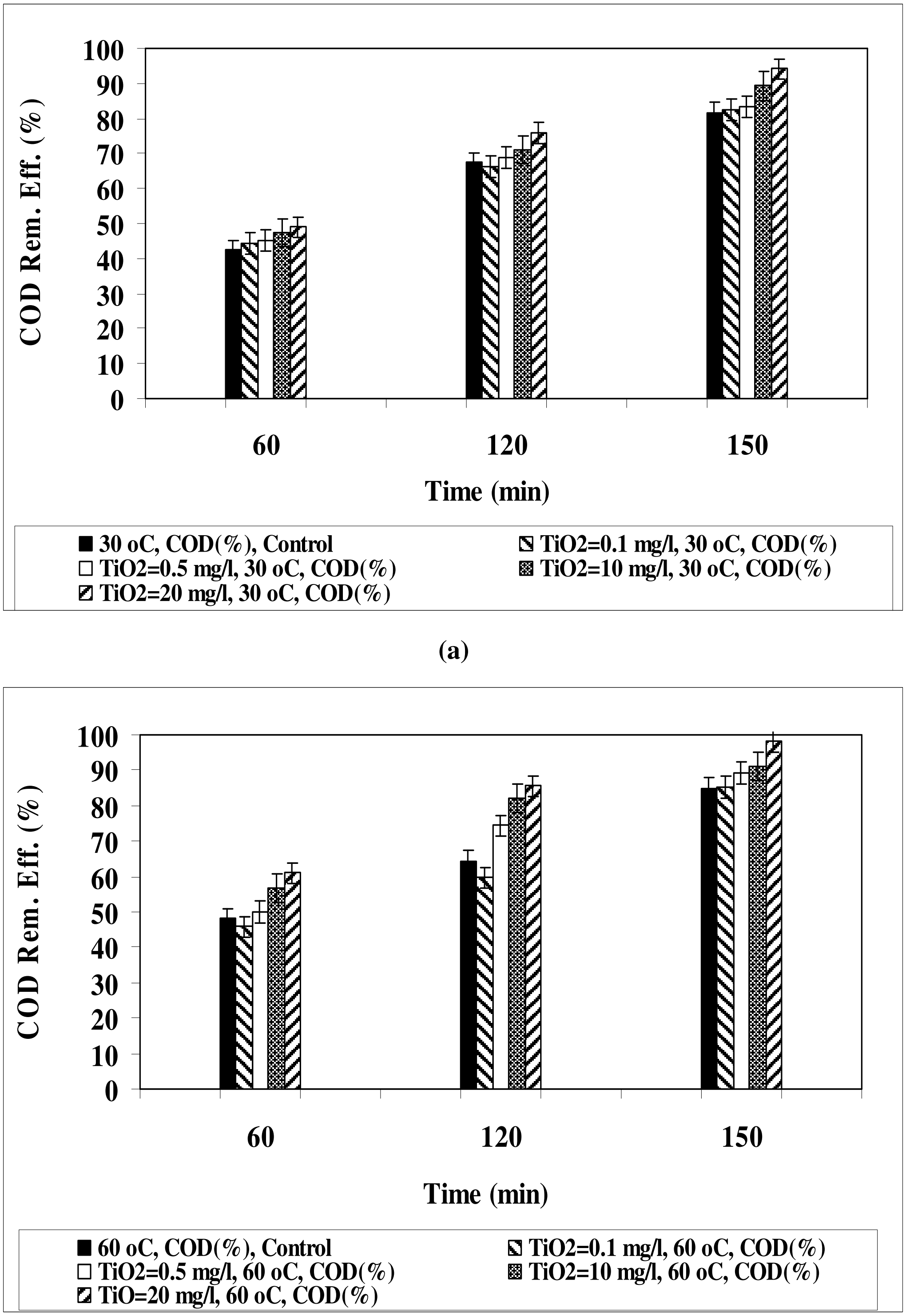
In a study performed by Yavuz et al. (2009) 50.00% TAAs removal was achieved in a TI ww containing 20.00 mg/l Basic Red 29 at 40 kHz frequency, at 25 W power, 0.25 W/ml power density after 30 min sonication time at 40°C with H_2O_2=1000 mg/l addition. In this study, 80.16% TAAs removal was observed in H_2O_2=2000 mg/l after 150 min sonication time at 60°C. The TAAs yield in the present study is higher than the yield observed by Yavuz et al. (2009) at 40°C as mentioned above.

Behnajady et al. (2008a) achieved 75.00% TAAs yield in a TI ww containing 10 mg/l Rhodamine B, at 35 kHz frequency, at 170 W power, 0.163 W/ml power density after 180 min sonication time at 60°C in H_2O_2=1000 mg/l. In this study, 80.16% TAAs removal was measured in H_2O_2=2000 mg/l after 150 min sonication time at 60°C. The TAAs yield in the present study is higher than the yield obtained by Behnajady et al. (2008a) at 60°C as mentioned above.

In a study performed by Inoue, M. et al. (2006) 37.30% TAAs removal was accomplished in a TI ww containing 50.00 mg/l Orange II, at 404 kHz frequency, at 41.50 W power, in H_2O_2=20.00 mg/l, after 240 min sonication time at 30°C. In this study, 68.40% TAAs removal was measured in H_2O_2=2000 mg/l after 150 min sonication time at 30°C. The TAAs yield in the present study is higher than the yield found by Inoue, M. et al. (2006) at 30°C as mentioned above.

5.11.9 Effect of TiO_2 Concentrations on the Removals of COD_{dis} in TI ww

82.31%, 83.43%, 89.27% and 94.11% COD_{dis} removals were observed in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.95a). 0.78%, 1.90%, 7.74% and 12.58% increase in COD_{dis} removals were obtained in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without TiO_2 while E=81.53% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing TiO_2 concentrations was observed (R^2=0.83, F=17.80, p=0.01) (Figure 5.95a).



(a)

(b)

Figure 5.95 Effect of increasing TiO_2 concentrations on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

85.24%, 89.20%, 91.17% and 98.13% COD_{dis} yields were found in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.95b). The contribution of TiO_2 concentrations on COD_{dis} removals were 0.32%, 4.28%, 6.25% and 13.21% in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=84.92% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 98.13% in TiO_2=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing TiO_2 concentrations was observed (R^2=0.79, F=16.52, p=0.01) (Figure 5.95b).

In a study performed by Mrowetz et al. (2003) 36.00% COD removal was found in a TI ww containing 75.00 mg/l Acid Orange 8, at 20 kHz frequency, at 250 W power, in TiO_2=0.10 g/l, after 100 min sonication time at 35°C. In this study, 94.11% COD_{dis} removal was measured in TiO_2=20.00 mg/l after 150 min sonication time at 30°C. The COD_{dis} yield in the present study is higher than the yield observed by Mrowetz et al. (2003) at 30°C as mentioned above.

5.11.9.1 Effect of TiO_2 Concentrations on the Color Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

80.73%, 84.14%, 88.60% and 90.13% color removals were observed in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.91). 2.47%, 5.88%, 10.34% and 11.87% increase in the color removals were obtained in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E= 78.26% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing TiO_2 concentrations was observed (R^2=0.84, F=13.76, p=0.01) (Table 5.91).

Table 5.91 Effect of increasing TiO_2 concentrations on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
TiO_2=0.10 mg/l	58.28	78.38	80.73	79.79	83.31	89.42
TiO_2=0.50 mg/l	59.34	79.67	84.14	80.38	85.78	91.19
TiO_2=10.00 mg/l	60.40	82.84	88.60	80.49	88.60	94.95
TiO_2=20.00 mg/l	62.40	83.78	90.13	81.67	90.83	96.24

89.42%, 91.19%, 94.95% and 96.24% color yields were found in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.91). The contribution of TiO_2 concentrations on color removals were 1.76%, 3.53%, 7.29% and 8.58% in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=87.66% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 96.24% in TiO_2=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing TiO_2 concentrations was observed (R^2=0.87, F=16.73, p=0.01) (Table 5.91).

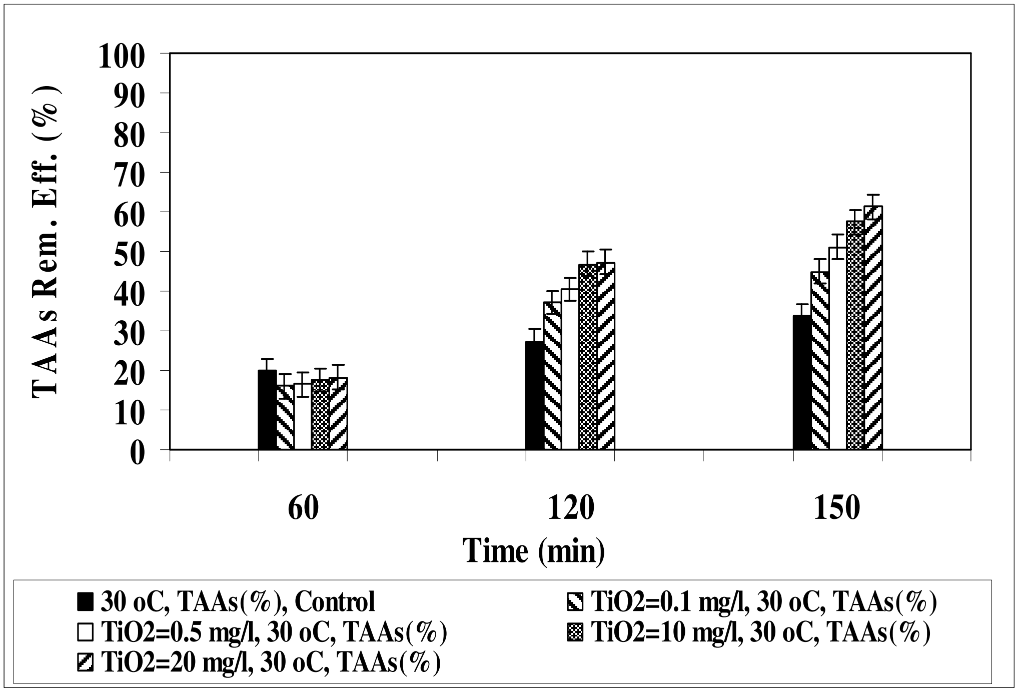
In the presence of TiO_2 active radicals produced. The reason would be due to increased surface area of TiO_2 powder which provides more active sites to produce radicals. However, the most ideal condition for dye degradation could be achieved by simultaneous usage of ultrasound and TiO_2 with H_2O_2 (Abbasi & Asl, 2008; Wang, J. et al., 2007).

Wang, J. et al. (2008) obtained 60.00% color yield in a TI ww containing 100 mg/l Azo Funchsine solution at 40 kHz frequency, at 50 W power after 60 min sonication time at 30^{o}C with TiO_2=50.00 mg/l concentration. In this study, 90.13% color removal was found in TiO_2=20.00 mg/l after 150 min sonication time at 30^{o}C. The color yield in the present study is higher than the yield obtained by Wang, J. et al. (2008) at 30^{o}C as mentioned above.

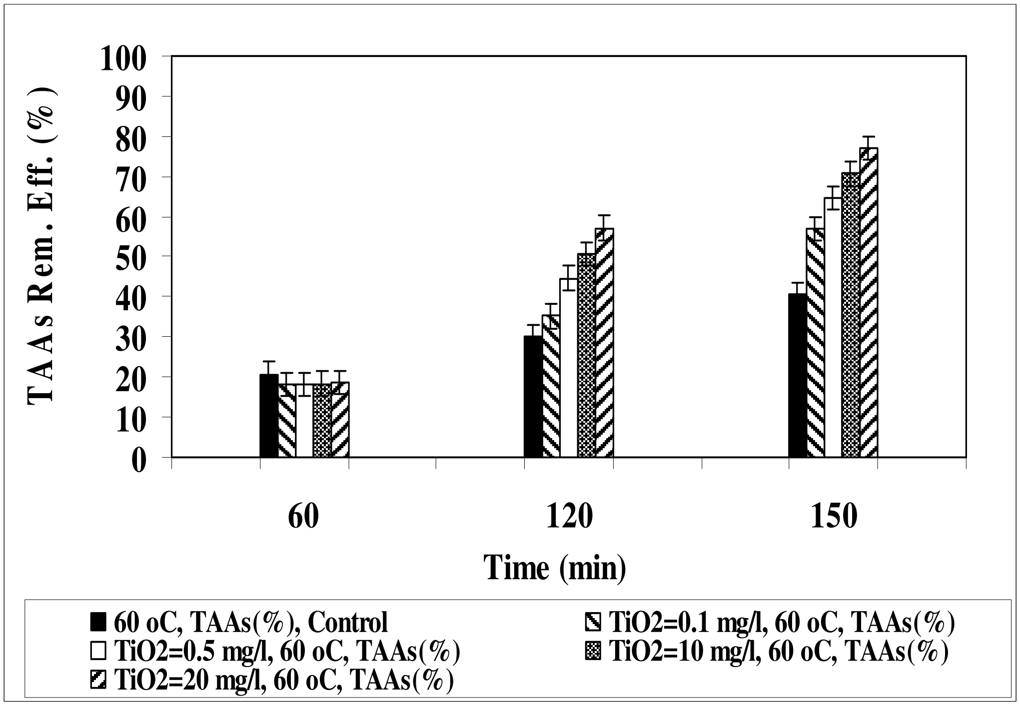
In a study performed by Abbasi & Asl (2008) 90.00% color removal was achieved in a TI ww containing 15.00 mg/l Basic Blue 41, at 35 kHz frequency, at 160 W power, after 180 min sonication time at 30^{o}C with TiO_2=0.10 g/l. In this study, 90.13% color removal was observed in TiO_2=20.00 mg/l after 150 min sonication time at 30^{o}C. In this study, similar result was obtained by Abbasi & Asl (2008) at 30^{o}C as mentioned above.

5.11.9.2 Effect of TiO_2 Concentrations on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

44.89%, 51.18%, 57.46% and 61.27% TAAs removals were observed in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.96a). 11.00%, 17.29%, 23.57% and 27.38% increase in TAAs removals were obtained in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=33.89% TAAs at pH=7.0 and at 30^{o}C). A significant linear correlation between TAAs yields and increasing TiO_2 concentrations was observed (R^2=0.97, F=18.11, p=0.01) (Figure 5.96a).



(a)



(b)

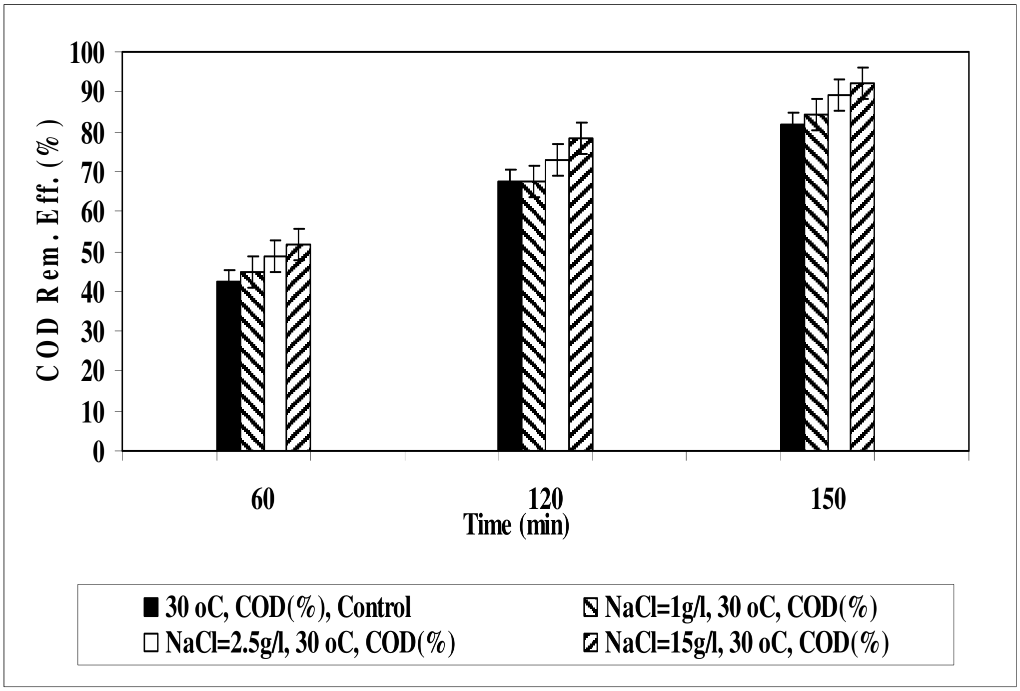
Figure 5.96 Effect of increasing TiO_2 concentrations on the TAAs removal efficiencies in TI ww at (a) 30^oC and (b) 60^oC versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

57.05%, 64.56%, 70.68% and 77.02% TAAs yields were found in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.96b). The contribution of concentrations on removals were 16.43%, 23.94%, 30.06% and 36.40% in 0.10 mg/l, 0.50 mg/l, 10.00 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=40.62% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 77.02% in TiO_2=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing TiO_2 concentrations was observed (R^2=0.92, F=18.62, p=0.01) (Figure 5.96b).

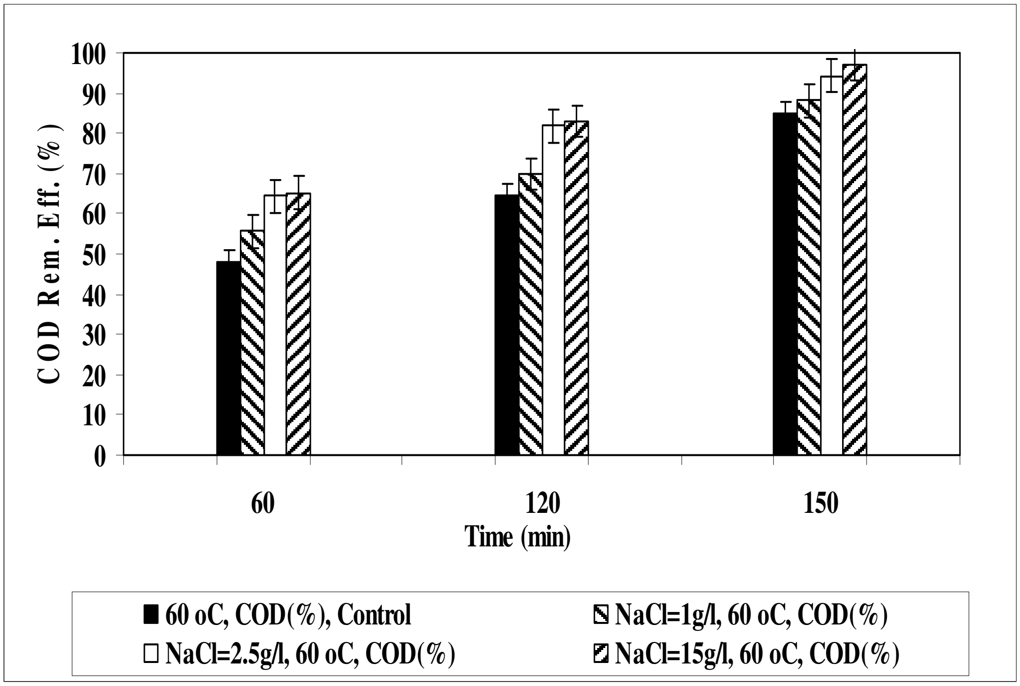
In a study performed by Wu & Yu (2009) 63.00% TAAs removal was accomplished in a TI ww containing 20.00 mg/l C.I. Reactive Red 2, in TiO_2=2000 mg/l, at 40 kHz frequency, at 400 W power, 10 W/cm^2 power intensity after 120 min sonication time at pH=7.0 at 60°C. In this study, 77.02% TAAs removal was observed in TiO_2=20.00 mg/l after 150 min sonication time at 60°C. The TAAs yield in the present study is higher than the yield observed by Wu & Yu (2009) at 60°C as mentioned above.

5.11.10 Effect of NaCl Concentrations on the Removals of COD_{dis} in TI ww

84.10%, 89.15% and 92.10% COD_{dis} removals were observed in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.97a). 2.57%, 7.62% and 10.57% increase in COD_{dis} yields were obtained in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without NaCl while E=81.53% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing NaCl concentrations was observed (R^2=0.84, F=16.75, p=0.01) (Figure 5.97a).



(a)



(b)

Figure 5.97 Effect of increasing NaCl concentrations on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

88.13%, 94.35% and 97.32% COD_{dis} yields were found in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.97b). The contribution of NaCl concentrations on COD_{dis} removals were 3.21%, 9.43% and 12.40% in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=84.92% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 97.32% in NaCl=15.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing NaCl concentrations was observed (R^2=0.79, F=17.32, p=0.01) (Figure 5.97b).

Addition of NaCl increases the ionic strength of the aqueous phase, driving the organic compounds to the bulk–bubble interface in ultrasound-related systems (Wu, C.-H, 2009). Other properties of the solution, such as viscosity, vapor pressure could affect the effect COD_{dis} removal in TI ww. The enhancement of COD_{dis} yields in the presence of NaCl can be attributed to the increase in partitioning of the pollutant species upon cavitation implosion in ultrasound-related system. Beyond the partitioning enhancement, the presence of salt reduces vapor pressure and increases surface tension. All of these factors help to collapse the bubbles more violently, causing high pollutant degradation (Wu, C.-H, 2009).

Zhang, J. et al. (2009) found 50.00% COD removal in a TI ww containing 25.00 mg/l C.I. Acid Orange 7, in NaCl=10.00 g/l, at 20 kHz frequency, at 250 W power, 201 W/l power density after 90 min sonication time at pH=4.1-9.4 and at 60°C. In this study, 97.32% COD_{dis} removal was measured in NaCl=15.00 g/l after 150 min sonication time at 60°C. The COD_{dis} yield in the present study is higher than the yield observed by Zhang, J. et al. (2009) at 60°C as mentioned above.

In a study performed by Wu, C.-H. (2008) 75.00% COD removal was accomplished in a TI ww containing 15.00 mg/l C.I. Reactive Red 198, in NaCl=5.00 g/l, at 40 kHz frequency, at 400 W power after 120 min sonication time at pH=7.0 and at 60°C. In this study, 97.32% COD_{dis} removal was found in NaCl=15.00 g/l 150 min sonication time at 60°C. The COD_{dis} yield in the present study is higher than the yield obtained by Wu, C.-H. (2008) at 60°C as mentioned above.

Maezawa et al. (2007) achieved 87.00% COD yield in a TI ww containing 25.00 mg/l Acid Orange 52, at 200 kHz frequency, at 600 W power, after 240 min sonication time at 30°C. In this study, 92.10% COD_{dis} removal was observed in NaCl=15.00 g/l after 150 min sonication time at 30°C. The COD_{dis} yield in the present study is higher than the yield measured by Maezawa et al. (2007) at 30°C as mentioned above.

5.11.10.1 Effect of NaCl Concentrations on the Color Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

83.43%, 84.96% and 87.19% color removals were observed in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.92). 5.17%, 6.70% and 8.93% increase in the color yields were obtained in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=78.26% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing NaCl concentrations was not observed (R^2=0.32, F=3.24, p=0.01) (Table 5.92).

Table 5.92 Effect of increasing NaCl concentrations on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
NaCl=1.00 g/l	78.03	80.14	83.43	83.31	94.95	96.71
NaCl=2.50 g/l	78.50	80.61	84.96	91.66	96.36	97.06
NaCl=15.00 g/l	78.61	83.20	87.19	92.95	96.94	97.53

96.71%, 97.06% and 97.53% color yields were found in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Table 5.92). The contribution of NaCl concentrations on color removals were 9.05%, 9.40% and 9.87% in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=87.66% Color at pH=7.0 and at 60^{o}C). The maximum color removal efficiency was 97.53% in NaCl=15.00 g/l after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between color yields and increasing NaCl concentrations was observed (R^2=0.87, F=12.98, p=0.01) (Table 5.92).

Addition of salts increases the color in TI ww (Ghodbane & Hamdaoui, 2009a). Addition of salts to dye aqueous solution pushes dyestuff molecules from the bulk aqueous phase to the bulk–bubble interface. The presence of salts may increase the hydrophilicity, the surface tension and ionic strength of the aqueous phase and decrease the vapor pressure. All these factors help in collapsing of the bubbles more violently, resulting in high degradation of dye (Ghodbane & Hamdaoui, 2009a).

In a study performed by Wu, C.-H. (2008) 99.00% color yield was accomplished in a TI ww containing 12.00 mg/l C.I. Reactive Red 198, in NaCl=5.00 g/l, at 40 kHz frequency, at 400 W power after 120 min sonication time at pH=7.0 and at 60^{o}C. In this study, 97.53% color removal was observed in NaCl=15.00 g/l after 150 min sonication time at 60^{o}C. In this study, similar result observed by Wu, C-H. (2008) at 60^{o}C as mentioned above.

Lorimer et al. (2000) observed 97.00% color removal in a TI ww containing 50 mg/l Sandolon Yellow, at 40 kHz frequency, at 100 W power, in NaCl=0.10 mol/l, after 80 min sonication time at 60^{o}C. In this study, 97.53% color removal was observed in NaCl=15.00 g/l after 150 min sonication time at 60^{o}C. In this study, similar result obtained by Lorimer et al. (2000) at 60^{o}C as mentioned above.

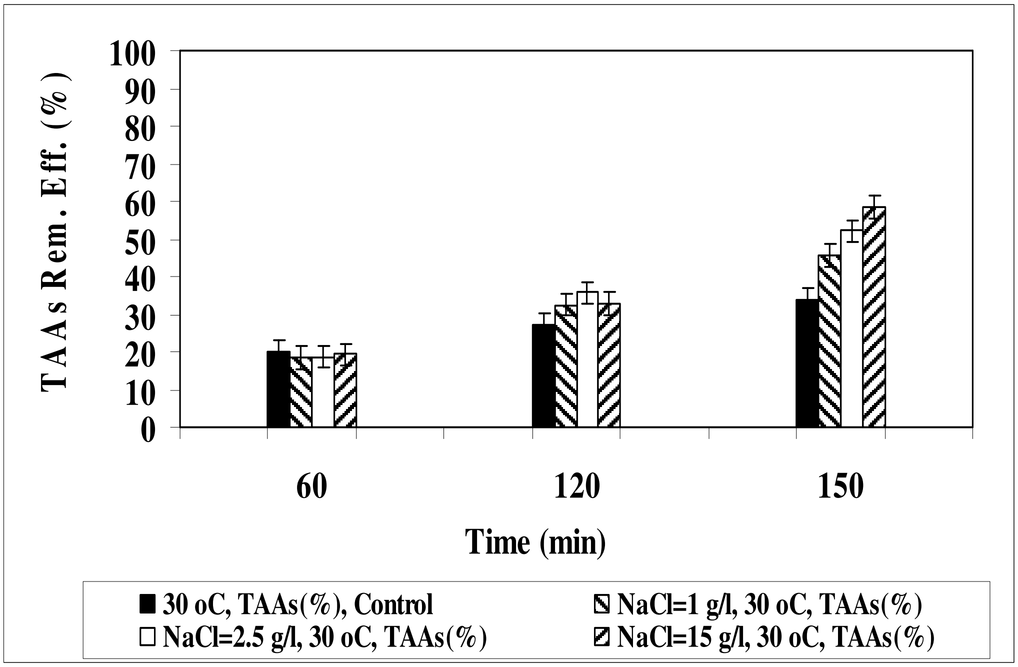
In a study performed by Maezawa et al. (2007) and Wang, X. et al. (2008) 95.00% and 68.90% color removals were obtained in a TI ww containing 25.00 mg/l Acid

Orange 52 and 10.00 mg/l Reactive Brilliant Red K-BP, in 20.00 and 35.00 g/l NaCl concentrations at 200 and 20 kHz frequencies, at 600 and 150 W powers, after 240 min sonication time at 60^{o}C and at pH=5.5, respectively. In this study, 97.53% color removal was observed in NaCl=15.00 g/l after 150 min sonication time at 60^{o}C. The color yield is higher than the yield observed by Maezawa et al. (2007) and Wang, X. et al. (2008) at 60^{o}C as mentioned above.

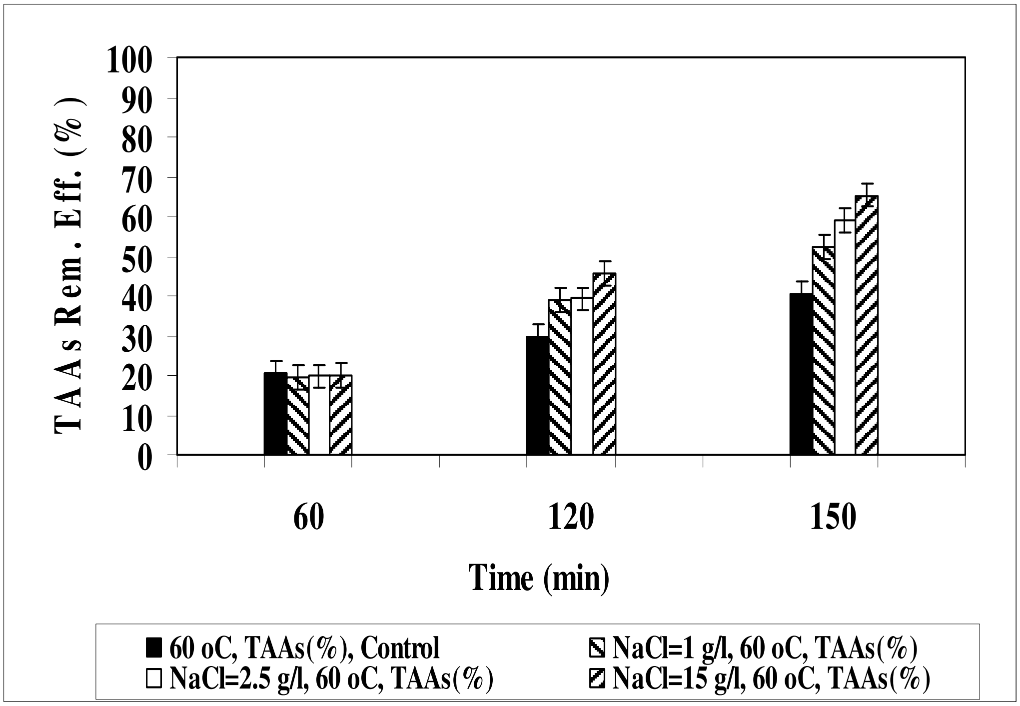
5.11.10.2 Effect of NaCl Concentrations on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

45.55%, 52.11% and 58.28% TAAs removals were observed in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.98a). 11.66%, 18.22% and 24.39% increase in TAAs removals were obtained in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=33.89% TAAs at pH=7.0 and at 30^{o}C). A significant linear correlation between TAAs yields and increasing NaCl concentrations was observed (R^2=0.76, F=13.45, p=0.01) (Figure 5.98a).

52.44%, 59.00% and 65.33% TAAs yields were found in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.98b). The contribution of NaCl concentrations on TAAs removals were 11.82%, 18.38% and 24.71% in 1.00 g/l, 2.50 and 15.00 g/l NaCl, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=40.62% TAAs at pH=7.0 and at 60^{o}C). The maximum TAAs removal efficiency was 65.33% in NaCl=15.00 g/l after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between TAAs yields and increasing NaCl concentrations was observed (R^2=0.87, F=15.58, p=0.01) (Figure 5.98b).



(a)



(b)

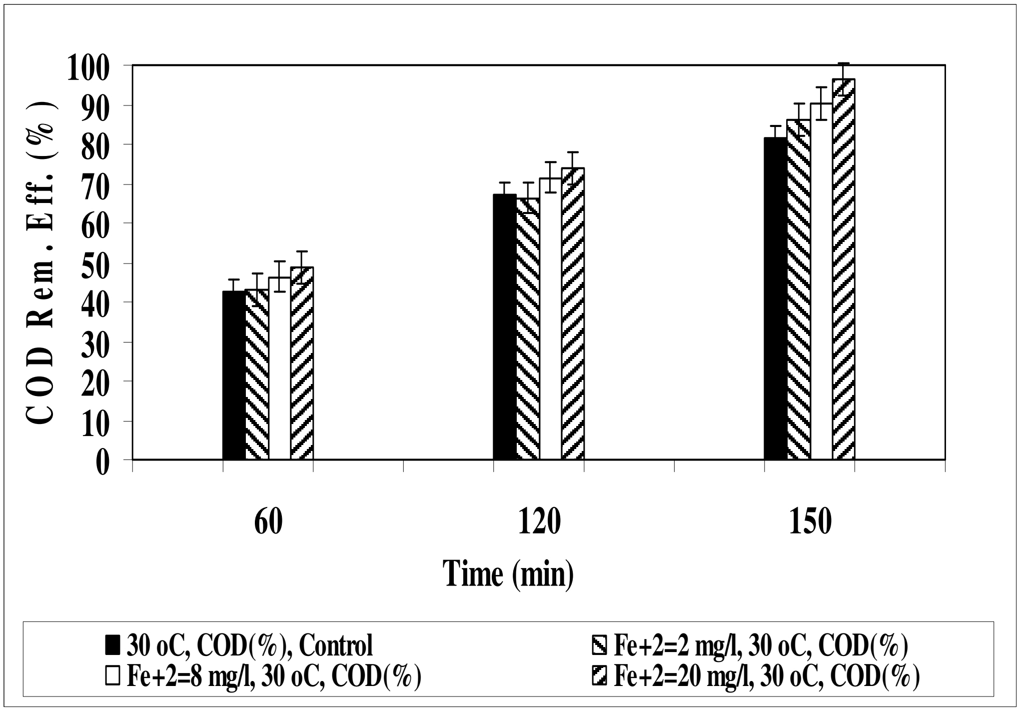
Figure 5.98 Effect of increasing NaCl concentrations on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

Addition of NaCl can increase the hydrophilicity, the surface tension and ionic strength of the aqueous phase and decrease the vapor pressure. All these factors help in collapsing of the bubbles more violently, and resulting in high degradation degrees of pollutant (Wang, J. et al., 2008). In this study, TAAs removal increased with increasing NaCl concentrations, increasing temperature and increasing sonication time during sonication experiments.

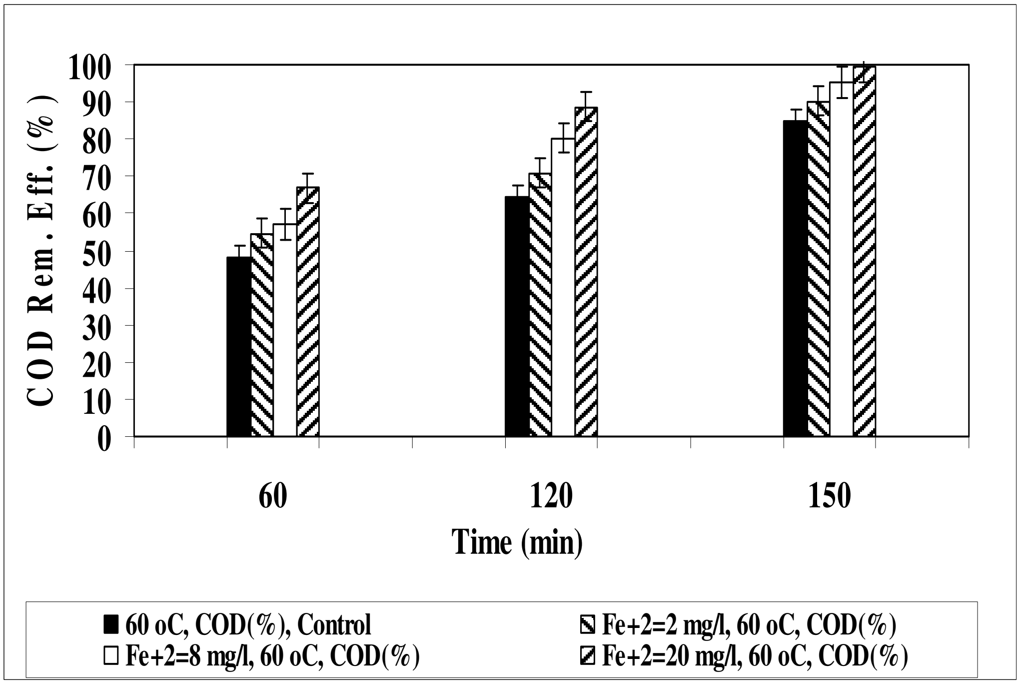
In a study performed by Behnajady et al. (2008a) 60.00% TAAs removal was achieved in a TI ww containing 10.00 mg/l Rhodamine B, at 35 kHz frequency, at 170 W power, 0.163 W/ml power density after 180 min sonication time at 60^oC with NaCl=0.625 g/l. In this study, 65.33% TAAs removal was obtained in NaCl=15.00 g/l after 150 min sonication time at 60^oC. The TAAs yield in the present study is higher than the yield observed by Behnajady et al. (2008a) at 60^oC as mentioned above.

5.11.11 Effect of Fe^{+2} Concentrations on the Removals of COD_{dis} in TI ww

86.27%, 90.31% and 96.53% COD_{dis} removals were observed in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30^oC (Figure 5.99a). 4.74%, 8.78% and 15.00% increase in COD_{dis} removals were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30^oC, compared to the control (without Fe^{+2} while E=81.53% COD_{dis} at pH=7.0 and at 30^oC). A significant linear correlation between COD_{dis} yields and increasing Fe^{+2} concentrations was observed (R^2=0.73, F=10.21, P=0.01) (Figure 5.99a).



(a)



(b)

Figure 5.99 Effect of increasing Fe^{+2} concentrations on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

90.29%, 95.31% and 99.26% COD_{dis} yields were found in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.99b). The contribution of Fe^{+2} concentrations on COD_{dis} removals were 5.37%, 10.39% and 14.34% in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=84.92% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 99.26% in Fe^{+2}=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing Fe^{+2} concentrations was observed (R^2=0.79, F=9.73, P=0.01) (Figure 5.99b).

In H_2O ultrasound can cause the formation of $OH^{\bullet}$, which is very strong and nonspecific oxidizing species. Since $OH^{\bullet}$ are major free radical and important precursors for many products formed in sonolysis, the production rate of $OH^{\bullet}$ strongly influence the sonolysis efficiency of pollutants. However, a lot of $OH^{\bullet}$ generated in cavitation bubbles would combine each other to form H_2O_2 in H_2O and lead to the decreasing of the sonolysis efficiency. According to the fenton reaction, Fe^{+2} can react with H_2O_2 to produce $OH^{\bullet}$ in weakly acidic media (pH=2.0–3.0), so Fe^{+2} can accelerate the sonolysis of pollutants (Wang, J. et al., 2008) Eqs. (5.89), (5.90), (5.91) and (5.92):

$$H_2O \ \rightarrow \ OH^{\bullet} + H^{\bullet} \tag{5.89}$$

$$OH^{\bullet} + OH^{\bullet} \ \rightarrow \ H_2O_2 \tag{5.90}$$

$$Fe^{+2} + H_2O_2 \ \rightarrow \ FeOH^{+2} + OH^{\bullet} \tag{5.91}$$

$$FeOH^{+2} + H_2O_2 \ \rightarrow \ Fe(O_2H)^{+2} \tag{5.92}$$

It has been reported that the sonochemical degradation of phenols can be enhanced by the addition of Fe^{+2}. The much higher degradation rate was observed when Fe^{+2} were added in the dye aqueous solution during sonication. This increment was mainly due to the higher $OH^\bullet$ concentration produced from the reaction. Similarly, the addition of Fenton reagent can increase the yield of $OH^\bullet$ and accelerate the sonochemical reactions. The coupled ultrasound and fenton reagent process has been investigated to improve the efficiency of sonolysis of contaminants in H_2O (Wang, J. et al., 2008).

In a study performed by Merouani et al. (2010) 58.00% COD removal was achieved in 5.00 mg/l Rhodamine B, in Fe^{+2}=5.00 mg/l, at a 300 kHz frequency, at a 60 W power after 140 min sonication time at 30°C and at pH=5.3. In this study, 96.53% COD_{dis} removal was found in Fe^{+2}=20.00 mg/l after 150 min sonication time at 30°C. The COD_{dis} yield is higher than the yield obtained by Merouani et al. (2010) at 30°C as mentioned above.

Guzman-Duque et al. (2011) it was reported that 50.00% COD was achieved in Crystal Violet (1125 μmol/l) in Fe^{+2}=20.00 mg/l after 180 min sonication time at 800 kHz frequency, at 80 W power, at pH=3.0 and at 30°C. In this study, 96.53% COD_{dis} removal was measured in Fe^{+2}=20.00 mg/l after 150 min sonication time at 30°C. The COD_{dis} yield is higher than the yield observed by Guzman-Duque et al. (2011) at 30°C as mentioned above.

Zhang, H. et al. (2009a) obtained 30.00% COD removal in 79.50 mg/l C.I. Acid Orange 7, in Fe^{+2}=86.00 mg/l, at 20 kHz frequency, at 250 W power, 10 W/cm^2 power intensity after 30 min sonication time at pH=7.0 at 30°C. In this study, 96.53% COD_{dis} removal was found in Fe^{+2}=20.00 mg/l after 150 min sonication time at 30°C. The COD_{dis} yield is higher than the yield observed by Zhang, H. et al. (2009a) at 30°C as mentioned above.

In a study performed by Sundararaman et al. (2009) 80.00% COD removal was observed with sono-fenton process in 50.00 mg/l Reactive Yellow 16, at 34 kHz frequency, at 120 W power, in Fe^{+2}=1.00 g/l, after 30 min sonication time at 60°C and at pH > 8.0. In this study, 96.53% COD_{dis} removal was obtained in Fe^{+2}=20.00

mg/l after 150 min sonication time at 60°C. The COD_{dis} yield is higher than the yield found by Sundararaman et al. (2009) at 60°C as mentioned above.

5.11.11.1 Effect of Fe^{+2} Concentrations on the Color Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

88.13%, 87.78% and 88.13% color removals were observed in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.93). 9.87%, 9.52% and 9.87% increase in the color yields were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=78.26% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing Fe^{+2} concentrations was not observed (R^2=0.30, F=0.22, P=0.01) (Table 5.93).

Table 5.93 Effect of increasing Fe^{+2} concentrations on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. Min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
Fe^{+2}=2.00 mg/l	79.91	84.96	88.13	87.19	90.72	95.30
Fe^{+2}=8.00 mg/l	81.20	85.31	87.78	87.54	90.95	96.12
Fe^{+2}=20.00 mg/l	83.20	86.96	88.13	88.72	91.89	96.59

95.30%, 96.12% and 96.59% color yields were found in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.93). The contribution of Fe^{+2} concentrations on color removals were 7.64%, 8.46% and 8.93% in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=87.66% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 96.59% in

Fe^{+2} =20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing Fe^{+2} concentrations was not observed (R^2=0.33, F=0.38, P=0.01) (Table 5.93).

Joseph et al. (2000) investigated the effect of fenton's reaction on the degradation of azo-benzene and some related azo dyes at 500 kHz. As in the previous work of Vinodgopal & Kamat (1998), these authors also reported that the first step in the reaction scheme was the cleavage of the azo-double bond upon $OH^\bullet$ attack. Fenton's reaction at optimal Fe^{+2} concentrations was found to induce a threefold increase in the reaction rates. Finally, they reported that saturating the solution with Ar instead of O_2 accelerated the reactions by 10.00%.

However, the degradation of dyestuff occurred by fenton oxidation. This is due to active species such as $OH^\bullet/O_2H^\bullet$ that can be generated by the inter-reaction of H_2O_2 with Fe^{+2} and Fe^{+3} in acid solution according to Eqs. (5.93) and (5.94). The main reaction pathway for the degradation of dyestuff in solution is the oxidation by $OH^\bullet$ attack in Eq. (5.88) (See Eq. (5.88) in 5.11.2.1 Section).

$$Fe^{+2} + H_2O_2 + H^+ \quad \rightarrow \quad Fe^{+3} + OH^\bullet + H_2O \tag{5.93}$$

$$Fe^{+3} + H_2O_2 \quad \rightarrow \quad Fe^{+2} + O_2H^\bullet + H^+ \tag{5.94}$$

Zhang, H. et al. (2009b) 95.00% color removal was achieved in C.I. Acid Orange 7 (C_0=79.5 mg/l), in Fe^{+2}=16.00 mg/l, at 20 kHz frequency, 250 W power, 10 W/cm^2 power intensity after 30 min sonication time at pH=7.0 at 60°C. In this study, 96.59% color removal was observed in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60°C. The color yield is higher than the yield observed by Zhang, H. et al. (2009b) at 60°C as mentioned above.

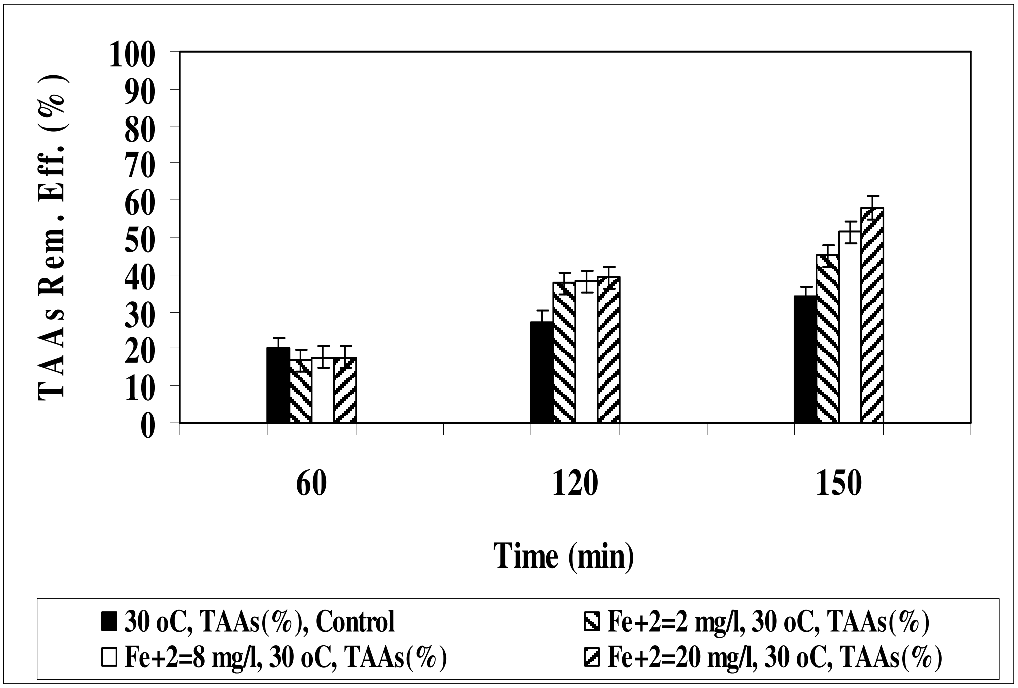
In a study performed by Sundararaman et al. (2009) 90.00% color yield was accomplished with sono-fenton process in 50 mg/l Reactive Yellow 16, at 34 kHz frequency, at 120 W power, in Fe^{+2}=1.00 g/l, after 30 min sonication time at 60°C and at pH > 8.00. In this study, 96.59% color removal was measured for Fe^{+2}=20.00 mg/l after 150 min sonication time at 60°C. The color yield is higher than the yield observed by Sundararaman et al. (2009) at 60°C as mentioned above.

Wang, X. et al. (2008) found 54.00% color yield in Reactive Brilliant Red K-BP, at 20 kHz frequency, at 150 W power, in Fe^{+2}=26.00 mg/l, after 240 min sonication time at 30°C and at pH=5.5. In this study, 88.13% color removal was observed in Fe^{+2}=20.00 mg/l after 150 min sonication time at 30°C. The color yield is higher than the yield measured by Wang, X. et al. (2008) at 30°C as mentioned above.

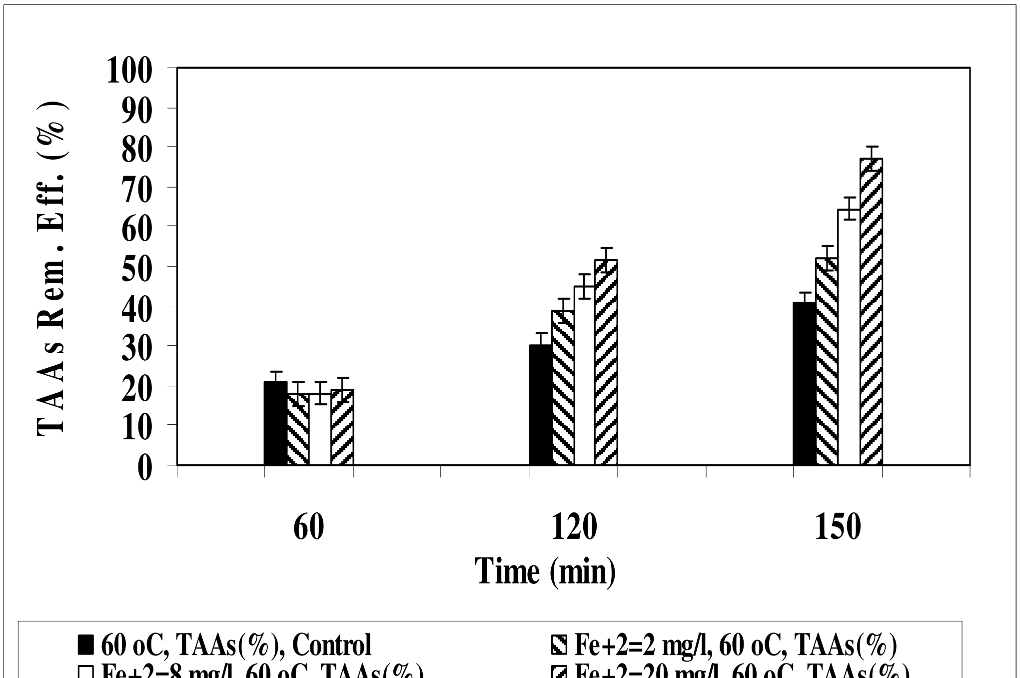
In a study performed by Ghodbane & Hamdaoui (2009a) 85.00% color removal was observed in Acid Blue 25, at 1700 kHz frequency, at 14 W power, in Fe^{+2}=10.00 mg/l, after 30 min sonication time at 55°C and at pH=5.0-8.0. In this study, 96.59% color removal was found in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60°C. The color yield is higher than the yield obtained by Ghodbane & Hamdaoui (2009a) at 55°C as mentioned above.

5.11.11.2 Effect of Fe^{+2} Concentrations on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

44.95%, 51.50% and 58.01% TAAs removals were observed in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.100a). 11.06%, 17.61% and 24.12% increase in TAAs removals were obtained in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=33.89% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing Fe^{+2} concentrations was observed (R^2=0.91, F=10.20, P=0.01) (Figure 5.100a).



(a)



(b)

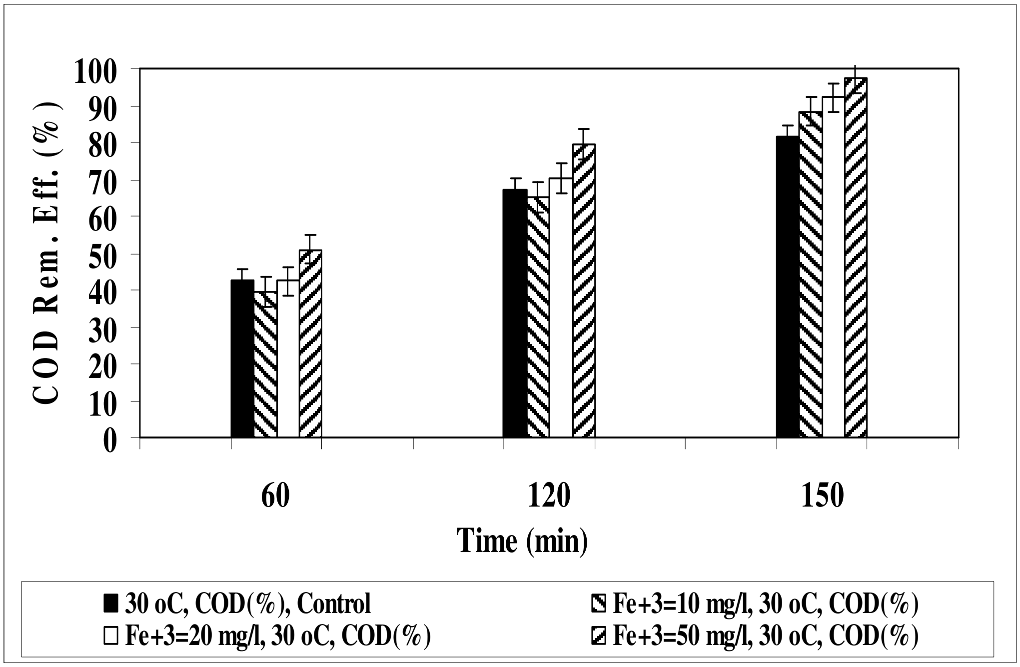
Figure 5.100 Effect of increasing Fe^{+2} concentrations on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

52.11%, 64.51% and 76.91% TAAs yields were found in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60^oC (Figure 5.100b). The contribution of Fe^{+2} concentrations on TAAs removals were 11.49%, 23.89% and 36.29% in 2.00 mg/l, 8.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at pH=7.0 and at 60^oC, compared to the control (E=40.62% TAAs at pH=7.0 and at 60^oC). The maximum TAAs removal efficiency was 76.91% in Fe^{+2}=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60^oC. A significant linear correlation between TAAs yields and increasing Fe^{+2} concentrations was observed (R^2=0.96, F=14.67, P=0.01) (Figure 5.100b).

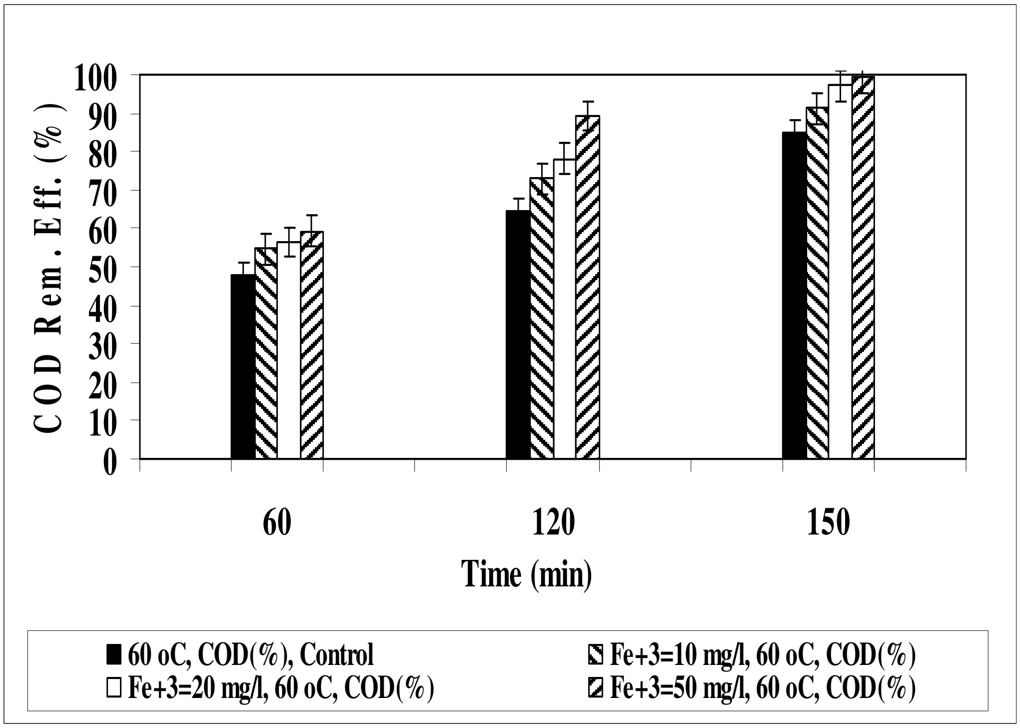
In a study performed by Sun et al. (2007) 36.94% TAAs removal was accomplished in 2.00 mg/l Acid Black 1, at 40 kHz frequency, at 50 W power, 50 W/l power density, in Fe^{+2}=10.00 mg/l, after 30 min sonication time at 40^oC and at pH=7.0. In this study, 76.91% TAAs removal was observed in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60^oC. The TAAs yield is higher than the yield found by Sun et al. (2007) at 40^oC as mentioned above.

5.11.12 Effect of Fe^{+3} Concentrations on the Removals of COD_{dis} in TI ww

88.41%, 92.15% and 97.39% COD_{dis} removals were observed in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30^oC (Figure 5.101a). 6.88%, 10.62% and 15.86% increase in COD_{dis} removals were obtained in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30^oC, compared to the control (without Fe^{+3} while E=81.53% COD_{dis} at pH=7.0 and at 30^oC). A significant linear correlation between COD_{dis} yields and increasing Fe^{+3} concentrations was observed (R^2=0.79, F=10.14, P=0.01) (Figure 5.101a).



(a)



(b)

Figure 5.101 Effect of increasing Fe^{+3} concentrations on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

91.18%, 97.20% and 99.37% COD_{dis} yields were found in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.101b). The contribution of Fe^{+3} concentrations on COD_{dis} removals were 6.26%, 12.28% and 14.45% in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=84.92% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 99.37% in Fe^{+3} =50.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing Fe^{+3} concentrations was observed (R^2=0.78, F=12.83, P=0.01) (Figure 5.101b).

For the combined Fe^{+2}/ultrasound experiments, Fe^{+2} was initially added using $FeSO_4$ to the desired target initial concentration. The pH was adjusted to 3 using H_2SO_4, in order to avoid Fe precipitation as $Fe(OH)_2$. The rate of dye degradation was significantly enhanced by the addition of Fe^{+2}. Sonochemically generated H_2O_2 can be effectively utilized when Fe^{+2} is added to the system, because additional $OH^\bullet$ generation is achieved by the fenton and fenton-like processes. If reaction proceeds at a high rate, the reduction of Fe^{+3} to Fe^{+2} by H_2O_2 occurs at a lower rate. Then, the initial degradation rate in the Fe^{+2}/ultrasound process is higher than that observed in the case of ultrasound alone (Ghodbane & Hamdaoui, 2009b) in Eqs. (5.95), (5.96), (5.97) and (5.98):

$$Fe^{+2} + H_2O_2 \quad \rightarrow \quad Fe^{+3} + OH^\bullet + OH^- \tag{5.95}$$

$$Fe^{+2} + H_2O_2 \quad \rightarrow \quad Fe - O_2H^{+2} + H^+ \tag{5.96}$$

$$Fe - O_2H^{+2} \quad \rightarrow \quad Fe^{+2} + O_2H^\bullet \tag{5.97}$$

$$Fe^{+3} + O_2H^\bullet \quad \rightarrow \quad Fe^{+2} + O_2 + H^+ \tag{5.98}$$

The fact that at high Fe^{+2} concentrations, the solution undergoes self-quenching of $OH^{\bullet}$ by the added amounts of Fe^{+2} to produce Fe^{+3} (Ghodbane & Hamdaoui, 2009b). Eq. (5.99):

$$Fe^{+2} + OH^{\bullet} \quad \rightarrow \quad Fe^{+3} + OH^{-} \tag{5.99}$$

The proper Fe^{+3} content as dopant can inhibit the crystallization and phase transformation of TiO_2 powder and preserve the anatase phase TiO_2 with high catalytic activity (Figure 5.102) However, the catalytic activity gradually decreases as the Fe^{+3} content increases unceasingly after 0.25%. There were two possible reasons. One is that the effective surface area of TiO_2 particles for absorbing light and heat energies decreases on a large scale. Another is that lots of chemical bonds of Ti–O– Fe^{+3} elements could occur so that the contents of surface O_2 vacancy and defect also decrease (Wang, J. et al., 2008).

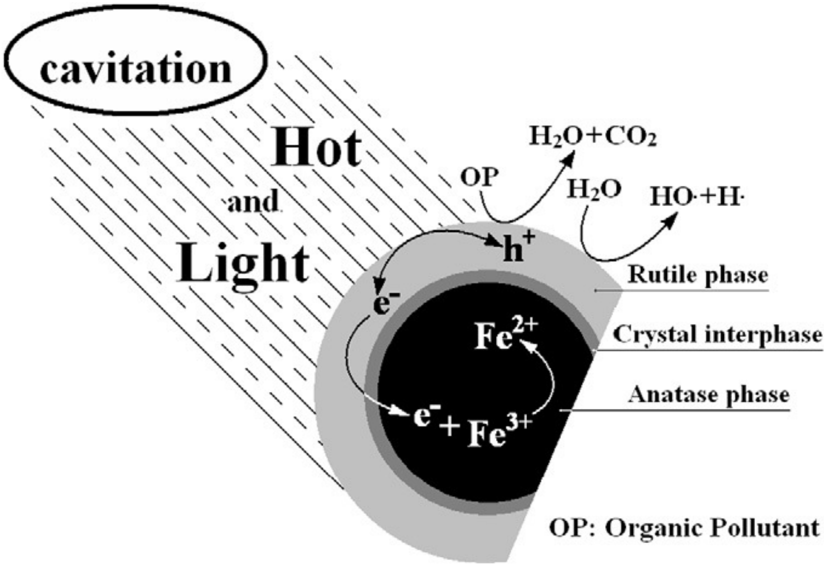


Figure 5.102 Possible exciton processes of Fe-doped mixed crystal TiO_2 particles under Ultrasonic irradiation, separation of hole and electron, and degradation of organic pollutants.

Merouani et al. (2010) found 45.00% COD yield in Rhodamine B (5.00 mg/l), in Fe^{+3}=7.00 mg/l, at a 300 kHz frequency, at a 60 W power after 140 min sonication time at 30°C and at pH=5.3. In this study, 97.39% COD_{dis} removal was measured in

Fe^{+3}=50.00 mg/l after 150 min sonication time at 30°C. The COD_{dis} yield is higher than the yield observed by Merouani et al. (2010) at 30°C as mentioned above.

In a study performed by Wang, J. et al. (2008) 65.00% COD removal was achieved in azo funchsine solution at 40 kHz frequency, at 50 W power after 60 min sonication time at 30°C with Fe^{+3}=50.00 mg/l concentration. In this study, 97.39% COD_{dis} removal was observed after 150 min sonication time at 30°C. The COD_{dis} yield is higher than the yield obtained by Wang, J. et al. (2008) at 30°C as mentioned above.

5.11.12.1 Effect of Fe^{+3} Concentrations on the Color Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

89.31%, 91.07% and 93.42% color yields were observed in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.94). 11.05%, 12.81% and 15.16% increase in the color removals were obtained for 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=78.26% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing Fe^{+3} concentrations was not observed (R^2=0.33, F=0.25, P=0.01) (Table 5.94).

91.42%, 93.89% and 93.07% color yields were found in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.94). The contribution of Fe^{+3} concentrations on color removals were 3.76%, 6.23% and 5.41% in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=87.66% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 93.89% in Fe^{+3}=20.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing Fe^{+3} concentrations was not observed (R^2=0.30, F=0.17, P=0.01) (Table 5.94).

Table 5.94 Effect of increasing Fe^{+3} concentrations on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
Fe^{+3}=10.00 mg/l	84.14	87.31	89.31	87.31	88.95	91.42
Fe^{+3}=20.00 mg/l	84.84	88.37	91.07	88.13	90.60	93.89
Fe^{+3}=50.00 mg/l	84.96	89.31	93.42	88.72	91.30	93.07

Gopinath et al. (2010) 90.00% color removal of Congo Red was accomplished with Fe^{+3}=20.00 mg/l, at 30 kHz frequency, at 300 W power after 60 min sonication time at pH=3.0-4.0 and at 60°C. In this study, 93.89% color removal was observed in Fe^{+3}=20.00 mg/l after 150 min sonication time at 60°C. The color yield is higher than the yield obtained by Gopinath et al. (2010) at 60°C as mentioned above.

In a study performed by Mrowetz et al. (2003) 30.00% color yield was accomplished in Acid Orange 8, at 20 kHz frequency, at 250 W power, in Fe^{+3}=50.00 mg/l, after 100 min sonication time at 35°C. In this study, 93.42% color removal was measured in Fe^{+3}=50.00 mg/l after 150 min sonication time at 30°C. The color yield is higher than the yield observed by Mrowetz et al. (2003) at 35°C as mentioned above.

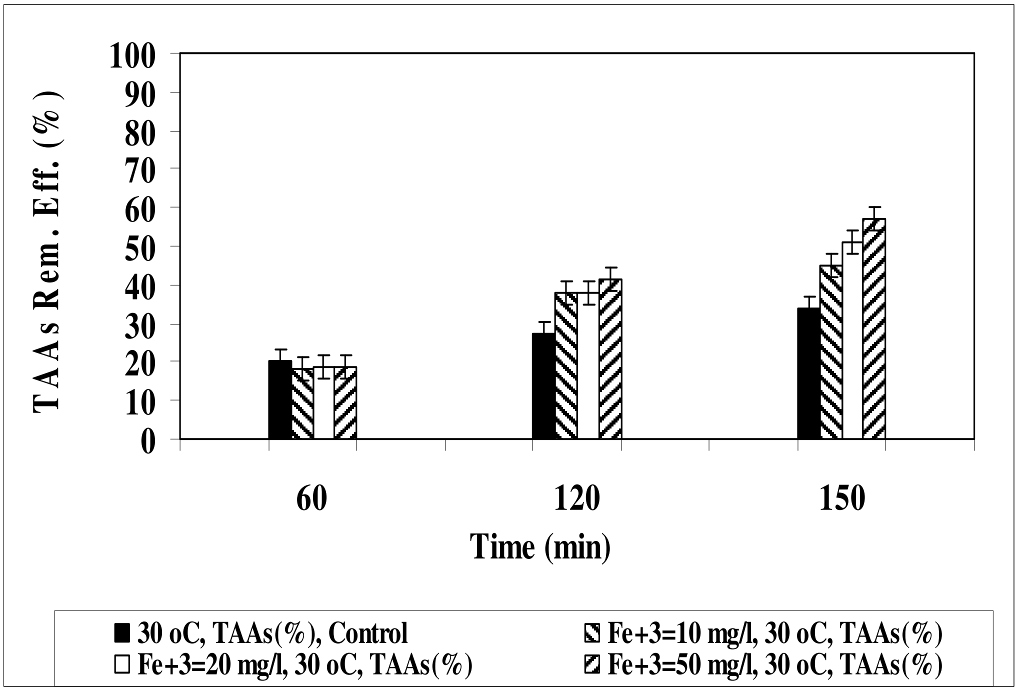
Zhang, H. et al. (2009b) 60.00% color removal was observed in 15.00 mg/l C.I. Acid Orange 7, at 20 kHz frequency, at 250 W power, in Fe^{+3}=5.00 g/l, after 30 min sonication time at 30°C and at pH=3.0. In this study, 93.42% color removal was observed in Fe^{+3}=50.00 mg/l after 150 min sonication time at 30°C. The color yield is higher than the yield obtained by Zhang, H. et al. (2009b) at 30°C as mentioned above.

In a study performed by Ghodbane & Hamdaoui (2009a) 81.00% color yield was accomplished in 20.00 mg/l Acid Blue 25, at 1700 kHz frequency, at 14 W power, in Fe^{+3}=35.00 mg/l, after 30 min sonication time at 55°C and at pH=5.0-8.0. In this study, 93.89% color removal was measured in Fe^{+3}=20.00 mg/l after 150 min sonication time at 60°C. The color yield is higher than the yield observed by Ghodbane & Hamdaoui (2009a) at 55°C as mentioned above.

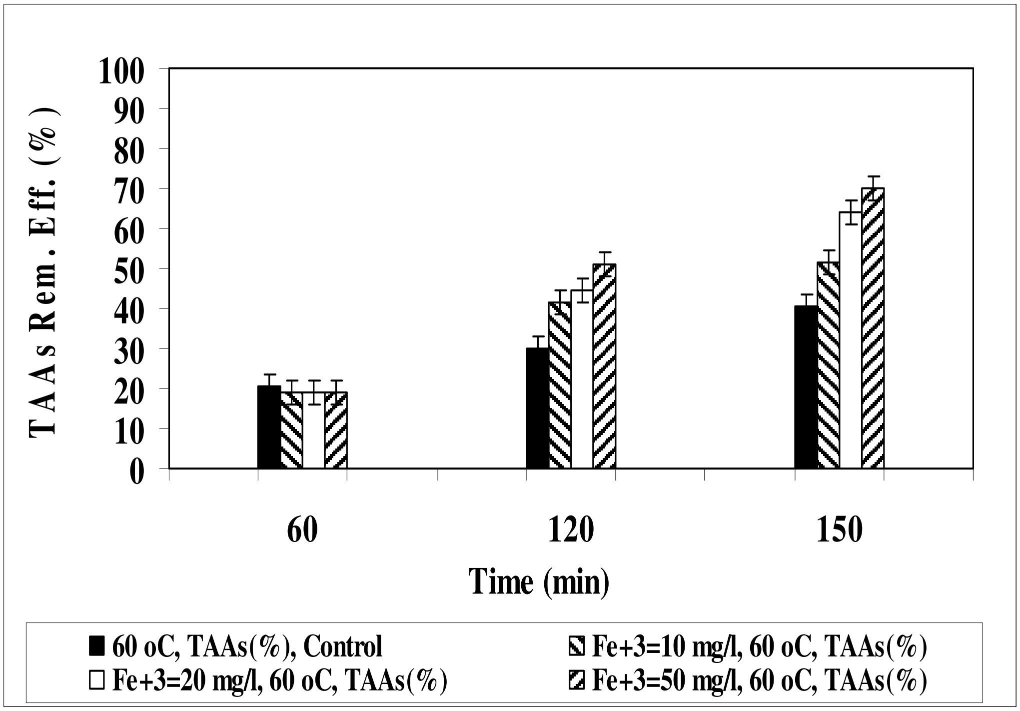
Jamalluddin & Abdullah (2010) obtained 90.00% color yield in 70.00 mg/l Reactive Blue 4, at 35 kHz frequency, at 50 W power, in Fe^{+3}=20.00 mg/l, after 60 min sonication time at 30°C and at pH=4.0. In this study, 91.07% color removal was measured in Fe^{+3}=20.00 mg/l after 150 min sonication time at 30°C. The color yield is higher than the yield found by Jamalluddin & Abdullah (2010) at 30°C as mentioned above.

5.11.12.2 Effect of Fe^{+3} Concentrations on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

44.78%, 51.01% and 57.24% TAAs removals were observed in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.103a). 10.89%, 17.12% and 23.35% increase in TAAs yields were obtained in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=33.89% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing Fe^{+3} concentrations was observed (R^2=0.84, F=11.25, P=0.01) (Figure 5.103a).



(a)



(b)

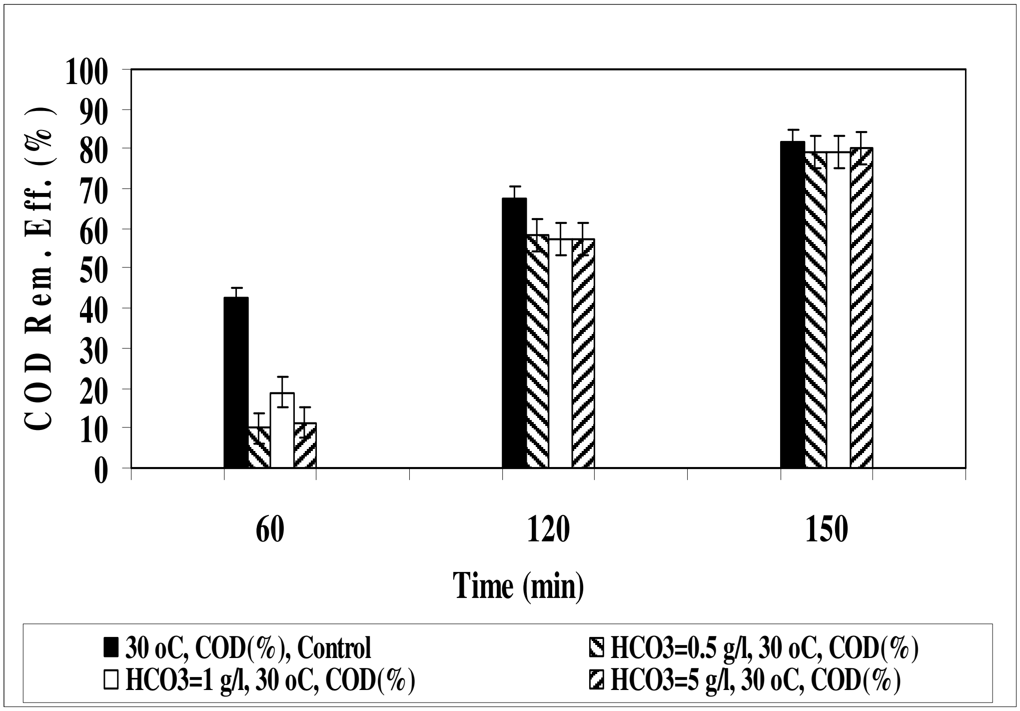
Figure 5.103 Effect of increasing Fe^{+3} concentrations on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

51.56%, 64.02% and 70.24% TAAs yields were found in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.103b). The contribution of Fe^{+3} concentrations on TAAs removals were 10.94%, 23.40% and 29.62% in 10.00 mg/l, 20.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=40.62% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 70.24% in Fe^{+3} =50.00 mg/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing Fe^{+3} concentrations was observed (R^2=0.73, F=12.38, P=0.01) (Figure 5.103b).

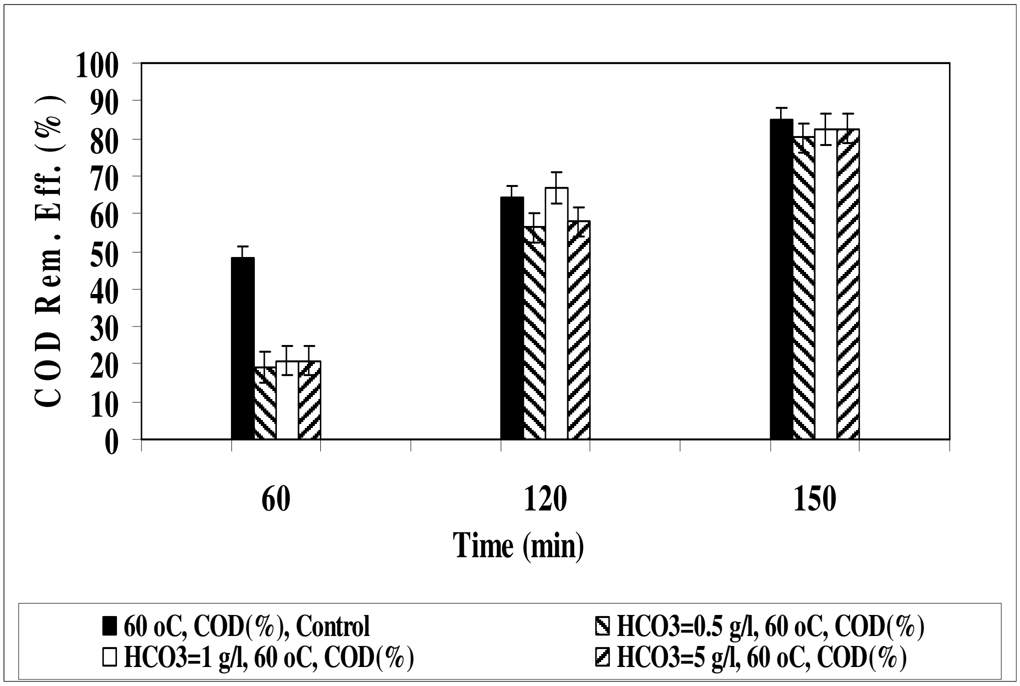
In a study performed by Fukushima et al. (2000) 70.00% TAAs removal was achieved in Fe^{+3}=50.00 mg/l, at 35 kHz frequency, at 500 W power after 100 min sonication time at 60°C at pH=3.0-5.0. In this study, 70.24% TAAs removal was observed in Fe^{+3}=50.00 mg/l after 150 min sonication time at 60°C. In this study, similar result obtained by Fukushima et al. (2000) at 60°C as mentioned above.

5.11.13 Effect of HCO_3^{-1} Concentrations on the Removals of COD_{dis} in TI ww

79.00%, 79.15% and 80.31% COD_{dis} removals were observed in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.104a). The contribution of increasing HCO_3^{-1} concentrations on COD_{dis} removals were not significant after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without HCO_3^{-1} while E=81.53% COD_{dis} at pH=7.0 and 30°C). A significant linear correlation between COD_{dis} yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.39, F=0.27, P=0.01) (Figure 5.104a).



(a)



(b)

Figure 5.104 Effect of increasing HCO_3^{-1} concentrations on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

80.19%, 82.33% and 82.50% COD_{dis} yields were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.104b). The contribution of increasing HCO_3^{-1} concentrations on COD_{dis} removals were not significant after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=84.92% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 82.50% in HCO_3^{-1}=5.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.33, F=0.21, P=0.01) (Figure 5.104b).

The degradation rate was increased in the presence of CO_3 and HCO_3, with a maximum around 0.10 M total concentration at pH=9.0 and a saturation trend at pH=11.0. The increasing concentration of the added ions would increase the ionic strength of the solution, but the expected salting effect would enhance volatility and therefore, gas-phase pyrolysis of neutral, volatile compounds, less likely of a charged species such as Acid Blue 40. Degradation enhancement is not limited to CO_3 and HCO_3. A linear increase of degradation rate with concentration was observed in the case of NO_2. Because CO_3 and HCO_3, Br_2 and I_2 are all $OH^\bullet$ scavengers, the experimental results reported so far are quite unexpected. In the absence of scavengers, the degradation of dyestuff would be accounted for by the $OH^\bullet$ that is present at the bubble surface and in the solution bulk. The air–water interface of the cavitation bubbles is thus a very reactive environment, although it accounts for a limited fraction of the solution volume. Not all the sonochemically formed $OH^\bullet$ can induce substrate degradation because, with such an elevated $OH^\bullet$ at the air–water interface, radical–radical recombination to yield H_2O_2 and H_2O would be much more important than the reaction with the substrates, and would also limit the diffusion of reactive radical species to the solution bulk. In the following reactions, (s)=bubble surface and (aq)=solution bulk (Minero et al., 2008) in Eqs. (5.100), (5.101), (5.102), (5.103), (5.104) and (5.105):

$$2OH^\bullet_{(s)} \rightarrow H_2O_{2\,(s)} \tag{5.100}$$

$$OH^{\bullet}{}_{(s)} + H^{\bullet}{}_{(s)} \rightarrow H_2O_{(s)} \quad (5.101)$$

$$H^{\bullet}{}_{(s)} + O_{2(s)} \rightarrow O_2H^{\bullet}{}_{(s)} \quad (5.102)$$

$$OH^{\bullet}{}_{(s)} \rightarrow OH^{\bullet}{}_{(aq)} \quad (5.103)$$

$$H^{\bullet}{}_{(s)} \rightarrow H^{\bullet}{}_{(aq)} \quad (5.104)$$

$$H^{\bullet}{}_{(aq)} + O_{2\,(aq)} \rightarrow O_2H^{\bullet}{}_{(aq)} \quad (5.105)$$

Guzman-Duque et al. (2011) it was reported that 90.00% COD was accomplished in 15.00 mg/l Crystal Violet, in HCO_3^{-1}=3.00 g/l after 180 min sonication time at 800 kHz frequency, at 80 W power, at pH=9.0 and at 50^{o}C. In this study, 82.50% COD_{dis} removal was observed in HCO_3^{-1}=5.00 g/l after 150 min sonication time at 60^{o}C. The COD_{dis} yield is lower than the yield obtained by Guzman-Duque et al. (2011) at 50^{o}C as mentioned above.

In a study performed by Merouani et al. (2010b) 55.00% COD removal was accomplished in 5.00 mg/l Rhodomanie B, in HCO_3=3.00 g/l, at 300 kHz frequency, at 60 W power, after 50 min sonication time at 60^{o}C and at pH=8.3. In this study, 82.50% COD_{dis} removal was measured in HCO_3^{-1}=5.00 g/l after 150 min sonication time at 60^{o}C. The COD_{dis} yield is higher than the yield observed by Merouani et al. (2010b) at 60^{o}C as mentioned above.

5.11.13.1 Effect of HCO_3^{-1} Concentrations on the Color Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

86.96%, 88.95% and 89.31% color removals were observed in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Table 5.95). 8.70%, 10.69% and 11.05% increase in the color removals were obtained in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=78.26% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.31, F=0.25, P=0.01) (Table 5.95).

Table 5.95 Effect of increasing HCO_3^{-1} concentrations on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
HCO_3^{-1}=0.50 g/l	78.73	83.78	86.96	87.66	90.36	93.30
HCO_3^{-1}=1.00 g/l	80.02	84.14	88.95	87.90	90.60	94.95
HCO_3^{-1}=5.00 g/l	82.02	85.78	89.31	88.72	91.89	96.12

93.30%, 94.95% and 96.12% color yields were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Table 5.95). The contribution of HCO_3^{-1} concentrations on color removals were 5.64%, 7.29% and 8.46% in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=87.66% Color at pH=7.0 and at 60°C. The maximum color removal was 96.12% in HCO_3^{-1}=5.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and increasing HCO_3^{-1} concentrations was not observed (R^2=0.36, F=0.31, P=0.01) (Table 5.95).

Differently from the surface of the cavitation bubbles, in the solution bulk the lower $OH^{\bullet}$ would cause organic substrates to be by far the main sink of $OH^{\bullet}$. Note that the $OH^{\bullet}$ that reaches the bulk is those that escape recombination or reaction on the bubble surface. There could be some exception for NO_2, Br_2 and I_2 at the highest adopted concentration values, due to their very fast reaction with $OH^{\bullet}$. The scavenging of $OH^{\bullet}$ by the anions would yield radical species such as $CO_3\bullet^{-}$, reactive toward organic compounds although less than $OH^{\bullet}$ (Minero et al., 2008) in Eqs. (5.106) and (5.107):

$$OH^{\bullet} + HCO_3^{-} \quad \rightarrow \quad H_2O + CO_3^{\bullet\,-} \tag{5.106}$$

$$OH^{\bullet} + CO_3^{-2} \quad \rightarrow \quad OH^{-} + CO_3^{\bullet\,-} \tag{5.107}$$

It is possible to account for the enhancement of dyestuff sonochemical degradation by the studied anions under the hypothesis that the $CO_3\bullet^{-}$ here after $X^{\bullet}$ undergo more limited radical–radical recombination compared to $OH^{\bullet}$ on the surface of the cavitation bubbles (Minero et al., 2008).

Merouani et al. (2010b) 66.00% color yield was found in 5.00 mg/l Rhodomanie B, in HCO_3^{-1}=3.00 g/l, at 300 kHz frequency, at 60 W power, after 50 min sonication time at 60^{o}C and at pH=8.3. In this study, 96.12% color removal was measured in HCO_3^{-1}=5.00 g/l after 150 min sonication time at 60^{o}C. The color yield is higher than the yield observed by Merouani et al. (2010b) at 60^{o}C as mentioned above.

In a study performed by Sun et al. (2007) 97.00% color removal was accomplished in 20.00 mg/l Acid Black 1, at 40 kHz frequency, at 50 W power, 50 W/l power density, in HCO_3^{-1}=1.00 g/l, after 30 min sonication time at 40^{o}C and at pH=3.0. In this study, 96.12% color removal was observed in HCO_3^{-1}=5.00 g/l after 150 min sonication time at 60^{o}C. In this study, similar result obtained by Sun et al. (2007) at 60^{o}C as mentioned above.

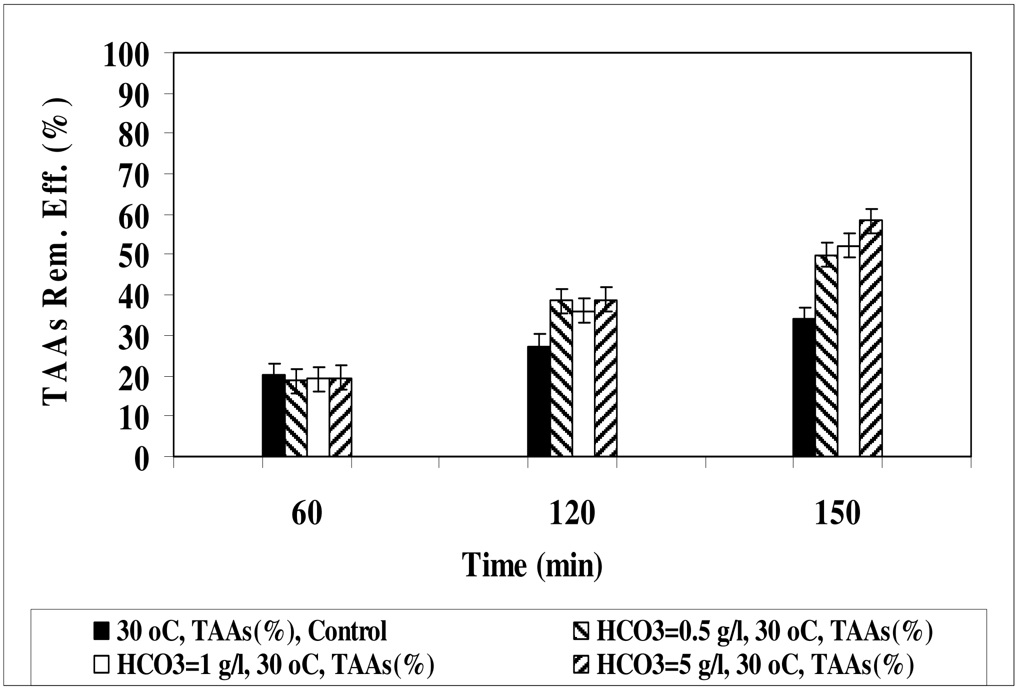
Guzman-Duque et al. (2011) 90.00% color removal was found in Orange-G, at 800 kHz frequency, at 80 W power, in HCO_3^{-1}=3.00 g/l, after 180 min sonication time at 30°C and at pH=3.0-9.0. In this study, 89.31% color yield was measured in HCO_3^{-1}=5.00 g/l after 150 min sonication time at 30°C. In this study, similar result observed by Guzman-Duque et al. (2011) at 30°C as mentioned above.

In a study performed by Wang, J. et al. (2011) 94.20% color removal was accomplished in 20.00 mg/l Brilliant Red K-2BP, at 20 kHz frequency, at 150 W power, in HCO_3^{-1}=1.50 g/l, after 120 min sonication time at 60°C and at pH=5.5. In this study, 96.12% color removal was found in HCO_3^{-1}=5.00 g/l after 150 min sonication time at 60°C. The color yield is higher than the yield obtained by Wang, J. et al. (2011) at 60°C as mentioned above.

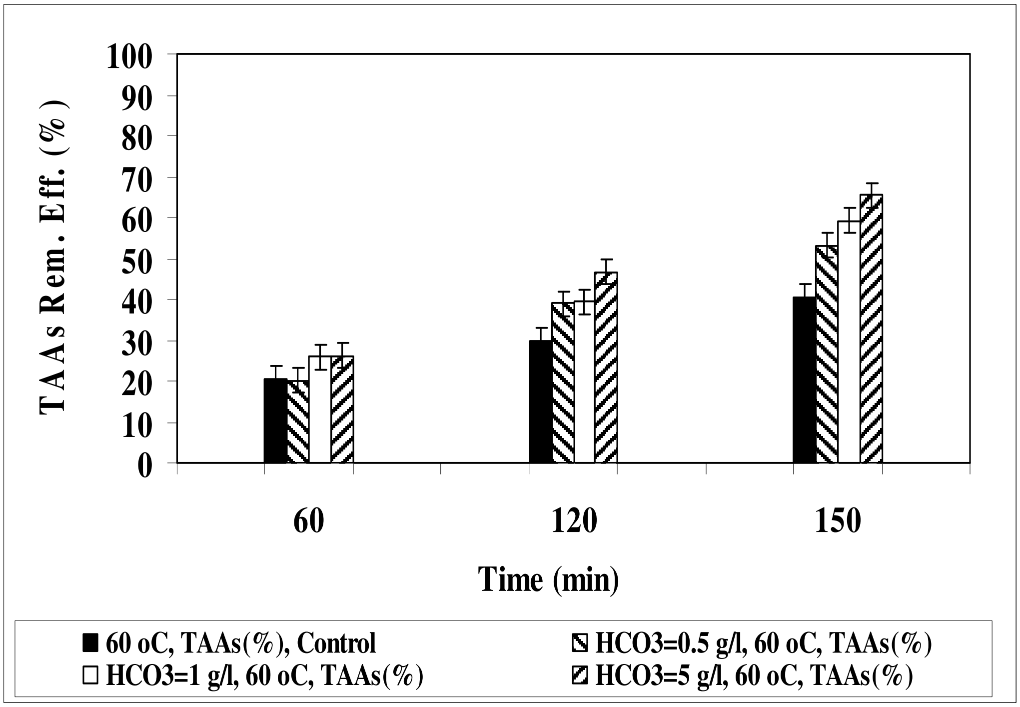
5.11.13.2 Effect of HCO_3^{-1} Concentrations on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

49.87%, 52.20% and 58.47% TAAs removals were observed in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.105a). 15.98%, 18.31% and 24.58% increase in TAAs removals were obtained in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (E=33.89% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing HCO_3^{-1} concentrations was observed (R^2=0.82, F=14.25, P=0.01) (Figure 5.105a).

53.06%, 59.61% and 65.52% TAAs yields were found in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.105b). The contribution of HCO_3^{-1} concentrations on TAAs removals were 12.44%, 18.99% and 24.90% in 0.50 g/l, 1.00 and 5.00 g/l HCO_3^{-1}, respectively, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=40.62% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 65.52% in HCO_3^{-1}=5.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between TAAs yields and increasing HCO_3^{-1} concentrations was observed (R^2=0.79, F=13.26, P=0.01) (Figure 5.105b).



(a)



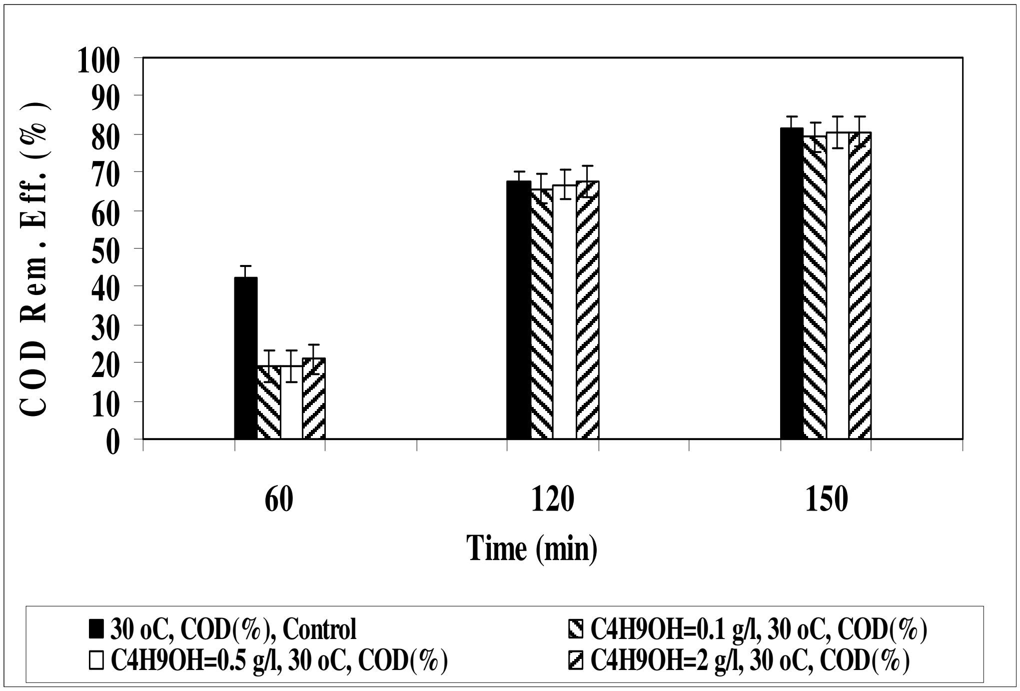
(b)

Figure 5.105 Effect of increasing HCO_3^{-1} concentrations on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

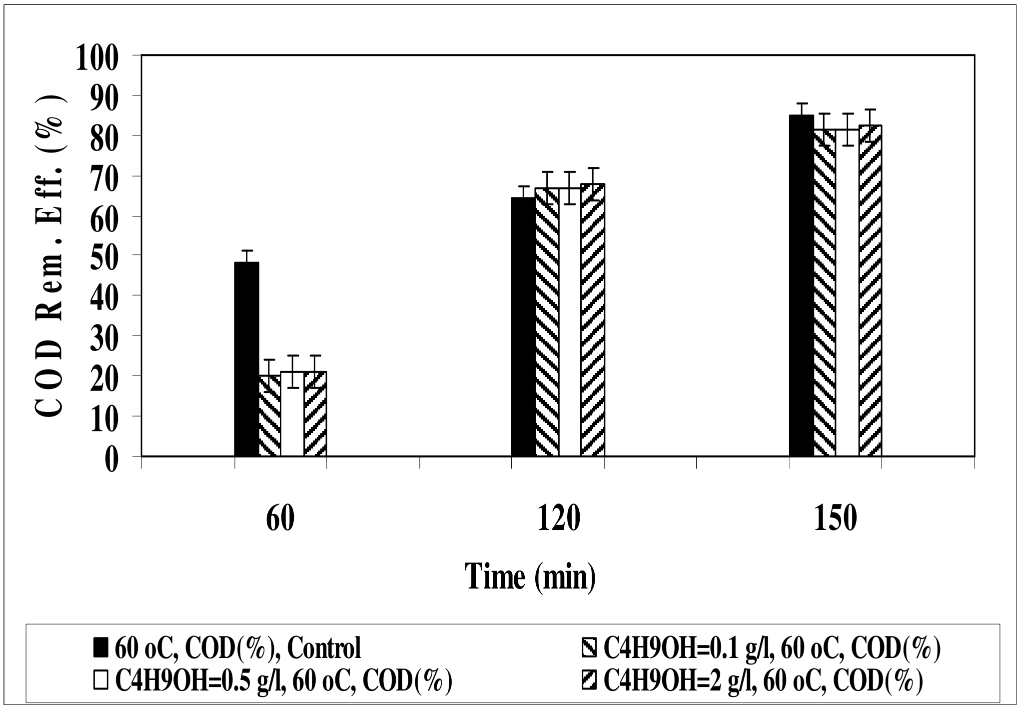
5.11.14 Effect of C_4H_9OH Concentrations on the Removals of COD_{dis} in TI ww

79.22%, 80.29% and 80.63% COD_{dis} removals were observed in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30°C (Figure 5.106a). The contribution of C_4H_9OH concentrations on COD_{dis} removals were not significant, after 150 min sonication time at pH=7.0 and at 30°C, compared to the control (without C_4H_9OH while E=81.53% COD_{dis} at pH=7.0 and at 30°C). A significant linear correlation between COD_{dis} yields and increasing C_4H_9OH concentrations was not observed ($R^2=0.33$, F=0.27, P=0.01) (Figure 5.106a).

81.23%, 81.50% and 82.40% COD_{dis} yields were found in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60°C (Figure 5.106b). The contribution of C_4H_9OH concentrations on COD_{dis} removals were not significant, after 150 min sonication time at pH=7.0 and at 60°C, compared to the control (E=84.92% COD_{dis} at pH=7.0 and at 60°C). The maximum COD_{dis} removal efficiency was 82.40% in C_4H_9OH=2.00 g/l after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing C_4H_9OH concentrations was not observed ($R^2=0.34$, F=0.38, P=0.01) (Figure 5.106b).



(a)



(b)

Figure 5.106 Effect of increasing C_4H_9OH concentrations on the COD_{dis} removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg/l, n=3, mean values).

The degradation was effectively quenched, but not completely, by the addition of tert-butyl alcohol. Because tert-butyl alcohol molecules pass in the cavitation bubbles, they are able to scavenge oxidizing species in the bubble and reduce significantly the decolorization rate of dye. Another factor that also affects the rate of dyestuff bleaching is the formation of volatile products from the tert-butyl alcohol degradation that accumulate inside the bubble and react with oxidizing species, conducting to the deceleration of the decolorization of dye. It seems that tert-butyl alcohol and its degradation products inhibited the bleaching of dyestuff by scavenging active species, such as HClO, Cl_2 and Cl_2-containing radicals ($^{\bullet}Cl$, $^{\bullet}CCl_3$ and $^{\bullet}CCl_2$), having strong oxidizing properties which will markedly inhibit the decolorization of dyestuff in aqueous solution. The increase of the tert-butyl alcohol concentration leads to the decrease of the decolorization rate. The observed differences can be due to the increase of the accumulation of tert-butyl alcohol and its degradation products in the cavitation bubbles with increasing alcohol concentration, conducting to more scavenging effect. Regardless of the absence and presence of tert-butyl alcohol, the pH of the reaction matrix decreased from the initial value of 5.7 to a final of 2.9 after 30 min of ultrasonic irradiation, which was attributed to the formation of HClO and HCl (Ghodbane & Hamdaoui, 2009a).

Merouani et al. (2010a) found 40.00% COD yield in 5.00 mg/l Rhodamine B, in tert-butyl alcohol=20.00 mg/l, at 300 kHz frequency, at 60 W power after 240 min sonication time at 30^{o}C and at pH=5.3. In this study, 80.63% COD_{dis} removal was measured in C_4H_9OH=2.00 g/l after 150 min sonication time at 30^{o}C. The COD_{dis} yield is higher than the yield observed by Merouani et al. (2010a) at 30^{o}C as mentioned above.

In a study performed by Behnajady et al. (2008b) 80.00% COD removal was accomplished in 10.00 mg/l Malachite Oxalate Green, at 35 kHz frequency, at 170 W power, in iso-butanol=1000 mg/l, 0.049-1.16 W/l power density, after 200 min sonication time at 60^{o}C with 400 rpm mechanical agitation. In this study, 82.40% COD_{dis} removal was observed in C_4H_9OH=2.00 g/l after 150 min sonication time at

60^{o}C. The COD$_{dis}$ yield is higher than the yield obtained by Behnajady et al. (2008b) at 60^{o}C as mentioned above.

5.11.14.1 Effect of C_4H_9OH Concentrations on the Color Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

88.13%, 91.30% and 93.54% color removals were observed in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Table 5.96). 9.87%, 13.04% and 15.28% increase in the color yields were obtained in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=78.26% color at pH=7.0 and at 30^{o}C). A significant linear correlation between color yields and increasing C_4H_9OH concentrations was not observed (R^2=0.31, F=0.23, P=0.01) (Table 5.96).

Table 5.96 Effect of increasing C_4H_9OH concentrations on the color removal efficiencies in TI ww at 30^{o}C and at 60^{o}C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 m^{-1}, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30^{o}C			**60^{o}C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
C_4H_9OH=0.10 g/l	83.90	87.19	88.13	87.19	88.95	91.07
C_4H_9OH=0.50 g/l	84.72	88.25	91.30	88.25	90.72	94.01
C_4H_9OH=2.00 g/l	84.96	89.42	93.54	88.84	91.66	94.48

91.07%, 94.01% and 94.48% color yields were found in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Table 5.96). The contribution of C_4H_9OH concentrations on color removals were 3.41%, 6.35% and 6.82% in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=87.66% color at pH=7.0 and at 60^{o}C). The maximum color yield was 94.48% in C_4H_9OH=2.00 g/l after 150 min sonication time at pH=7.0 and at 60^{o}C. A significant linear correlation between color yields and increasing C_4H_9OH concentrations was not observed (R^2=0.48, F=0.37, P=0.01) (Table 5.96).

It is expected that the sonolytic degradation of Rhodamine B would mainly occur by $OH^{\bullet}$ attack. In order to investigate the dependence of the $OH^{\bullet}$ during the degradation of Rhodamine B by ultrasonic irradiation, the sonolytic degradation of Rhodamine B in the presence of tert-butyl alcohol, known as an effective $OH^{\bullet}$ scavenger, was performed. Extensive work on the sonochemistry of tert-butyl alcohol has been reported by Tauber et al. (1999a, 1999b). The tert-butyl alcohol is able to scavenge $OH^{\bullet}$ in the bubble and prevent the accumulation of $OH^{\bullet}$ at the interface of the bubble.

At low tert-butyl alcohol concentrations (7.00 and 20.00 mg/l), unexpectedly, the rate of dye degradation was accelerated. This enhancement may be attributed to the relatively low dose of tert-butyl alcohol, at which competition for $OH^{\bullet}$ is unlikely and the rapid decomposition of the additive to produce reactive $CH_3^{\bullet}$, which are the main products of high-temperature pyrolysis of the additive (Tauber et al., 1999a, 1999b). Additionally, tert-butyl alcohol, a surfactant substance, can reduce the surface tension of the liquid and thus reduce the cavitation threshold and facilitate the generation of bubbles and, therefore, the production of $OH^{\bullet}$. At high tert-butyl alcohol concentrations (250–2500 mg/l), the degradation was effectively quenched, but not completely, by the addition of tert-butyl alcohol, suggesting that the main mechanism of Rhodamine B destruction is chemical oxidation by $OH^{\bullet}$. The degradation efficiency of Rhodamine B decreased with the increase of concentration of tert-butyl alcohol in solution. Another factor that also affects the rate of Rhodamine B degradation is the formation of volatile products from the tert-butyl alcohol degradation that accumulate inside the bubble. Such volatile products decrease the temperature inside the bubble, which, in turn, slow the sonolytic reactions (Tauber et al., 1999a, 1999b).

Wu, C.-H. (2008) achieved 92.00% color removal in 10.00 mg/l C.I. Reactive Red 198, C_4H_9OH=1.20 g/l, at 40 kHz frequency, at 400 W power after 120 min sonication time at pH=7.0 and at 60^{o}C. In this study, 94.48% color removal was found in C_4H_9OH=2.00 g/l after 150 min sonication time at 60^{o}C. The color yield is higher than the yield obtained by Wu, C.-H. (2008) at 60^{o}C as mentioned above.

In a study performed by Eren & Ince (2010) 49.50% color removal was accomplished in 15.00 mg/l C.I. Reactive Red 141, in C_4H_9OH=1.00 g/l, at 1145 kHz frequency, at 40 W power, after 30 min sonication time at 60^{o}C. In this study, 94.48% color removal was observed in C_4H_9OH=2.00 g/l after 150 min sonication time at 60^{o}C. The color yield is higher than the yield observed by Eren & Ince (2010) at 60^{o}C as mentioned above.

In a study performed by Eren & Ince (2010) 22.58% color removal was accomplished in 30.00 mg/l C.I. Direct Yellow 9, in C_4H_9OH=1.00 g/l, at 577 kHz frequency, at 48.9 W power, after 30 min sonication time at 60^{o}C. In this study, 94.48% color removal was measured in C_4H_9OH=2.00 g/l after 150 min sonication time at 60^{o}C. The color yield is higher than the yield found by Eren & Ince (2010) at 60^{o}C as mentioned above.

Behnajady et al. (2008b) observed 94.00% color yield in 10.00 mg/l Malachite Oxalate Green, at 35 kHz frequency, at 170 W power, in iso-butanol=1000 mg/l, 0.049-1.16 W/l power density, after 200 min sonication time at 30^{o}C with 400 rpm mechanical agitation. In this study, 93.54% color removal was observed in C_4H_9OH=2.00 g/l after 150 min sonication time at 30^{o}C. In this study, similar result obtained by Behnajady et al. (2008b) at 30^{o}C as mentioned above.

Ghodbane & Hamdaoui (2009a) obtained 92.00% color removal in 15.00 mg/l Acid Blue 25, at 1700 kHz frequency, at 14 W power, in tert-butyl alcohol=1570 mg/l, after 35 min sonication time at 50^{o}C and at pH=5.7. In this study, 94.48% color removal was observed in C_4H_9OH=2.00 g/l after 150 min sonication time at 60^{o}C.

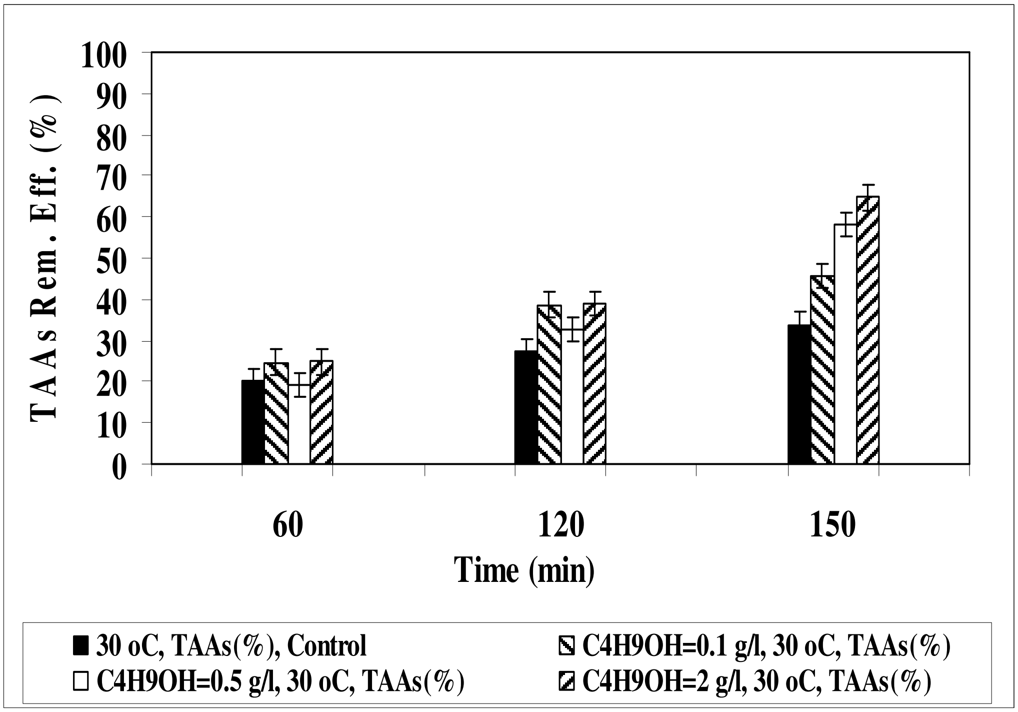
The color yield is higher than the yield observed by Ghodbane & Hamdaoui (2009) at 60^{o}C as mentioned above.

In a study performed by Gultekin et al. (2009) 72.00% color removal was accomplished in 20.00 mg/l C.I. Acid Orange 8, at 300 kHz frequency, at 25 W power, in tert-butyl alcohol=1.50 g/l, after 30 min sonication time at 30^{o}C and at pH=5.7. In this study, 93.54% color removal was measured in C_4H_9OH=2.00 g/l after 150 min sonication time at 30^{o}C. The color yield is higher than the yield obtained by Gultekin et al. (2009) at 30^{o}C as mentioned above.

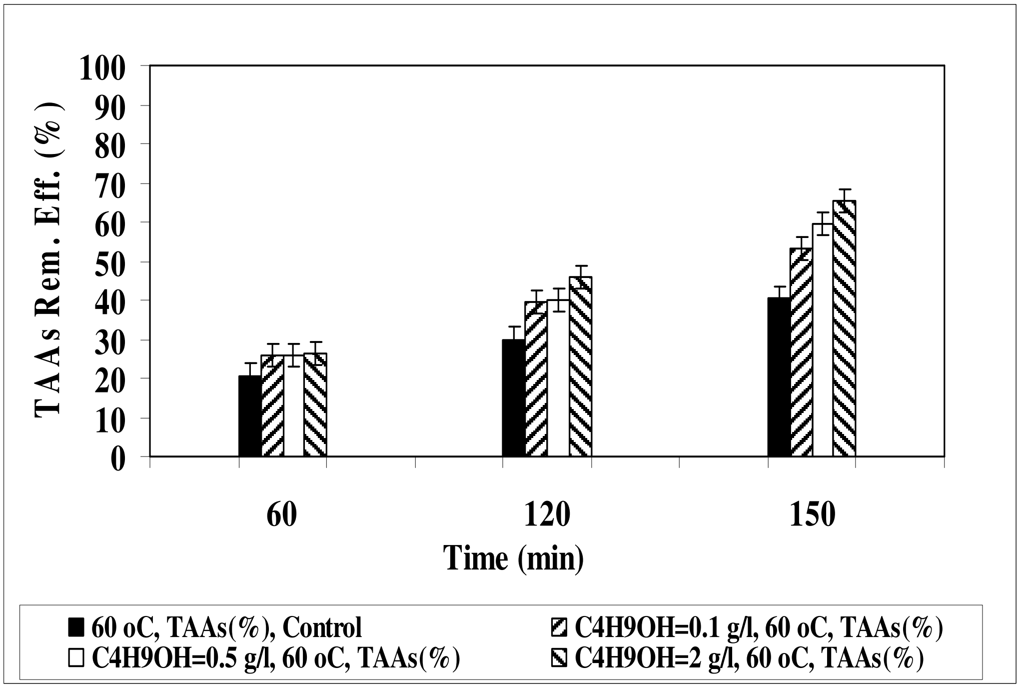
5.11.14.2 Effect of C_4H_9OH Concentrations on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

45.71%, 58.28% and 52.39% TAAs removals were observed in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C (Figure 5.107a). 11.82%, 24.39% and 18.50% increase in TAAs removals were obtained in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 30^{o}C, compared to the control (E=33.89% TAAs at pH=7.0 and at 30^{o}C). A significant linear correlation between TAAs yields and increasing C_4H_9OH concentrations was not observed (R^2=0.30, F=0.22, P=0.01) (Figure 5.107a).

53.06%, 59.61% and 65.52% TAAs yields were found in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C (Figure 5.107b). The contribution of C_4H_9OH concentrations on TAAs removals were 12.44%, 18.99% and 24.90% in 0.10 g/l, 0.50 and 2.00 g/l C_4H_9OH, respectively, after 150 min sonication time at pH=7.0 and at 60^{o}C, compared to the control (E=40.62% TAAs at pH=7.0 and at 60^{o}C). The maximum TAAs removal efficiency was 65.52% in C_4H_9OH=2.00 g/l after 150 min sonication at pH=7.0 and at 60^{o}C. A significant linear correlation between TAAs yields and increasing C_4H_9OH concentrations was observed (R^2=0.89, F=12.58, P=0.01) (Figure 5.107b).



(a)



(b)

Figure 5.107 Effect of increasing C_4H_9OH concentrations on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

In a study performed by Behnajady et al. (2008a) 70.00% TAAs removal was achieved in 10.00 mg/l Rhodamine B, at 35 kHz frequency, at 170 W power, 0.163 W/ml power density after 180 min sonication time at 60^{o}C with C_4H_9OH=1.00 g/l. In this study, 65.52% TAAs removal was observed in C_4H_9OH=2.00 g/l after 150 min sonication time at 60^{o}C. The TAAs yield is lower than the yield obtained by Behnajady et al. (2008a) at 60^{o}C as mentioned above.

5.12 Removal Kinetic of PAHs

5.12.1 Reaction Kinetic of PAHs at 35 kHz Frequency and at a Temperature of 60^{o}C

The sonical removal of PAHs in the raw PCI ww was found to be pseudo first order with respect to PAHs concentrations at a frequency of 35 kHz and at a temperature of 60^{o}C after 150 min of sonication time in Eqs. (5.108) and (5.109):

$$-\frac{d\,[PAH]}{dt} = k_1\,[PAH]_t \tag{5.108}$$

$$\frac{d\,[\,PAH\,]}{dt} = k_0 \tag{5.109}$$

In this run the maximun PAHs removals were between 91.72% and 98.48% for mostly PAHs. The degradation rates for PAHs were reduced from the slopes of the curves given by Eqs. (5.110) and (5.111):

$$\frac{[PAH\,]_t}{[PAH\,]_0} = k_1\,[PAH\,] \tag{5.110}$$

and

$$\ln\frac{[PAH\,]_t}{[\,PAH\,]_0} = k_1\,[PAH\,]\,t \tag{5.111}$$

where, k.[PAH] is the rate constant at 35 kHz frequency, $[PAH]_0$ the initial PAHs concentration and $[PAH]_t$ its value at time t. k_0 and k_1 are the zero and first order reaction kinetic rate constants, respectively.

In this study, the rate constants of sono-destruction have been calculated for only seven PAHs representing PAHs with 3 benzene rings (FLN), with 4 benzene rings

(FL and CHR) with 5 benzene rings (BbF) and with 6 benzene rings (IcdP, DahA and BghiP). Figure 5.108 illustrated the ln $[(PAH_t)/(PAH_0)]$ concentration versus sonication time. The maximum removals were 98.48%, 97.12% and 96.34% in less hydrophobic PAHs (NAP, ACL and PHE) while the maximum removals in more hydrophobic PAHs were 95.97% BaA, 95.94% CHR and 95.98% BbF.

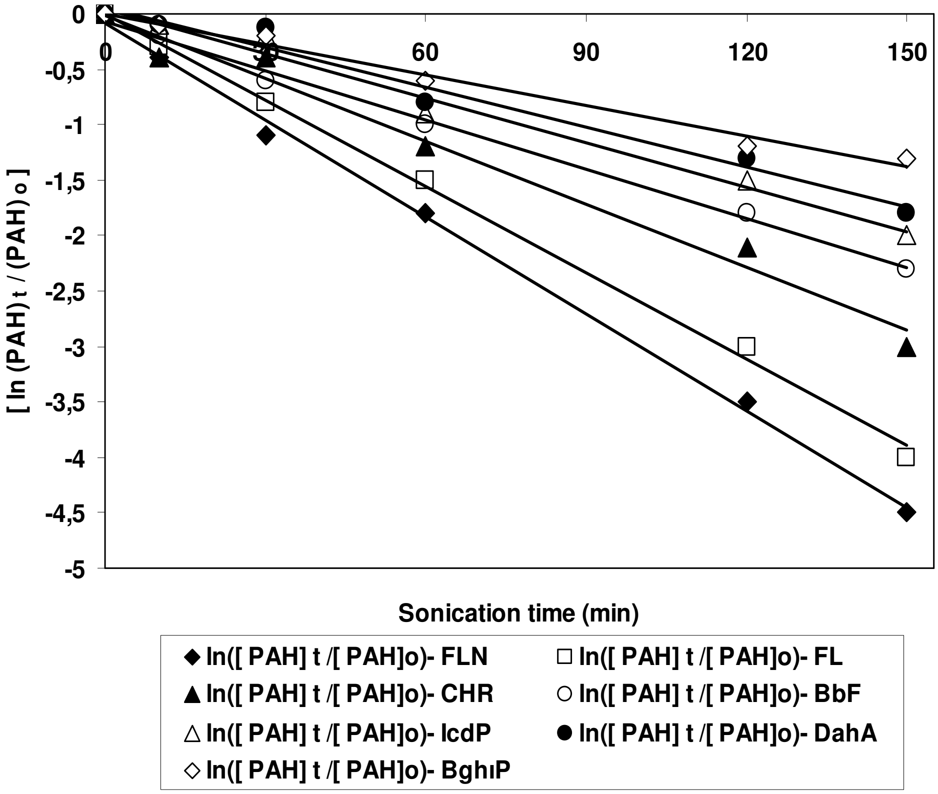


Figure 5.108 Effects of sonication time on the removal kinetic of seven PAHs according to pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

The rate constants of the PAHs are tabulated in Table 5.97. It was found that the pseudo first order rate constants decreased from PAHs with three benzene rings to PAHs with five and seven rings at all sonication times. The kinetic rate constants obtained in this study agree with the literature data of low frequencies (20 and 32 kHz) for powers varying between 390 and 640 W after 120-150 min sonication times and at temperatures 40–65^{o}C (Benabdallah El-Hadj et al., 2007; David, 2009; Taylor Jr. et al., 1999; Wheat & Tumeo, 1997). Although, the PAH removal yields exhibited similar ranges (86.21% and 97.98%) in all PAHs with low and high benzene rings after 150 min sonication time at 60^{o}C, the removal rate constants decreased from the low to the high molecular weight PAHs. The reaction kinetic constants of PAHs depend on their properties, such as the number of benzene rings, the vapor pressure, the water solubility and Henry's law constant after 150 min sonication time at 60^{o}C, as reported by David (2009). The removal rate constants increased as the vapor pressure, the water solubility and the Henry's law constants increased and the benzene rings of PAHs decreased.

Table 5.97 Calculated pseudo-first order reaction kinetics for seven PAHs after 150 min sonication time at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**Benzene Ring Number**	**k_{pf} [a]**
FLN	3	0.016
FL	4	0.014
CHR	4	0.015
BbF	5	0.011
DahA	5	0.008
IcdP	6	0.009
BghiP	6	0.008

a: Experimental pseudo first order reaction of PAH, (1/min).

In this study, it was found that the most hydrophobic PAHs, with five and six benzene rings (BbF, DahA, IcdP and BghiP) (which have low water solubiliy and Henry's law constant) have the lowest reacton rate constants compared to three and four ring PAHs (FLN, FL and CHR) (which have high water solubility and Henry's law constant) (Table 5.98). In other words, the lower molecular weight PAHs tend to be more volatile (i.e., have a higher vapour pressure) and more readily partition into air from pure water (i.e., have a higher Henry's law constant) have high reaction kinetic constants througout sonication. Although, the high molecular weight PAHs tending to less volatile (i.e., have a low vapour pressure) and low partition into air from pure water (i.e., have a low Henry's law constant), the untreated percentages of PAHs with five, six and seven rings at a sonication time of 150 min reached the same levels as PAHs which had low ring numbers after 150 min sonication time at 60^{o}C (Table 5.98 and Figure 5.109).

Table 5.98 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**CAS-No**	**MF**	**MW**	**T_M**	**T_B**	**S_W (25°C)**	**V_P (25°C)**	**H (25°C)**	**log K_{OA} (25°C)**	**log K_{OW}**	**IPC**
FLN	86-73-7	$C_{13}H_{10}$	166	115	295	1.69	$6.00 x 10^{-4}$	$9.62 x 10^{-5}$	6.90	4.18	55.57
FL	206-44-0	$C_{16}H_{10}$	202	108	384	$2.60 x 10^{-1}$	$9.22 x 10^{-6}$	$8.86 x 10^{-6}$	8.76	5.16	19.36
CHR	218-01-9	$C_{18}H_{12}$	228	258	448	$2.00 x 10^{-3}$	$6.23 x 10^{-9}$	$5.23 x 10^{-6}$	10.30	5.81	$2.68 x 10^{-1}$
BbF	205-99-2	$C_{20}H_{12}$	252	168	-	$1.50 x 10^{-3}$	$5.00 x 10^{-7}$	$6.57 x 10^{-7}$	11.34	5.78	$7.90 x 10^{-1}$
IcdP	193-39-5	$C_{22}H_{12}$	276	164	536	$1.94 x 10^{-3}$	$1.25 x 10^{-10}$	$3.48 x 10^{-7}$	12.43	6.70	$10.93 x 10^{-2}$
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	$2.49 x 10^{-4}$	$1.00 x 10^{-10}$	$1.23 x 10^{-7}$	12.59	6.75	45.7810^{-2}
BghiP	191-24-2	$C_{22}H_{12}$	276	278	> 500	$2.67 x 10^{-4}$	$1.00 x 10^{-10}$	$3.31 x 10^{-7}$	12.55	6.63	$51.30 x 10^{-2}$

fluorene (FLN), fluoranthene (FL), chrysene (CHR), benz[*b*]fluoranthene (BbF), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g/mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg/l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 /mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng/ml)

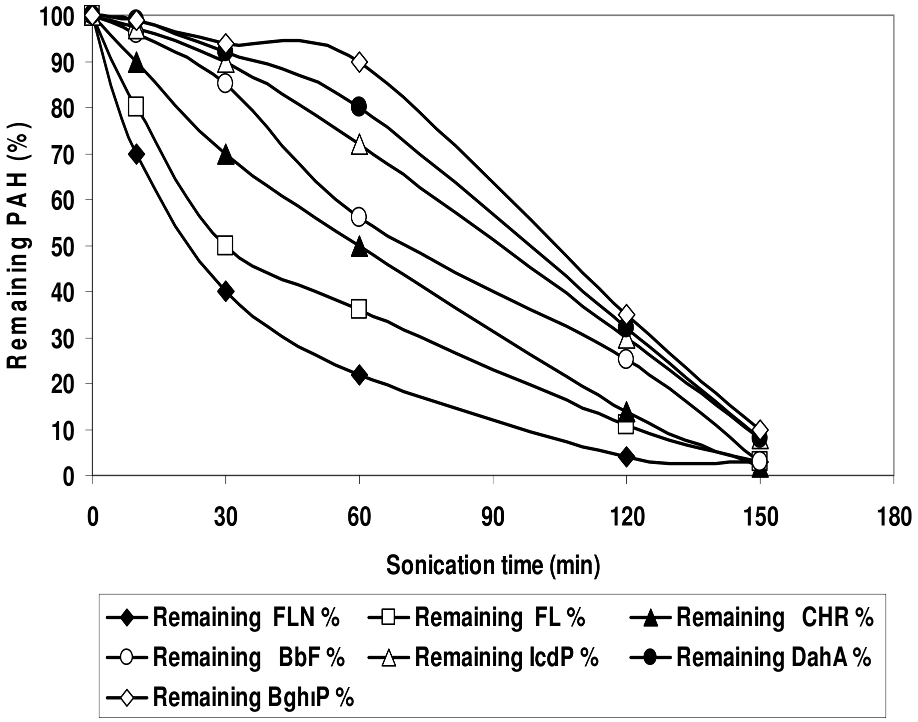


Figure 5.109 The remaining (untreated) PAHs percentages versus sonication time in pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

As seen in Figure 5.109 the remaining percentages in PAHs with low benzene rings (FLN and FL) were low (20.24% and 35.43%) after 60 min of sonication time while the untreated PAHs percentages were high (90.30%, 80.11% and 67.42%) in PAHs with high benzene rings (BghiP, DahA and IcdP) for the same sonication time. A similar result was obtained after 30 and 120 min sonication times. However, similar remaining PAHs percentages was obtained (0.04% - 10.15%) after 150 min of sonication time.

The results of this study showed that although, a strict correlation between the remaining percentage of the aforementioned PAHs and physicochemical properties was observed after 30 min, 60 and 120 min sonication times (R^2=0.89, P=16.89, p=0.001), a significant correlation was not observed between the remaining percentages of PAHs and their properties after 150 min sonication time (R^2=0.45, p=3.56, P=0.01) and over 90.00% removal rates of the all PAHs was achieved.

Furthermore, it becomes evident that a larger hydrophobicity resulted in smaller reaction kinetic constants of the PAHs. Low initial PAHs concentrations led to low reaction rates and also to smaller residual concentrations. The coefficient of the correlation between the residual concentration and the total initial concentration of the single PAHs was strong and highly significant ($R^2=0.85$, $p < 0.001$).

A more energetic implosion of cavitation bubbles is expected to occur at low frequency because a larger bubble radius is observed at low frequency after long sonication times (90-180 min) at high temperatures (60-80^oC) (De Visscher et al., 1996; Wu & Ondruschka, 2005). The larger the bubble size, the greater the water vapor within the bubble, leading to a more important damping of the collapse at a low frequency such as 20-30 kHz (David, 2009). This contributes to enhancing the penetration of water containing PAHs inside the bubbles. Sigman et al. (1998) showed that non linear bubble implosions play a significant role at low frequency. De Visscher et al. (1996) demonstrated that the equilibrium time of a partitioning process between the liquid and the bubble phases is 560 times longer at low frequencies such as 20 and 30 kHz. The data obtained in this study are in good agreement with the rate constants obtained by David (2009), Psillakis et al. (2004), Wu & Ondruschka (2005).

5.12.2 Reaction Kinetic of PAHs at 35 kHz and at 60^oC in the Presence of 6.00 mg/l DO

The sonic degradation of PAHs in the raw PCI ww was found to be pseudo first order with respect to PAHs concentrations at a frequency of 35 kHz and at 60^oC in the presence of 6.00 mg/l DO, according to Eqs. (5.110) and (5.111).

In this study, the rate constants of sonodegradation are given for only five PAHs. These rate constants are tabulated in Table 5.99. The pseudo first order rate constants ranged between 0.011 and 0.026 1/min. The pseudo first order kinetic rate constants obtained in this study agree with the literature data of low frequencies (20 and 32 kHz) (Benabdallah El-Hadj et al., 2007; Taylor Jr. et al., 1999; Wheat & Tumeo, 1997). The biodegradation rate constants of the PAHs depend on their properties, such as the benzene ring numbers, the vapor pressure, the water solubility and Henry's law constant, as reported by David (2009). The biodegradation rate constants increased as the vapor pressure, the water solubility and the Henry's law constants increased and the number of benzene rings of PAHs decreased. The most hydrophobic PAHs, with four, five and six benzene rings, (PY, BkF and BghiP) (low water solubility and Henry's law constant) have the lowest degradation constants compared to two and three ring PAHs (NAP, ACL and PHE) with high water solubility and Henry's law constants. The data obtained in this study are in good agreement with the rate constants obtained by David (2009) and Wu & Ondruschka (2005).

Table 5.99 Calculated pseudo-first order reaction kinetics for six PAHs in DO=6.00 mg/l concentration after 150 min sonication time at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**Benzene Ring Number**	**k_{pf} [a]**
NAP	2	0.026
ACL	3	0.024
PHE	3	0.017
PY	4	0.015
BkF	5	0.013
BghiP	6	0.011

[a] : Experimental pseudo first order reaction of PAH, (1/min).

The pseudo first order rate constants decreased from PAHs with one benzene ring to PAHs with five rings at low sonication times such as 60 min sonication time (Table 5.3). However, the untreated percentages of PAHs with four and five rings at a sonication time of 150 min reached the same levels as PAHs with low ring numbers after 150 min sonication time (Figure 5.110). Therefore, the removal efficiencies for all PAHs were > 95.00% after 150 min sonication time (Figure 5.110).

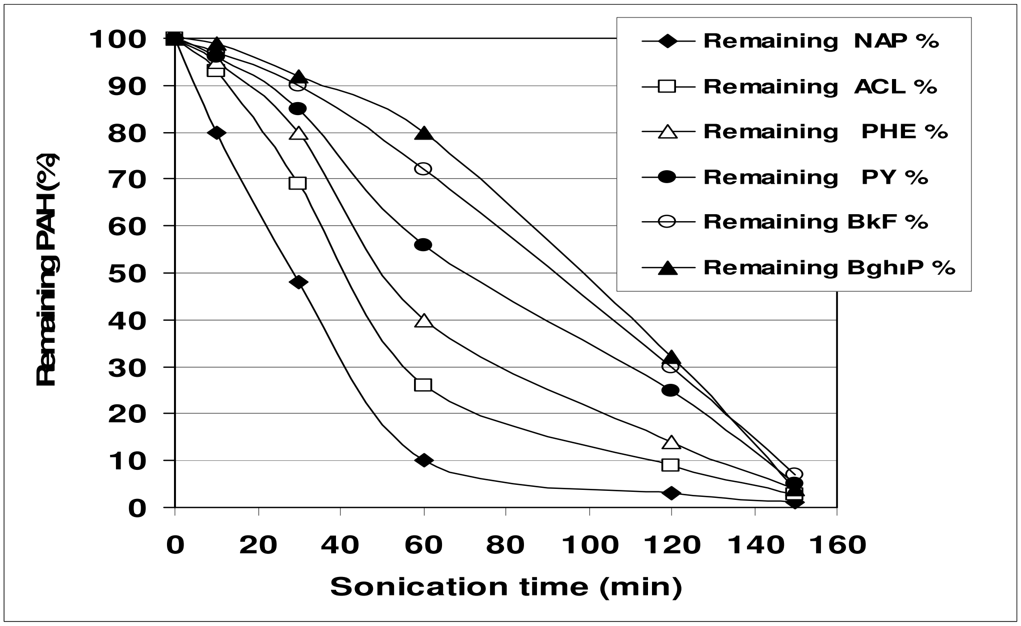


Figure 5.110 Effects of sonication time on the residual PAHs percentages (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

5.12.3 PAHs Removal Kinetic at 35 kHz and at 60^{o}C in the Presence of 6.00 mg/l NaCl

In this step of the study, the rate constants of sonodegradation are given for only seven PAHs (Table 5.100). The pseudo first order rate constants ranged between 0.007 and 0.046 1/min (Table 5.101). The pseudo first order kinetic rate constants obtained in this study agree with the literature data of low frequencies (20 and 32 kHz) (Benabdallah El-Hadj et al., 2007; David, 2009). The sono-degradation rate constants increased as the vapor pressure and the water solubility increased whereas the Henry's law constants and the number of benzene rings of PAHs decreased. The most hydrophobic PAHs, with five and six benzene rings, (BbF, DahA and BghiP) (with low water solubiliy and Henry law constant) had the lowest sono-degradation rate constants compared to three and four benzene ring PAHs (PHE, ANT, PY and CHR) with higher water solubility and Henry's law constants. The pseudo first order rate constants decreased from PAHs with three, four benzene ring to PAHs with five, six rings at 60 and 120 min sonication times. A significant correlation was found between PAHs yields and sono-degradation rate constants after 60 and 120 min sonication times (R^2=0.87, F=15.98, p=0.001).

Table 5.100 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**CAS-No**	**MF**	**MW**	**T_M**	**T_B**	**S_W**	**V_P (25°C)**	**H (25°C)**	**log K_{OA} (25°C)**	**log K_{OW}**	**IPC**
PHE	85-01-8	$C_{14}H_{10}$	178	99	340	1.15	$1.21x10^{-4}$	$3.35x10^{-5}$	7.68	4.46	125.58
ANT	120-12-7	$C_{14}H_{10}$	178	215	340	$4.34x10^{-2}$	$2.67x10^{-6}$	$5.56x10^{-5}$	7.71	4.45	3.63
PY	129-00-0	$C_{16}H_{10}$	202	151	404	$1.35x10^{-1}$	$4.50x10^{-6}$	$1.19x10^{-5}$	8.81	4.88	14.49
CHR	218-01-9	$C_{18}H_{12}$	228	258	448	$2.00x10^{-3}$	$6.23x10^{-9}$	$5.23x10^{-6}$	10.30	5.81	2.32
BbF	205-99-2	$C_{20}H_{12}$	252	168	-	$1.50x10^{-3}$	$5.00x10^{-7}$	$6.57x10^{-7}$	11.34	5.78	0.23
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	$2.49x10^{-3}$	$1.00x10^{-10}$	$1.23x10^{-7}$	12.59	6.75	5.42
BghiP	191-24-2	$C_{22}H_{12}$	276	278	> 500	$2.60x10^{-4}$	$1.00x10^{-10}$	$3.31x10^{-7}$	12.55	6.63	0.58

phenanthrene (PHE), anthracene (ANT), pyrene (PY), chrysene (CHR), benz[*b*]fluoranthene (BbF), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g / mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg / l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 / mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng / ml).

Table 5.101 Calculated pseudo-first order reaction kinetics for seven PAHs in NaCl=6.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**Benzene Ring Number**	$\mathbf{k_{pf}}$ [a]
ANT	3	0.046
PHE	3	0.037
PY	4	0.025
CHR	4	0.019
BbF	5	0.011
DahA	5	0.009
BghiP	6	0.007

a: Experimental pseudo first order reaction of PAH, (1/min).

The untreated percentages of more hydrophobic PAHs (BbF, DahA and BghiP) were higher than those of less hydrophobic PAHs (PHE, PY, CHR and ANT) after 60 and 120 min sonication times. A strongly significant correlation was observed between the PAHs properties and the remaining PAHs percentages after 60 and 120 min sonication time (R^2=0.83, F=14.78, p=0.001) (Figure 5.111). The untreated PAHs percentages in PAHs with low Henry's low constant, vapor pressure and solubility were higher in PAHs with high benzene rings than in PAHs with low benzene rings for the aforementioned sonication times (Table 5.100). However, the untreated percentages of hydrophobic PAHs with four and five rings at 150 min sonication time reached the same levels as less hydrophobic PAHs with low ring numbers after 150 min sonication time (Table 5.101).

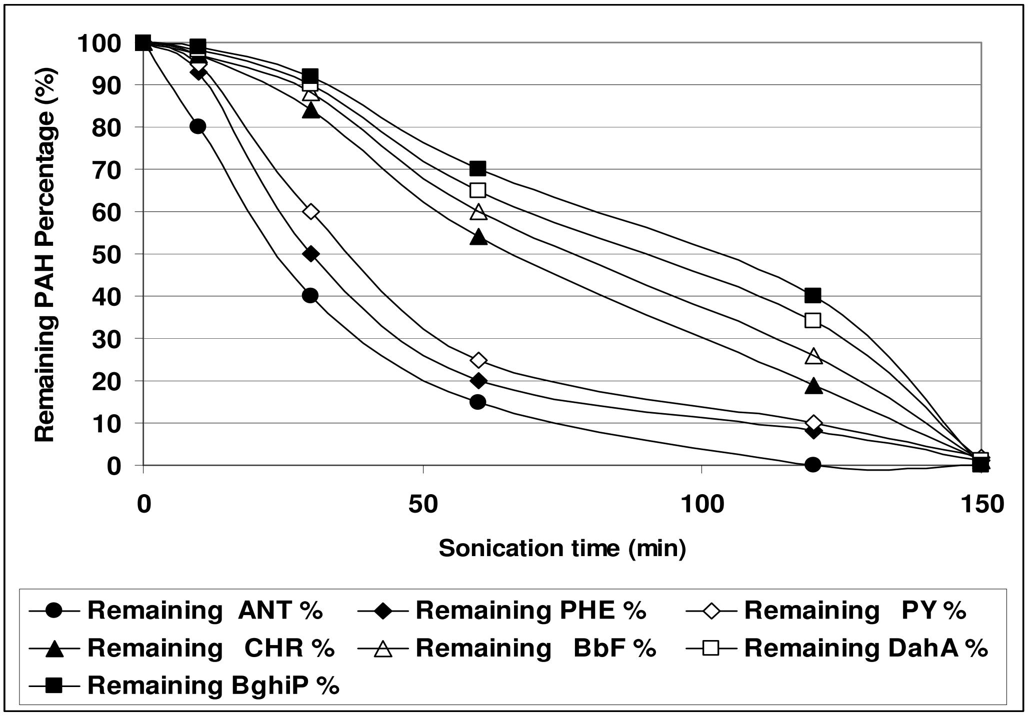


Figure 5.111 Effects of sonication time on the residual PAHs percentages after 150 min sonication at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

A weak correlation was found between PAHs properties and remaining PAHs percentage and this correlation was not significant (R^2=0.56, F=6.78, p=0.001). Therefore, the removal efficiencies for all PAHs were > 95.00% after 150 min sonication time.

5.12.4 Reaction Kinetic of PAHs at 35 kHz and at 60°C in the Presence of 6.00 mg/l Al_2O_3

In this step of this study, the pseudo first order rate constants of sonodegradation onyl six PAHs, namely, BkF, BaP and IcdP (more hydrophobic) and ACT, FL and BaA (less hydrophobic) PAHs ranged between 0.010 and 0.056 1/min (Table 5.102). The pseudo first order kinetic rate constants obtained in this study agree with the literature data of low frequencies (20 and 32 kHz) (Benabdallah El-Hadj et al., 2007; David, 2009). Physical and chemical properties of these PAHs as shown in Table 5.103.

Table 5.102 Calculated pseudo-first order reaction kinetics for six PAHs in Al_2O_3=6.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**Benzene Ring Number**	**k_{pf} [a]**
ACT	3	0.056
FL	4	0.047
BaA	4	0.038
BkF	5	0.029
BaP	5	0.019
IcdP	6	0.010

a: Experimental pseudo first order reaction of PAH, (1/min).

Table 5.103 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**CAS-No**	**MF**	**MW**	**T_M**	**T_B**	**S_W (25°C)**	**V_P (25°C)**	**H (25°C)**	**log K_{OA} (25°C)**	**log K_{OW}**	**IPC**
ACT	83-32-9	$C_{12}H_{10}$	154	93	279	3.90	$2.15x10^{-3}$	$1.84x10^{-4}$	6.52	3.92	66.82
FL	206-44-0	$C_{16}H_{10}$	202	108	384	$2.60x10^{-1}$	$9.22x10^{-6}$	$8.86x10^{-5}$	8.76	5.16	19.36
BaA	56-55-3	$C_{18}H_{12}$	228	84	438	$9.40x10^{-2}$	$2.10x10^{-7}$	$1.20x10^{-5}$	10.28	5.76	$5.50x10^{-1}$
BkF	207-08-9	$C_{20}H_{12}$	252	217	480	$8.00x10^{-3}$	$9.70x10^{-10}$	$5.84x10^{-6}$	11.37	6.11	$8.00x10^{-1}$
BaP	50-32-8	$C_{20}H_{12}$	252	177	495	$1.62x10^{-4}$	$5.49x10^{-9}$	$4.57x10^{-7}$	11.56	6.13	$7.50x10^{-2}$
IcdP	193-39-5	$C_{22}H_{12}$	276	164	536	$1.94x10^{-4}$	$1.25x10^{-10}$	$3.48x10^{-7}$	12.43	6.70	$10.93x10^{-2}$

acenaphthene (ACT), fluoranthene (FL), benz[*a*]anthracene (BaA), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP)

MF: Molecular formula, MW: Molecular weight (g/mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg/l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3/mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng/ml)

The sono-degradation rate constants increased as the vapor pressure and the H_2O solubility increased whereas, the Henry’s law constants and the number of benzene rings of PAHs decreased. The more hydrophobic PAHs, with four and five benzene rings (BaP and IcdP) with low H_2O solubiliy and Henry law constant had the lowest sono-degradation rate constants compared to less hydrophobic PAHs (FL and BaA) with higher H_2O solubility and Henry’s law constants. The pseudo first order rate constants decreased from PAHs with one, two benzene ring to PAHs with five, six rings at sonication times of 60 and 120 min. A significant correlation was found between PAHs yields and sono-degradation rate constants after 60 and 120 min sonication times (R^2=0.77, F=12.77, p=0.001). The untreated percentages of more hydrophobic PAHs (BaP and IcdP) were higher than those of less hydrophobic PAHs (FL and BaA) after 60 and 120 min sonication times (Figure 5.112).

However, the untreated percentages of more hydrophobic PAHs reached the same levels as less hydrophobic PAHs after 150 min sonication time. A weak correlation was found between PAHs properties and the remaining PAHs percentage and this correlation was not significant (R^2=0.49, F=2.11, p=0.001). Therefore, the removal efficiencies for all PAHs were > 92.00% after 150 min sonication time.

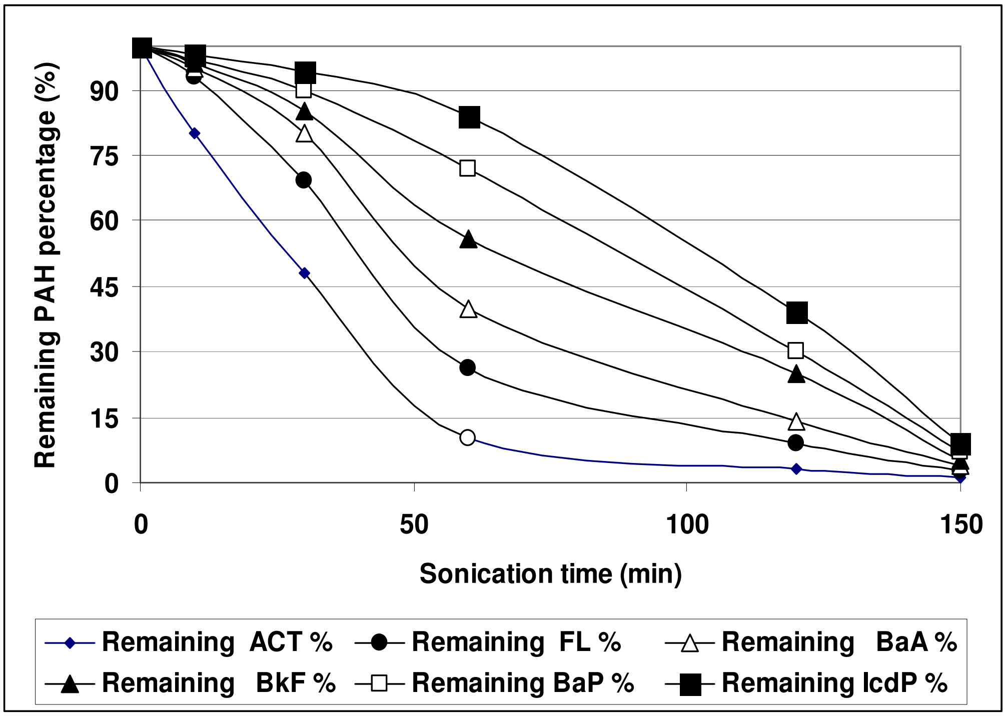


Figure 5.112 Effects of sonication time on the residual PAHs percentages after 150 min at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

5.12.5 Reaction Kinetic of PAHs at 35 kHz and at 60°C in the Presence of 15.00 mg/l $CaCl_2$

In this step of this study the PAHs removal kinetics were researched according to the pseudo zero, first and second order reaction kinetics at the operational conditions in which the maximum PAHs removals were obtained.

The maximum yields in less (BaA, CHR, BbF, BkF) and more (BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 98.33% and 99.44% and at between 99.57% and 99.76%, respectively, in $CaCl_2$=15.00 g/l after 150 min sonication time at 60°C (Table 5.104).

At a $CaCl_2$ concentration of 15.00 g/l the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 3.128 and 4.305 mg/l.h (R^2=0.92) and at betweeen 1.450 and 2.280 mg/l.h (R^2=0.92), respectively, after 150 min sonication time at 60°C (Table 5.104).

At the same $CaCl_2$ concentration, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.057 and 0.081 1/h (R^2=0.99) and at betweeen 0.038 and 0.049 1/h (R^2=0.99), respectively, after 150 min sonication time at 60°C (Table 5.104; Figure 5.113).

At a $CaCl_2$ concentration of 15.00 g/l, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 41.70x10^{-4} and 55.60x10^{-4} l/mg.h (R^2=0.54 - 0.77) and at betweeen 28.60x10^{-4} and 33.50x10^{-4} l/mg.h (R^2=0.64 - 0.88), respectively, after 150 min sonication time at 60°C (Table 5.104).

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less (BaA, CHR, BkF, BbF) and more (BaP, IcdP, DahA, BghiP) hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.104; Figure 5.113).

In this study, no significant difference in yields between less (BaA, CHR, BbF and BkF) and more (BaP, IcdP, DahA, BghiP) hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and $CaCl_2$ concentration was observed after 150 min sonication time at 60°C (R^2=0.91, F=14.27, p=0.001).

Table 5.104 The pseudo zero, first and second order reaction kinetic constants of eight PAHs obtained at maximum removal efficiencies in the presence of 15.00 g/l $CaCl_2$ concentration after 150 min sonication time at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC (A) (ng/ml) ± SD**	**Eff. (B) T=150 min PAH (ng/ml) ± SD**	**T=150 min PAH (%)**	**ZORKC (C)**	**ZORKC (R^2)**	**FORKC (D)**	**FORKC (R^2)**	**SORKC (E)**	**SORKC (R^2)**
BaA	0.55 ± 0.01	0.002 ± $7.00x10^{-5}$	99.06	4.305	0.92	0.081	0.99	$55.60x10^{-4}$	0.67
CHR	2.69 ± 0.09	0.01 ± $4.00x10^{-4}$	99.44	4.072	0.92	0.063	0.99	$48.00x10^{-4}$	0.77
BbF	0.80 ± 0.02	0.003 ± $1.00x10^{-4}$	98.33	3.167	0.92	0.060	0.99	$43.20x10^{-4}$	0.54
BkF	0.80 ± 0.02	0.003 ± $1.00x10^{-4}$	99.17	3.128	0.92	0.057	0.99	$41.70x10^{-4}$	0.76
BaP	0.07 ± 0.002	0.0002 ± $7.00x10^{-4}$	99.73	2.280	0.92	0.049	0.99	$33.50x10^{-4}$	0.88
IcdP	1.09 ± 0.03	0.004 ± $1.00x10^{-4}$	99.76	2.101	0.92	0.045	0.99	$32.60x10^{-4}$	0.87
DahA	4.60 ± 0.16	0.02 ±$7.00x10^{-4}$	99.59	1.634	0.92	0.043	0.99	$30.70x10^{-4}$	0.88
BghiP	0.51 ± 0.01	0.002 ± $7.00x10^{-5}$	99.57	1.450	0.92	0.038	0.99	$28.60x10^{-4}$	0.64

IPC (A): Initial PAH concentration (ng/ml), (B) Eff. = Effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

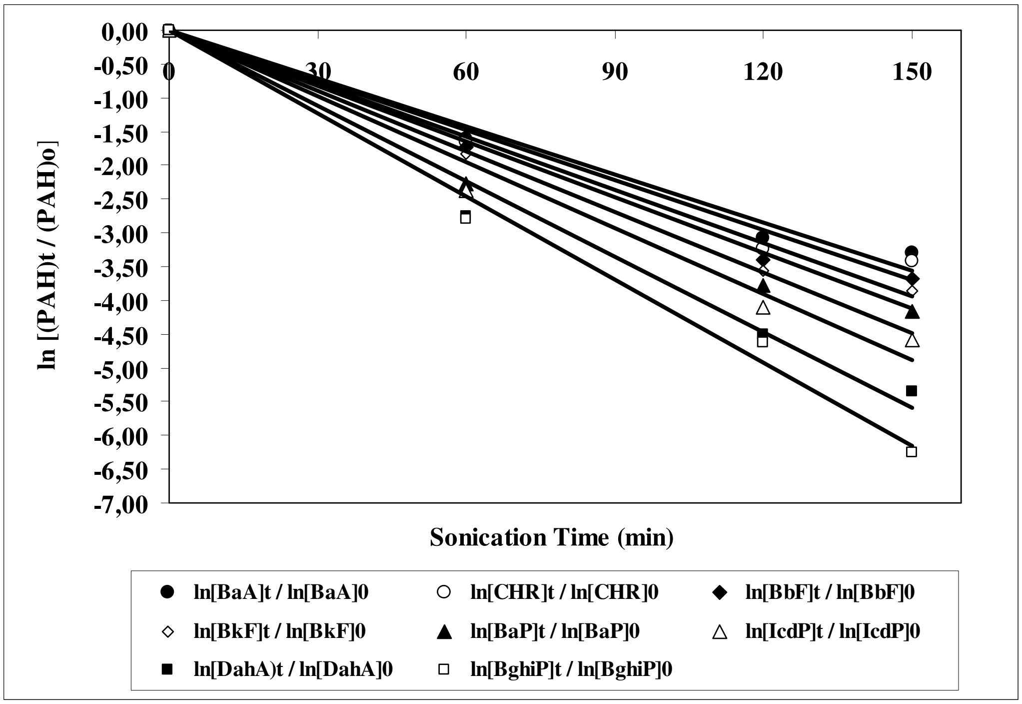


Figure 5.113 In the presence of 15.00 g/l $CaCl_2$ concentrations the removal kinetic of eight PAHs according to pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

5.12.6 Reaction Kinetic of PAHs at 35 kHz and at 60^{o}C in the Presence of pH=7.0

The maximum yields in less (BaA, CHR, BbF, BkF) and more (BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 87.57% and 95.81% and at between 96.80% and 98.18%, respectively, at pH=7.0 after 150 min sonication time at 60^{o}C (Table 5.105).

At pH=7.0 value, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 2.747 and 4.112 mg/l.h (R^2=0.96 - 0.98) and at betweeen 1.326 and 2.195 mg/l.h (R^2=0.97 - 0.98), respectively, after 150 min sonication time at 60^{o}C (Table 5.105).

At pH=7.0, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.048 and 0.070 1/h (R^2=0.99) and at betweeen 0.034 and 0.046 1/h (R^2=0.99), respectively, after 150 min sonication time at 60^{o}C (Table 5.105; Figure 5.114).

At pH=7.0, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 10.70x10^{-4} and 31.10x10^{-4} l/mg.h (R^2=0.55) and at betweeen 2.70x10^{-4} and 7.10x10^{-4} l/mg.h (R^2=0.55), respectively, after 150 min sonication time at 60^{o}C (Table 5.105).

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less and more hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 at pH=7.0 after 150 min sonication time at 60^{o}C (Table 5.105; Figure 5.114).

In this study, the significant difference in yields between less (BaA, CHR, BbF and BkF) and more (BaP, IcdP, DahA, BghiP) hydrophobic PAHs were obtained, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and pH values was observed after 150 min sonication time at 60^{o}C (R^2=0.88, F=10.29, p=0.001).

Table 5.105 The pseudo zero, first and second order reaction kinetic constants of eight PAHs obtained at maximum removal efficiencies at pH=7.0 after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC $^{(A)}$ (ng/ml) ± SD**	**Eff. $^{(B)}$ T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC $^{(C)}$**	**ZORKC (R^2)**	**FORKC $^{(D)}$**	**FORKC (R^2)**	**SORKC $^{(E)}$**	**SORKC (R^2)**
BaA	0.55 ± 0.019	0.022 ± 7.00x10^{-4}	93.01	4.112	0.98	0.070	0.99	31.10x10^{-4}	0.55
CHR	2.69 ± 0.09	0.106 ± 0.004	95.81	3.472	0.97	0.056	0.99	19.50x10^{-4}	0.55
BbF	0.80 ± 0.003	0.031 ± 0.001	87.57	2.954	0.96	0.049	0.99	17.30x10^{-4}	0.55
BkF	0.80 ± 0.003	0.031 ± 0.001	93.84	2.747	0.98	0.048	0.99	10.70x10^{-4}	0.55
BaP	0.07 ± 0.002	0.003 ± 1.00x10^{-4}	97.99	2.195	0.98	0.046	0.99	7.10x10^{-4}	0.55
IcdP	1.09 ± 0.04	0.043 ± 0.001	98.18	1.914	0.97	0.043	0.99	6.20x10^{-4}	0.55
DahA	4.60 ± 0.161	0.183 ± 0.006	96.94	1.421	0.97	0.037	0.99	3.78x10^{-4}	0.55
BghiP	0.51 ± 0.018	0.02 ± 7.00x10^{-4}	96.80	1.326	0.98	0.034	0.99	2.70x10^{-4}	0.55

IPC $^{(A)}$: Initial PAH concentration (ng/ml), $^{(B)}$ Eff. = Effluent, $^{(C)}$ ZORKC: Zero order reaction kinetic constant (mg/l . h), $^{(D)}$ FORKC: First order reaction kinetic constant (1/h), $^{(E)}$ SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

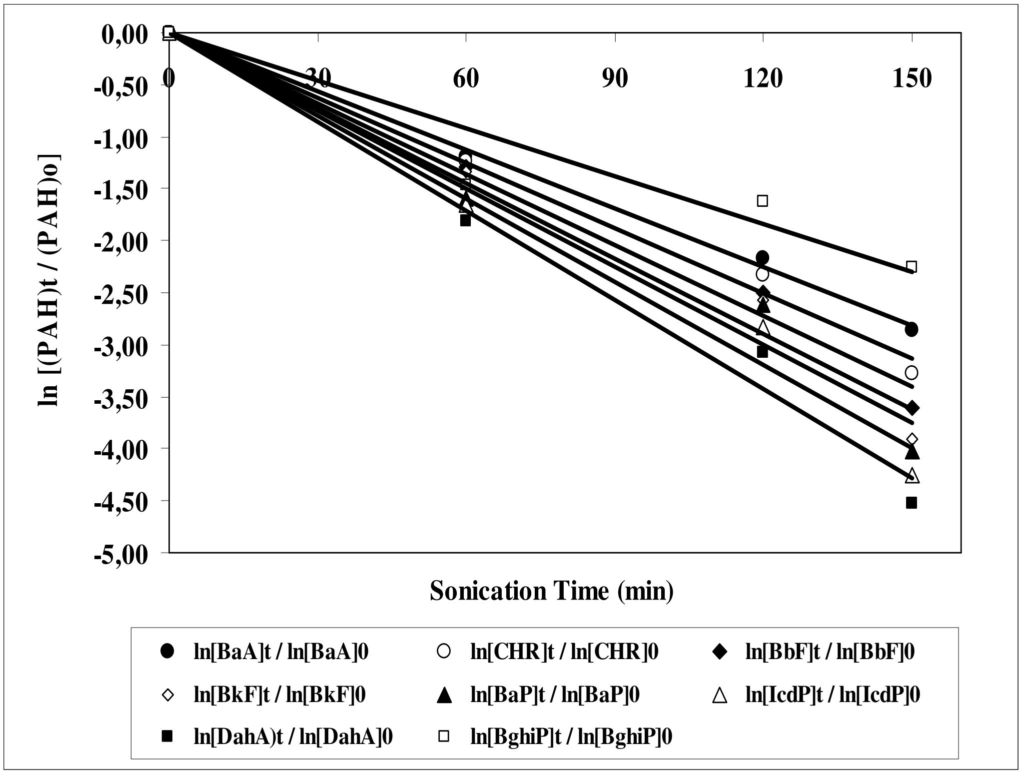


Figure 5.114 In the presence of pH=7.0 the removal kinetic of eight PAHs according to pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

In most studies on sonodegradation of pollutants in water, the pseudo first order kinetic constant has been found to depend on inital concentration of pollutant (Weavers et al., 2000). Pseudo first order rate constants of PAHs degradation are linked to the physico-chemical properties of PAHs, since higher the Henry's constant, higher the vapor pressure and higher the water solubility, higher the rate constants of sonodegradation (David, 2009).

5.12.7 Reaction Kinetic of PAHs at Different Experimental Conditions

5.12.7.1 Reaction Kinetic of PAHs at 35 kHz and at 60^{o}C

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 91.72% and 98.48% and at between 95.88% and 95.98%, respectively, after 150 min sonication time at 60^{o}C (Table 5.106).

At 60^{o}C, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 3.360 and 6.717 mg/l.h (R^2=0.97) and at betweeen 1.232 and 2.451 mg/l.h (R^2=0.96 - 0.97), respectively, after 150 min sonication time at 60^{o}C (Table 5.106).

At 60^{o}C, the pseudo first order rate constants of less and more hydrophobic PAHs varied at between 0.052 and 0.100 1/h (R^2=0.99) and at between 0.028 and 0.044 17h (R^2=0.98 - 0.99) after 150 min sonication time at 60^{o}C (Table 5.106).

At 60^{o}C, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 19.00x10^{-4} and 41.60x10^{-4} l/mg.h (R^2=0.53 - 0.67) and at between 0.67x10^{-4} and 12.10x10^{-4} l/mg.h (R^2=0.53 - 0.60) after 150 min sonication time at 60^{o}C (Table 5.106).

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less and more hydrophobic PAHs with the highest linear correlation coefficients of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.106).

In this study, no significant difference in yields between less (FLN, PHE, CRB, FL, PY BaA, CHR) and more (BbF, BkF, BaP, IcdP, DahA, BghiP) hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and increasing temperature was observed (R^2=0.89, F=11.15, p=0.001).

Table 5.106 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD$_{dis}$ concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC (A) (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC (C)**	**ZORKC (R^2)**	**FORKC (D)**	**FORKC (R^2)**	**SORKC (E)**	**SORKC (R^2)**
NAP	2164.51 ± 75.76	614.16 ± 21.50	98.48	6.717	0.97	0.100	0.99	41.60 x 10^{-4}	0.58
ACL	53.02 ± 1.86	2.76 ± 0.10	97.12	6.336	0.97	0.095	0.99	39.20 x 10^{-4}	0.58
ACT	71.83 ± 2.51	3.34 ± 0.12	94.16	5.978	0.97	0.089	0.99	37.10 x 10^{-4}	0.53
FLN	59.04 ± 2.07	2.89 ± 0.10	96.00	5.640	0.97	0.084	0.99	34.90 x 10^{-4}	0.67
PHE	143.28 ± 5.02	8.71 ± 0.31	96.34	5.321	0.97	0.080	0.99	32.90 x 10^{-4}	0.58
ANT	7.54 ± 0.26	0.31 ± 0.01	91.72	5.020	0.97	0.075	0.99	31.10 x 10^{-4}	0.53
CRB	14.41 ± 0.50	0.65 ± 0.02	97.85	4.735	0.97	0.071	0.99	29.30 x 10^{-4}	0.58
FL	19.78 ± 0.69	0.85 ± 0.03	95.41	4.467	0.97	0.067	0.99	27.60 x 10^{-4}	0.53
PY	15.81 ± 0.55	0.67 ± 0.02	95.69	4.214	0.97	0.063	0.99	26.10 x 10^{-4}	0.59
BaA	0.55 ± 0.19	0.02 ± 0.007	95.97	3.975	0.97	0.059	0.99	24.60 x 10^{-4}	0.57
CHR	2.68 ± 0.93	0.10 ± 0.03	95.94	3.360	0.97	0.052	0.99	19.00 x 10^{-4}	0.56
BbF	0.80 ± 0.28	0.03 ± 0.01	95.98	2.451	0.96	0.044	0.98	12.10 x 10^{-4}	0.60
BkF	0.80 ± 0.28	0.03 ± 0.01	95.97	2.384	0.97	0.039	0.99	6.70 x 10^{-4}	0.53
BaP	0.07 ± 0.02	0.003 ± 0.001	95.97	1.893	0.97	0.037	0.99	6.00 x 10^{-4}	0.59
IcdP	1.09 ± 0.38	0.05 ± 0.06	95.93	1.648	0.97	0.034	0.99	3.32 x 10^{-4}	0.53
DahA	4.58 ± 1.60	0.18 ± 0.06	95.88	1.345	0.97	0.030	0.99	2.84 x 10^{-4}	0.60
BghiP	0.51 ± 0.17	0.02 ± 0.007	95.97	1.232	0.97	0.028	0.99	0.67 x 10^{-4}	0.58

IPC (A) : Initial PAH concentration (ng/ml), (B) Eff. = Effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

5.12.7.2 Reaction Kinetic of PAHs at 35 kHz and at 60^{o}C in the Presence of 10.00 mg/l DO

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 92.70% and 98.66% and at between 87.84% and 98.22%, respectively, in DO=10.00 mg/l after 150 min sonication time at 60^{o}C (Table 5.11).

At a DO concentration of 10.00 mg/l the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 4.622 and 9.250 mg/l.h (R^2=0.94 - 0.96) and at betweeen 1.766 and 3.933 mg/l.h (R^2=0.95), respectively, after 150 min sonication time at 60^{o}C (Table 5.107).

At DO=10.00 mg/l, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.075 and 0.157 1/h (R^2=0.99) and at betweeen 0.045 and 0.066 1/h (R^2=0.99), respectively, after 150 min sonication time at 60^{o}C (Table 5.107).

At DO=10.00 mg/l, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 26.00x10^{-4} and 69.80x10^{-4} l/mg.h (R^2=0.54 - 0.69) and at betweeen 3.60x10^{-4} and 23.00x10^{-4} l/mg.h (R^2=0.57), respectively, after 150 min sonication time at 60^{o}C (Table 5.107).

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less and more hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 for DO=10.00 mg/l after 150 min sonication time at 60^{o}C (Table 5.107). In this study, no significant difference in yields between less (ACL, FLN, PHE, CRB, FL, PY and CHR) and more (BaP, IcdP, DahA, BghiP) hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and DO concentration was observed (R^2=0.86, F=9.40, p=0.001).

Table 5.107 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies in the presence of DO=10.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC (A) (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAH (%)**	**ZORKC (C)**	**ZORKC (R^2)**	**FORKC (D)**	**FORKC (R^2)**	**SORKC (E)**	**SORKC (R^2)**
NAP	1871.45 ± 65.50	455.54 ± 15.94	98.66	9.250	0.94	0.157	0.99	$69.80x10^{-4}$	0.69
ACL	52.30 ± 1.83	1.94 ± 0.07	97.46	8.724	0.96	0.149	0.99	$66.00x10^{-4}$	0.58
ACT	70.56 ± 2.47	2.33 ± 0.08	94.85	8.230	0.96	0.141	0.99	$62.30x10^{-4}$	0.56
FLN	58.16 ± 2.04	2.03 ± 0.07	96.47	7.767	0.96	0.132	0.99	$58.70x10^{-4}$	0.56
PHE	138.78 ± 4.86	6.20 ± 0.22	96.77	7.326	0.96	0.124	0.99	$55.40x10^{-4}$	0.58
ANT	7.52 ± 0.26	0.21 ± 0.007	92.70	6.910	0.95	0.118	0.99	$52.30x10^{-4}$	0.57
CRB	14.35 ± 0.50	0.45 ± 0.02	98.10	6.523	0.95	0.111	0.99	$49.40x10^{-4}$	0.58
FL	19.68 ± 0.50	0.59 ± 0.02	95.95	6.150	0.95	0.106	0.99	$46.60x10^{-4}$	0.57
PY	15.74 ± 0.55	0.47 ± 0.02	96.20	5.803	0.95	0.098	0.99	$43.90x10^{-4}$	0.57
BaA	0.55 ± 0.02	0.02 ± 7 x 10^{-4}	93.16	5.480	0.95	0.094	0.99	$41.40x10^{-4}$	0.57
CHR	2.69 ± 0.09	0.08 ± 0.003	95.90	4.622	0.95	0.075	0.99	$26.00x10^{-4}$	0.57
BbF	0.80 ± 0.03	0.02 ± 7 x 10^{-4}	87.84	3.933	0.95	0.066	0.99	$23.00x10^{-4}$	0.57
BkF	0.80 ± 0.03	0.02 ± 7 x 10^{-4}	93.98	3.656	0.95	0.064	0.99	$14.30x10^{-4}$	0.57
BaP	0.07 ± 0.003	0.002 ± 1 x 10^{-4}	98.04	2.926	0.95	0.062	0.99	$9.45x10^{-4}$	0.57
IcdP	1.09 ± 0.04	0.03 ± 0.001	98.22	2.552	0.95	0.057	0.99	$8.25x10^{-4}$	0.57
DahA	4.60 ± 0.16	0.13 ± 0.005	97.01	1.892	0.95	0.050	0.99	$5.03x10^{-4}$	0.57
BghiP	0.51 ± 0.02	0.01 ± 4 x 10^{-4}	96.87	1.766	0.95	0.045	0.99	$3.60x10^{-4}$	0.57

IPC (A) : Initial PAH concentration (ng/ml), (B) Eff. = Effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

5.12.7.3 Reaction Kinetic of PAHs at 35 kHz and at 60^{o}C in the Presence of 1 hour Aeration

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 92.54% and 98.63% and at between 87.57% and 98.18%, respectively, under 1 h aeration after 150 min sonication time at 60^{o}C (Table 5.108).

At 1 h aeration, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 5.084 and 10.175 mg/l.h (R^2=0.86 - 0.97) and at betweeen 1.943 and 4.326 mg/l.h (R^2=0.96 - 0.97), respectively, after 150 min sonication time at 60^{o}C (Table 5.108).

At 1 h aeration, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.083 and 0.173 1/h (R^2=0.99) and at betweeen 0.050 and 0.073 1/h (R^2=0.99), respectively, after 150 min sonication time at 60^{o}C (Table 5.108).

At 1 h aeration, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 23.50x10^{-4} and 76.90x10^{-4} l/mg.h (R^2=0.54 - 0.64) and at betweeen 3.95x10^{-4} and 25.30x10^{-4} l/mg.h (R^2=0.56), respectively, after 150 min sonication time at 60^{o}C (Table 5.108).

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less and more hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 under 1 h aeration after 150 min sonication time at 60^{o}C (Table 5.108). In this study, no significant difference in yields between less (NAP, ACL, FLN, PHE, CRB, FL, PY and CHR) and more (BaP, IcdP, DahA, BghiP) hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and aeration was observed (R^2=0.73, F=6.32, p=0.001).

Table 5.108 The pseudo zero, first and second order reaction kinetic constans of seventeen PAHs obtained at maximum removal efficiencies in the presence of 1 h aeration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC (A) (ng/ml) ± SD**	**Eff. (B)T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC (C)**	**ZORKC (R^2)**	**FORKC (D)**	**FORKC (R^2)**	**SORKC (E)**	**SORKC (R^2)**
NAP	2599.44 ± 90.98	821.42 ± 28.75	98.63	10.175	0.86	0.173	0.99	76.90x10^{-4}	0.64
ACL	54.09 ± 1.89	2.58 ± 0.09	97.40	9.597	0.97	0.164	0.99	72.60x10^{-4}	0.57
ACT	73.73 ± 2.58	2.97 ± 0.10	94.74	9.053	0.97	0.155	0.99	68.50x10^{-4}	0.54
FLN	60.35 ± 2.11	2.63 ± 0.09	96.39	8.544	0.97	0.145	0.99	64.60x10^{-4}	0.57
PHE	149.97 ± 5.25	8.93 ± 0.31	96.70	8.059	0.97	0.136	0.99	60.90x10^{-4}	0.56
ANT	7.56 ± 0.27	0.24 ± 0.008	92.54	7.601	0.97	0.130	0.99	57.50x10^{-4}	0.55
CRB	14.50 ± 0.51	0.55 ± 0.02	98.06	7.175	0.97	0.122	0.99	54.30x10^{-4}	0.57
FL	19.94 ± 0.70	0.70 ± 0.03	95.86	6.764	0.97	0.117	0.99	51.20x10^{-4}	0.56
PY	15.92 ± 0.56	0.55 ± 0.02	96.11	6.383	0.97	0.108	0.99	48.30x10^{-4}	0.56
BaA	0.55 ± 0.02	0.02 ± 0.0007	93.01	6.030	0.96	0.103	0.99	45.50x10^{-4}	0.56
CHR	2.69 ± 0.09	0.09 ± 0.003	95.81	5.084	0.97	0.083	0.99	28.50x10^{-4}	0.56
BbF	0.80 ± 0.03	0.02 ± 0.0007	87.57	4.326	0.96	0.073	0.99	25.30x10^{-4}	0.56
BkF	0.80 ± 0.03	0.02 ± 0.0007	93.84	4.022	0.96	0.070	0.99	15.70x10^{-4}	0.56
BaP	0.07 ± 0.003	0.002 ± 0.0001	97.99	3.220	0.96	0.068	0.99	10.40x10^{-4}	0.56
IcdP	1.09 ± 0.04	0.03 ± 0.001	98.18	2.808	0.96	0.063	0.99	9.08x10^{-4}	0.56
DahA	4.61 ± 0.16	0.15 ± 0.005	96.94	2.081	0.97	0.055	0.99	5.53x10^{-4}	0.56
BghiP	0.51 ± 0.02	0.02 ± 0.0007	96.80	1.943	0.96	0.050	0.99	3.95x10^{-4}	0.56

IPC (A) : Initial PAH concentration (ng/ml), (B) Eff. = Effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

5.12.7.4 Reaction Kinetic of PAHs at 35 kHz and at 60^{o}C in the Presence of 30 min N_2(g) (6.00 mg/l N_2) Sparging

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 90.39% and 98.12% and at between 82.91% and 97.49%, under 30 min N_2(g) (6.00 mg/l N_2) sparging after 150 min sonication time at 60^{o}C (Table 5.109).

At 30 min N_2(g) (6.00 mg/l N_2) sparging, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 3.820 and 7.642 mg/l.h (R^2=0.89 - 0.96) and at betweeen 1.459 and 3.250 mg/l.h (R^2=0.94), respectively, after 150 min sonication time at 60^{o}C (Table 5.109).

At 30 min N_2(g) (6.00 mg/l N_2) sparging, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.062 and 0.130 1/h (R^2=0.99) and at betweeen 0.037 and 0.054 1/h (R^2=0.99), respectively, after 150 min sonication time at 60^{o}C (Table 5.109).

At 30 min N_2(g) (6.00 mg/l N_2) sparging, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 21.50x10^{-4} and 57.80x10^{-4} l/mg.h (R^2=0.57 - 0.66) and at betweeen 2.97x10^{-4} and 19.00x10^{-4} l/mg.h (R^2=0.60 - 0.67), respectively, after 150 min sonication time at 60^{o}C (Table 5.109).

Table 5.109 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies in the presence of 30 min N_2(g) (6.00 mg/l N_2) sparging after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC $^{(A)}$ (ng/ml) ± SD**	**Eff. $^{(B)}$ T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC $^{(C)}$**	**ZORKC (R^2)**	**FORKC $^{(D)}$**	**FORKC (R^2)**	**SORKC $^{(E)}$**	**SORKC (R^2)**
NAP	2312.39 ± 80.93	684.88 ± 23.97	98.12	7.642	0.89	0.130	0.99	57.80x10^{-4}	0.66
ACL	53.39 ± 1.87	2.71 ± 0.10	96.43	7.210	0.95	0.123	0.99	54.60x10^{-4}	0.60
ACT	72.48 ± 2.54	3.23 ± 0.11	92.77	6.801	0.95	0.116	0.99	51.50x10^{-4}	0.57
FLN	59.48 ± 2.08	2.81 ± 0.10	95.04	6.416	0.95	0.109	0.99	48.50x10^{-4}	0.65
PHE	145.56 ± 5.10	8.81 ± 0.31	95.46	6.053	0.96	0.103	0.99	45.80x10^{-4}	0.58
ANT	7.55 ± 0.26	0.29 ± 0.01	89.74	5.710	0.94	0.097	0.99	43.20x10^{-4}	0.59
CRB	14.44 ± 0.51	0.62 ± 0.02	97.33	5.388	0.94	0.091	0.99	40.80x10^{-4}	0.60
FL	19.84 ± 0.69	0.80 ± 0.03	94.31	5.082	0.94	0.087	0.99	38.50x10^{-4}	0.59
PY	15.85 ± 0.56	0.63 ± 0.02	94.66	4.795	0.94	0.081	0.99	36.30x10^{-4}	0.59
BaA	0.55 ± 0.02	0.02 ± 7.00x10^{-4}	90.39	4.523	0.94	0.077	0.99	34.20x10^{-4}	0.60
CHR	2.69 ± 0.09	0.10 ± 0.004	94.24	3.820	0.94	0.062	0.99	21.50x10^{-4}	0.60
BbF	0.80 ± 0.03	0.03 ± 0.001	82.91	3.250	0.94	0.054	0.99	19.00x10^{-4}	0.62
BkF	0.80 ± 0.03	0.03 ± 0.001	91.53	3.022	0.94	0.053	0.99	11.80x10^{-4}	0.60
BaP	0.07 ± 0.003	0.003 ± 1.00x10^{-4}	97.24	2.415	0.94	0.051	0.99	7.81x10^{-4}	0.63
IcdP	1.09 ± 0.04	0.04 ± 0.001	97.49	2.105	0.94	0.047	0.99	6.82x10^{-4}	0.60
DahA	4.60 ± 0.16	0.18 ± 0.006	95.79	1.563	0.94	0.041	0.99	4.16x10^{-4}	0.60
BghiP	0.51 ± 0.02	0.02 ± 7.00x10^{-4}	95.60	1.459	0.94	0.037	0.99	2.97x10^{-4}	0.67

IPC $^{(A)}$: Initial PAH concentration (ng/ml), $^{(B)}$ Eff. = Effluent, $^{(C)}$ ZORKC: Zero order reaction kinetic constant (mg/l . h), $^{(D)}$ FORKC: First order reaction kinetic constant (1/h), $^{(E)}$ SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less and more hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 under 30 min N_2(g) (6.00 mg/l N_2) after 150 min sonication time at 60°C (Table 5.109). In this study, no significant difference in yields between less (ACL, FLN, PHE, CRB, FL, PY and CHR) and more (BaP, IcdP, DahA, BghiP) hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and N_2(g) sparging was observed (R^2=0.76, F=5.24, p=0.001).

5.12.7.5 Reaction Kinetic of PAHs at 35 kHz and at 60°C in the Presence of 2000 mg/l H_2O_2

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 95.00% and 99.08% and at between 91.68% and 98.78%, respectively, in H_2O_2=2000 mg/l after 150 min sonication time at 60°C (Table 5.110).

At H_2O_2=2000 mg/l, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 5.592 and 11.913 mg/l.h (R^2=0.93 - 0.97) and at betweeen 2.140 and 4.760 mg/l.h (R^2=0.96), respectively, after 150 min sonication time at 60°C (Table 5.110).

At H_2O_2=2000 mg/l, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.091 and 0.190 1/h (R^2=0.99) and at betweeen 0.055 and 0.080 1/h (R^2=0.99), respectively, after 150 min sonication time at 60°C (Table 5.110).

At H_2O_2=2000 mg/l, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 31.40×10^{-4} and 84.60×10^{-4} l/mg.h (R^2=0.53 -

0.68) and at betweeen $4.35x10^{-4}$ and $27.90x10^{-4}$ l/mg.h (R^2=0.53), respectively, after 150 min sonication time at 60°C (Table 5.110).

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less and more hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 in H_2O_2=2000 mg/l concentration after 150 min sonication time at 60°C (Table 5.110). In this study, no significant difference in yields between less (NAP, ACL, ACT, FLN, PHE, CRB, FL, PY, CHR) and more (BkF, BaP, IcdP, DahA, BghiP) hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and H_2O_2 concentration was observed (R^2=0.79, F=5.09, p=0.001).

Table 5.110 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies in the presence of 2000 mg/l H_2O_2 concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC (A) (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC (C)**	**ZORKC (R^2)**	**FORKC (D)**	**FORKC (R^2)**	**SORKC (E)**	**SORKC (R^2)**
NAP	1899.69 ± 66.50	461.41 ± 16.20	99.08	11.913	0.93	0.190	0.99	$84.60x10^{-4}$	0.68
ACL	52.37 ± 1.83	1.56 ± 0.06	98.26	10.560	0.96	0.180	0.99	$79.90x10^{-4}$	0.55
ACT	70.68 ± 2.47	1.81 ± 0.06	96.48	9.958	0.97	0.171	0.99	$75.40x10^{-4}$	0.53
FLN	58.24 ± 2.04	1.59 ± 0.06	97.59	9.398	0.96	0.160	0.99	$71.00x10^{-4}$	0.56
PHE	139.21 ± 4.87	5.28 ± 0.20	97.79	8.865	0.97	0.150	0.99	$67.00x10^{-4}$	0.55
ANT	7.53 ± 0.26	0.15 ± 0.005	95.00	8.361	0.96	0.143	0.99	$63.30x10^{-4}$	0.53
CRB	14.36 ± 0.50	0.34 ± 0.01	98.70	7.893	0.96	0.134	0.99	$59.80x10^{-4}$	0.54
FL	19.69 ± 0.70	0.43 ± 0.02	97.23	7.440	0.96	0.129	0.99	$56.40x10^{-4}$	0.53
PY	15.75 ± 0.55	0.34 ± 0.01	97.40	7.021	0.96	0.119	0.99	$53.10x10^{-4}$	0.53
BaA	0.55 ± 0.02	$0.01 \pm 4.00x10^{-4}$	95.32	6.633	0.96	0.113	0.99	$50.10x10^{-4}$	0.53
CHR	2.69 ± 0.09	0.05 ± 0.002	97.19	5.592	0.96	0.091	0.99	$31.40x10^{-4}$	0.53
BbF	0.80 ± 0.03	0.02 ± 0.0007	91.68	4.760	0.96	0.080	0.99	$27.90x10^{-4}$	0.53
BkF	0.80 ± 0.03	0.02 ± 0.0007	95.87	4.424	0.96	0.077	0.99	$17.30x10^{-4}$	0.53
BaP	0.07 ± 0.003	$0.001 \pm 4.00x10^{-5}$	98.66	3.542	0.96	0.075	0.99	$11.40x10^{-4}$	0.53
IcdP	1.09 ± 0.04	$0.02 \pm 7.00x10^{-4}$	98.78	3.090	0.96	0.069	0.99	$9.99x10^{-4}$	0.53
DahA	4.60 ± 0.16	0.09 ± 0.003	97.95	2.290	0.96	0.061	0.99	$6.09x10^{-4}$	0.53
BghiP	0.51 ± 0.02	$0.01 \pm 4.00x10^{-4}$	97.85	2.140	0.96	0.055	0.99	$4.35x10^{-4}$	0.53

IPC (A) : Initial PAH concentration (ng/ml), (B) Eff. = Effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

5.12.7.6 Reaction Kinetic of PAHs at 35 kHz and at 60^{o}C in the Presence of 20.00 mg/l TiO_2

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 90.92% and 96.99% and at between 92.92% and 96.00%, respectively, in TiO_2=20.00 mg/l after 150 min sonication time at 60^{o}C (Table 5.111).

At TiO_2=20.00 mg/l, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 6.151 and 12.312 mg/l.h (R^2=0.94 - 0.96) and at betweeen 2.354 and 5.236 mg/l.h (R^2=0.94), respectively, after 150 min sonication time at 60^{o}C (Table 5.111).

At TiO_2=20.00 mg/l, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.100 and 0.210 1/h (R^2=0.99) and at betweeen 0.060 and 0.088 1/h (R^2=0.99), respectively, after 150 min sonication time at 60^{o}C (Table 5.111).

At TiO_2=20.00 mg/l, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 34.60x10^{-4} and 93.00x10^{-4} l/mg.h (R^2=0.67 - 0.75) and at betweeen 4.80x10^{-4} and 30.70x10^{-4} l/mg.h (R^2=0.74), respectively, after 150 min sonication time at 60^{o}C (Table 5.111).

Table 5.111 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies in the presence of TiO_2=20.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC $^{(A)}$ (ng/ml) ± SD**	**Eff. $^{(B)}$ T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC $^{(C)}$**	**ZORKC (R^2)**	**FORKC $^{(D)}$**	**FORKC (R^2)**	**SORKC $^{(E)}$**	**SORKC (R^2)**
NAP	1871.45 ± 65.50	489.44 ± 17.13	96.99	12.312	0.95	0.210	0.99	$93.00x10^{-4}$	0.72
ACL	52.30 ± 1.83	3.62 ± 0.13	94.30	11.616	0.95	0.198	0.99	$87.90x10^{-4}$	0.72
ACT	70.56 ± 2.47	4.57 ± 0.16	95.47	10.954	0.95	0.188	0.99	$82.90x10^{-4}$	0.68
FLN	58.16 ± 2.04	3.89 ± 0.14	92.08	10.340	0.95	0.176	0.99	$78.10x10^{-4}$	0.75
PHE	138.78 ± 4.86	10.41 ± 0.36	92.75	9.752	0.96	0.165	0.99	$73.70x10^{-4}$	0.67
ANT	7.52 ± 0.26	0.46 ± 0.02	94.88	9.197	0.94	0.157	0.99	$69.60x10^{-4}$	0.73
CRB	14.35 ± 0.50	0.93 ± 0.03	95.74	8.682	0.94	0.147	0.99	$65.70x10^{-4}$	0.74
FL	19.68 ± 0.70	1.24 ± 0.04	90.92	8.184	0.94	0.142	0.99	$62.00x10^{-4}$	0.72
PY	15.74 ± 0.55	0.99 ± 0.03	91.47	7.723	0.94	0.131	0.99	$58.50x10^{-4}$	0.73
BaA	0.55 ± 0.02	0.03 ± 0.001	94.99	7.296	0.94	0.124	0.99	$55.10x10^{-4}$	0.74
CHR	2.69 ± 0.09	0.16 ± 0.006	94.32	6.151	0.94	0.100	0.99	$34.60x10^{-4}$	0.74
BbF	0.80 ± 0.03	0.05 ± 0.002	95.80	5.236	0.94	0.088	0.99	$30.70x10^{-4}$	0.74
BkF	0.80 ± 0.03	0.05 ± 0.002	92.92	4.866	0.94	0.085	0.99	$19.00x10^{-4}$	0.74
BaP	0.07 ± 0.003	0.004 ± $1.00x10^{-4}$	95.59	3.896	0.94	0.083	0.99	$12.60x10^{-4}$	0.74
IcdP	1.09 ± 0.04	0.07 ± 0.003	96.00	3.400	0.94	0.076	0.99	$11.00x10^{-4}$	0.74
DahA	4.60 ± 0.16	0.28 ± 0.01	93.28	2.520	0.94	0.067	0.99	$6.70x10^{-4}$	0.74
BghiP	0.51 ± 0.02	0.03 ± 0.001	92.97	2.354	0.94	0.060	0.99	$4.80x10^{-4}$	0.74

IPC $^{(A)}$: Initial PAH concentration (ng/ml), $^{(B)}$ Eff. = Effluent, $^{(C)}$ ZORKC: Zero order reaction kinetic constant (mg/l . h), $^{(D)}$ FORKC: First order reaction kinetic constant (1/h), $^{(E)}$ SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less and more hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 in TiO_2=20.00 mg/l concentration after 150 min sonication time at 60°C (Table 5.111). In this study, no significant difference in yields between less (ACL, ACT, ANT, CRB, BaA, CHR) and more (BbF, BaP, IcdP) hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and TiO_2 concentration was observed (R^2=0.83, F=6.45, p=0.001).

5.12.7.7 Reaction Kinetic of PAHs at 35 kHz and at 60°C in the Presence of 15.00 g/l NaCl

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 99.00% and 99.82% and at between 98.33% and 99.76%, respectively, in NaCl=15.00 g/l after 150 min sonication time at 60°C (Table 5.112).

At NaCl=15.00 g/l, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 6.766 and 13.543 mg/l.h (R^2=0.92 - 0.94) and at betweeen 2.589 and 5.760 mg/l.h (R^2=0.92), respectively, after 150 min sonication time at 60°C (Table 5.112).

At NaCl=15.00 g/l, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.112 and 0.231 1/h (R^2=0.99) and at betweeen 0.066 and 0.097 1/h (R^2=0.99), respectively, after 150 min sonication time at 60°C (Table 5.112).

At NaCl=15.00 g/l, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 38.00×10^{-4} and 102.30×10^{-4} l/mg.h (R^2=0.47 - 0.70) and at betweeen 5.26×10^{-4} and 33.70×10^{-4} l/mg.h (R^2=0.47 - 0.48), respectively, after 150 min sonication time at 60°C (Table 5.112).

Table 5.112 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies in the presence of NaCl=15.00 g/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC (A) (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC (C)**	**ZORKC (R^2)**	**FORKC (D)**	**FORKC (R^2)**	**SORKC (E)**	**SORKC (R^2)**
NAP	1891.53 ± 66.20	440.69 ± 15.42	99.82	13.543	0.94	0.231	0.99	102.30x10^{-4}	0.70
ACL	52.35 ± 1.83	0.72 ± 0.03	99.65	12.778	0.93	0.218	0.99	96.70x10^{-4}	0.52
ACT	70.65 ± 2.50	0.71 ± 0.03	99.30	12.050	0.94	0.207	0.99	91.20x10^{-4}	0.49
FLN	58.22 ± 2.04	0.68 ± 0.02	99.52	11.374	0.93	0.194	0.99	85.90x10^{-4}	0.53
PHE	139.09 ± 4.87	3.19 ± 0.11	99.56	10.727	0.94	0.182	0.99	81.10x10^{-4}	0.53
ANT	7.53 ± 0.26	0.03 ± 0.001	99.00	10.117	0.93	0.173	0.99	76.60x10^{-4}	0.47
CRB	14.36 ± 0.50	0.11 ± 0.004	99.74	9.550	0.93	0.162	0.99	72.30x10^{-4}	0.49
FL	19.68 ± 0.68	0.11 ± 0.004	99.45	9.002	0.93	0.158	0.99	68.20x10^{-4}	0.48
PY	15.75 ± 0.55	0.09 ± 0.003	99.48	8.495	0.93	0.144	0.99	64.30x10^{-4}	0.48
BaA	0.55 ± 0.02	0.002 ± 1.00x10^{-4}	99.06	8.026	0.92	0.136	0.99	60.60x10^{-4}	0.47
CHR	2.69 ± 0.10	0.01 ± 4.00x10^{-4}	99.44	6.766	0.92	0.112	0.99	38.00x10^{-4}	0.47
BbF	0.80 ± 0.03	0.003 ± 1.00x10^{-4}	98.33	5.760	0.92	0.097	0.99	33.70x10^{-4}	0.47
BkF	0.80 ± 0.03	0.003 ± 1.00x10^{-4}	99.17	5.353	0.92	0.094	0.99	21.00x10^{-4}	0.47
BaP	0.07 ± 0.003	0.0002 ± 1.00x10^{-5}	99.73	4.286	0.92	0.091	0.99	13.80x10^{-4}	0.47
IcdP	1.09 ± 0.04	0.004 ± 1.00x10^{-4}	99.76	3.740	0.92	0.084	0.99	12.90x10^{-4}	0.47
DahA	4.60 ± 0.16	0.02 ± 7.00x10^{-4}	99.59	2.772	0.92	0.074	0.99	7.37x10^{-4}	0.48
BghiP	0.51 ± 0.02	0.002 ± 1.00x10^{-4}	99.57	2.589	0.92	0.066	0.99	5.26x10^{-4}	0.47

IPC (A) : Initial PAH concentration (ng/ml), (B) Eff. = Effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less and more hydrophobic PAHs with the highest linear correlation coefficient of $R^2=0.99$ in NaCl=15.00 g/l after 150 min sonication time at 60°C (Table 5.112). In this study, no significant difference in yields between less and more hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and NaCl concentration was observed ($R^2=0.94$, F=11.56, p=0.001).

5.12.7.8 Reaction Kinetic of PAHs at 35 kHz and at 60°C in the Presence of 20.00 mg/l Fe^{+2}

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 94.59% and 98.94% and at between 90.37% and 98.59%, respectively, in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60°C (Table 5.113).

At Fe^{+2}=20.00 mg/l, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 4.202 and 8.406 mg/l.h (R^2=0.87 - 0.92) and at betweeen 1.605 and 3.575 mg/l.h (R^2=0.87), respectively, after 150 min sonication time at 60°C (Table 5.113).

At Fe^{+2}=20.00 mg/l, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.068 and 0.143 1/h (R^2=0.99) and at betweeen 0.041 and 0.060 1/h (R^2=0.99), respectively, after 150 min sonication time at 60°C (Table 5.113).

At Fe^{+2}=20.00 mg/l, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 23.60×10^{-4} and 63.50×10^{-4} l/mg.h (R^2=0.54 - 0.74) and at betweeen 3.27×10^{-4} and 21.00×10^{-4} l/mg.h (R^2=0.54 - 0.76), respectively, after 150 min sonication time at 60°C (Table 5.113).

Table 5.113 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies in the presence of Fe^{+2}=20.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC (A) (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC (C)**	**ZORKC (R^2)**	**FORKC (D)**	**FORKC (R^2)**	**SORKC (E)**	**SORKC (R^2)**
NAP	1884.52 ± 65.96	448.59 ± 15.70	98.94	8.406	0.92	0.143	0.99	$63.50x10^{-4}$	0.70
ACL	52.34 ± 1.83	1.28 ± 0.05	97.99	7.931	0.88	0.135	0.99	$60.00x10^{-4}$	0.56
ACT	70.61 ± 2.47	1.45 ± 0.05	95.93	7.481	0.89	0.128	0.99	$56.60x10^{-4}$	0.54
FLN	58.20 ± 2.04	1.30 ± 0.05	97.21	7.060	0.89	0.120	0.99	$53.40x10^{-4}$	0.55
PHE	138.98 ± 4.96	4.58 ± 0.16	97.44	6.660	0.90	0.113	0.99	$50.30x10^{-4}$	0.56
ANT	7.52 ± 0.26	0.11 ± 0.004	94.22	6.281	0.87	0.107	0.99	$47.60x10^{-4}$	0.84
CRB	14.36 ± 0.50	0.26 ± 0.009	98.50	5.930	0.88	0.101	0.99	$44.90x10^{-4}$	0.55
FL	19.68 ± 0.70	0.33 ± 0.012	96.80	5.590	0.88	0.096	0.99	$42.40x10^{-4}$	0.64
PY	15.75 ± 0.55	0.26 ± 0.009	96.99	5.275	0.88	0.089	0.99	$39.90x10^{-4}$	0.54
BaA	0.55 ± 0.02	0.01 ± $4.00x10^{-4}$	94.59	4.980	0.87	0.085	0.99	$37.60x10^{-4}$	0.74
CHR	2.69 ± 0.09	0.04 ± 0.001	96.76	4.202	0.87	0.068	0.99	$23.60x10^{-4}$	0.54
BbF	0.80 ± 0.03	0.01 ± $4.00x10^{-4}$	90.37	3.575	0.87	0.060	0.99	$21.00x10^{-4}$	0.64
BkF	0.80 ± 0.03	0.01 ± $4.00x10^{-4}$	95.23	3.324	0.87	0.058	0.99	$13.00x10^{-4}$	0.54
BaP	0.07 ± 0.003	0.001 ± $4.00x10^{-5}$	98.45	2.660	0.87	0.056	0.99	$8.60x10^{-4}$	0.84
IcdP	1.09 ± 0.04	0.02 ± $7.00x10^{-4}$	98.59	2.320	0.87	0.052	0.99	$7.50x10^{-4}$	0.76
DahA	4.60 ± 0.16	0.07 ± 0.003	97.63	1.720	0.87	0.045	0.99	$4.57x10^{-4}$	0.54
BghiP	0.51 ± 0.02	0.01 ± $4.00x10^{-4}$	97.52	1.605	0.87	0.041	0.99	$3.27x10^{-4}$	0.54

IPC (A) : Initial PAH concentration (ng/ml), (B) Eff. = Effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less (ACT, FLN, PHE, FL, PY, BaA, CHR) and more (BaP, IcdP, DahA, BghiP) hydrophobic PAHs with the highest linear correlation coefficient of $R^2=0.99$ in $Fe^{+2}=20.00$ mg/l concentration after 150 min sonication time at 60°C (Table 5.113). In this study, no significant difference in yields between less and more hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and Fe^{+2} concentration was observed ($R^2=0.78$, F=7.46, p=0.001).

5.12.7.9 Reaction Kinetic of PAHs at 35 kHz and at 60°C in the Presence of 50.00 mg/l Fe^{+3}

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 91.71% and 97.84% and at between 90.29% and 97.13%, respectively, in $Fe^{+3}=50.00$ mg/l after 150 min sonication time at 60°C (Table 5.114).

At $Fe^{+3}=50.00$ mg/l, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 3.450 and 6.890 mg/l.h ($R^2=0.88$ - 0.92) and at betweeen 1.305 and 2.830 mg/l.h ($R^2=0.88$), respectively, after 150 min sonication time at 60°C (Table 5.114).

At $Fe^{+3}=50.00$ mg/l, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.055 and 0.114 1/h ($R^2=0.99$) and at betweeen 0.033 and 0.048 1/h ($R^2=0.99$), respectively, after 150 min sonication time at 60°C (Table 5.114).

At $Fe^{+3}=50.00$ mg/l, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between $19.40x10^{-4}$ and $49.80x10^{-4}$ l/mg.h ($R^2=0.59$ - 0.70) and at betweeen $2.20x10^{-4}$ and $16.00x10^{-4}$ l/mg.h ($R^2=0.61$), respectively, after 150 min sonication time at 60°C (Table 5.114).

Table 5.114 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies in the presence of Fe^{+3}=50.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC (A) (ng/ml) ± SD**	**Eff. (B) T=150 min PAH (ng/ml) ± SD**	**T=150 min PAH (%)**	**ZORKC (C)**	**ZORKC (R^2)**	**FORKC (D)**	**FORKC (R^2)**	**SORKC (E)**	**SORKC (R^2)**
NAP	1896.53 ± 66.38	472.83 ± 16.55	97.84	6.890	0.92	0.114	0.99	49.80x10^{-4}	0.70
ACL	52.37 ± 1.83	2.20 ± 0.08	95.91	6.502	0.89	0.108	0.99	47.10x10^{-4}	0.62
ACT	70.67 ± 2.47	2.67 ± 0.09	91.71	6.135	0.90	0.101	0.99	44.40x10^{-4}	0.59
FLN	58.23 ± 2.04	2.31 ± 0.08	94.32	5.790	0.90	0.096	0.99	41.90x10^{-4}	0.60
PHE	139.17 ± 4.87	6.88 ± 0.24	94.80	5.460	0.91	0.091	0.99	39.40x10^{-4}	0.60
ANT	7.53 ± 0.26	0.25 ± 0.009	94.40	5.150	0.88	0.085	0.99	37.30x10^{-4}	0.61
CRB	14.36 ± 0.50	0.52 ± 0.02	96.94	4.860	0.89	0.080	0.99	35.30x10^{-4}	0.62
FL	19.69 ± 0.70	0.68 ± 0.02	93.48	4.590	0.89	0.076	0.99	33.20x10^{-4}	0.61
PY	15.75 ± 0.55	0.54 ± 0.02	93.88	4.330	0.89	0.072	0.99	31.30x10^{-4}	0.61
BaA	0.55 ± 0.02	0.02 ± 7.00x10^{-4}	94.58	4.080	0.88	0.068	0.99	30.60x10^{-4}	0.61
CHR	2.69 ± 0.09	0.09 ± 0.003	93.40	3.450	0.88	0.055	0.99	19.40x10^{-4}	0.61
BbF	0.80 ± 0.03	0.03 ± 0.001	95.80	2.830	0.88	0.048	0.99	16.00x10^{-4}	0.61
BkF	0.80 ± 0.03	0.03 ± 0.001	90.29	2.660	0.88	0.046	0.99	9.80x10^{-4}	0.61
BaP	0.07 ± 0.003	0.002 ± 1.00x10^{-4}	96.84	2.120	0.88	0.044	0.99	6.80x10^{-4}	0.61
IcdP	1.09 ± 0.04	0.04 ± 0.001	97.13	1.847	0.88	0.041	0.99	5.48x10^{-4}	0.61
DahA	4.60 ± 0.16	0.15 ± 0.005	95.18	1.403	0.88	0.036	0.99	3.55x10^{-4}	0.61
BghiP	0.51 ± 0.02	0.02 ± 7.00x10^{-4}	94.95	1.305	0.88	0.033	0.99	2.20x10^{-4}	0.61

IPC (A) : Initial PAH concentration (ng/ml), (B) Eff. = Effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less (ACL, PHE, ANT, FL, BaA, CHR) and more (BbF, BaP, IcdP, DahA, BghiP) hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 in Fe^{+3}=50.00 mg/l concentration after 150 min sonication time at 60°C (Table 5.114). In this study, no significant difference in yields between less and more hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and Fe^{+3} concentration was observed (R^2=0.73, F=3.56, p=0.001).

5.12.7.10 Reaction Kinetic of PAHs at 35 kHz and at 60°C in the Presence of 2.00 g/l C_4H_9OH

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 76.76% and 90.55% and at between 85.64% and 93.82%, respectively, in C_4H_9OH=2.00 g/l after 150 min sonication time at 60°C (Table 5.115).

At C_4H_9OH=2.00 g/l, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 3.390 and 6.780 mg/l.h (R^2=0.91 - 0.98) and at betweeen 1.258 and 2.580 mg/l.h (R^2=0.94 - 0.98), respectively, after 150 min sonication time at 60°C (Table 5.115).

At C_4H_9OH=2.00 g/l, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.053 and 0.105 1/h (R^2=0.99) and at betweeen 0.030 and 0.046 1/h (R^2=0.99), respectively, after 150 min sonication time at 60°C (Table 5.115).

Table 5.115 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies in the presence of C_4H_9OH=2.00 g/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC $^{(A)}$ (ng/ml) ± SD**	**Eff. $^{(B)}$ T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC $^{(C)}$**	**ZORKC (R^2)**	**FORKC $^{(D)}$**	**FORKC (R^2)**	**SORKC $^{(E)}$**	**SORKC (R^2)**
NAP	7840.86 ± 274.43	1379.26 ± 48.27	82.41	6.780	0.96	0.105	0.99	$44.40x10^{-4}$	0.84
ACL	114.33 ± 4.00	22.44 ± 0.79	80.38	6.395	0.98	0.100	0.99	$41.90x10^{-4}$	0.75
ACT	113.32 ± 3.97	38.88 ± 1.36	85.69	6.030	0.92	0.093	0.99	$39.50x10^{-4}$	0.87
FLN	91.64 ± 3.20	17.87 ± 0.63	80.50	5.700	0.98	0.088	0.99	$37.30x10^{-4}$	0.88
PHE	239.11 ± 8.37	22.60 ± 0.79	90.55	5.367	0.96	0.084	0.99	$35.10x10^{-4}$	0.89
ANT	9.32 ± 0.33	1.54 ± 0.05	83.48	5.065	0.98	0.079	0.99	$33.20x10^{-4}$	0.78
CRB	41.54 ± 1.45	5.80 ± 0.20	86.04	4.780	0.91	0.074	0.99	$31.40x10^{-4}$	0.84
FL	27.00 ± 0.95	6.28 ± 0.22	76.76	4.510	0.98	0.070	0.99	$29.50x10^{-4}$	0.83
PY	22.99 ± 0.80	4.70 ± 0.17	79.57	4.250	0.98	0.066	0.99	$27.90x10^{-4}$	0.82
BaA	0.66 ± 0.02	0.10 ± 0.004	85.27	4.010	0.97	0.062	0.99	$27.10x10^{-4}$	0.75
CHR	3.64 ± 0.13	0.52 ± 0.02	85.69	3.390	0.96	0.053	0.99	$19.20x10^{-4}$	0.79
BbF	0.98 ± 0.03	0.14 ± 0.005	85.64	2.580	0.94	0.046	0.99	$13.40x10^{-4}$	0.75
BkF	1.24 ± 0.04	0.14 ± 0.005	88.54	2.480	0.98	0.042	0.99	$8.10x10^{-4}$	0.77
BaP	0.21 ± 0.007	0.01 ± 0.0004	93.82	1.970	0.97	0.040	0.99	$6.30x10^{-4}$	0.81
IcdP	3.40 ± 0.12	0.21 ± 0.007	93.80	1.714	0.95	0.037	0.99	$4.04x10^{-4}$	0.84
DahA	8.52 ± 0.30	1.02 ± 0.04	88.08	1.365	0.94	0.032	0.99	$3.08x10^{-4}$	0.86
BghiP	0.91 ± 0.03	0.09 ± 0.003	89.91	1.258	0.96	0.030	0.99	$1.19x10^{-4}$	0.79

IPC $^{(A)}$: Initial PAH concentration (ng/ml), $^{(B)}$ Eff. = Effluent, $^{(C)}$ ZORKC: Zero order reaction kinetic constant (mg/l . h), $^{(D)}$ FORKC: First order reaction kinetic constant (1/h), $^{(E)}$ SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

At C_4H_9OH=2.00 g/l, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between 19.20x10^{-4} and 44.40x10^{-4} l/mg.h (R^2=0.75 - 0.89) and at betweeen 1.19x10^{-4} and 13.40x10^{-4} l/mg.h (R^2=0.75 - 0.86), respectively, after 150 min sonication time at 60°C (Table 5.115).

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less (NAP, ACL, FLN, ANT, PY) and more (BbF, BkF, DahA, BghiP) hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 in C_4H_9OH=2.00 g/l concentration after 150 min sonication time at 60°C (Table 5.115). In this study, no significant difference in yields between less and more hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and C_4H_9OH concentration was observed (R^2=0.85, F=7.12, p=0.001).

5.12.7.11 Reaction Kinetic of PAHs at 35 kHz and at 60°C in the Presence of pH=7.0

The maximum yields in less (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR) and more (BbF, BkF, BaP, DahA, IcdP, BghiP) hydrophobic PAHs varied at between 92.54% and 98.63% and at between 87.57% and 98.18%, respectively, at pH=7.0 after 150 min sonication time at 60°C (Table 5.116).

At pH=7.0, the pseudo zero order rate constants of less and more hydrophobic PAHs ranged at between 3.472 and 6.947 mg/l.h (R^2=0.97 - 0.99) and at betweeen 1.326 and 2.954 mg/l.h (R^2=0.96 - 0.98), respectively, after 150 min sonication time at 60°C (Table 5.116).

At pH=7.0, the pseudo first order rate constants of less and more hydrophobic PAHs ranged at between 0.056 and 0.118 1/h (R^2=0.99) and at betweeen 0.034 and 0.049 1/h (R^2=0.99), respectively, after 150 min sonication time at 60°C (Table 5.116).

Table 5.116 The pseudo zero, first and second order reaction kinetic constants of seventeen PAHs obtained at maximum removal efficiencies at pH=7.0 after 150 min sonication time at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, initial COD$_{dis}$ concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

PAHs	**IPC $^{(A)}$ (ng/ml) ± SD**	**Eff. $^{(B)}$ T=150 min PAHs (ng/ml) ± SD**	**T=150 min PAHs (%)**	**ZORKC $^{(C)}$**	**ZORKC (R^2)**	**FORKC $^{(D)}$**	**FORKC (R^2)**	**SORKC $^{(E)}$**	**SORKC (R^2)**
NAP	2011.57 ± 70.41	536.83 ± 18.80	98.63	6.947	0.90	0.118	0.99	$52.50x10^{-4}$	0.64
ACL	52.65 ± 1.84	2.60 ± 0.09	97.40	6.554	0.99	0.112	0.99	$49.60x10^{-4}$	0.56
ACT	71.17 ± 2.50	3.17 ± 0.11	94.74	6.183	0.99	0.105	0.99	$46.80x10^{-4}$	0.54
FLN	58.58 ± 2.05	2.74 ± 0.10	96.40	5.833	0.99	0.099	0.99	$44.10x10^{-4}$	0.61
PHE	140.93 ± 4.93	8.08 ± 0.28	96.70	5.503	0.98	0.094	0.99	$41.60x10^{-4}$	0.55
ANT	7.53 ± 0.26	0.30 ± 0.01	92.54	5.191	0.98	0.088	0.99	$39.30x10^{-4}$	0.55
CRB	14.38 ± 0.50	0.62 ± 0.02	98.06	4.898	0.98	0.083	0.99	$37.10x10^{-4}$	0.56
FL	19.73 ± 0.69	0.82 ± 0.03	95.86	4.620	0.97	0.079	0.99	$35.00x10^{-4}$	0.55
PY	15.78 ± 0.55	0.65 ± 0.02	96.11	4.359	0.98	0.074	0.99	$33.00x10^{-4}$	0.55
BaA	0.55 ± 0.02	0.02 ± $7.00x10^{-4}$	93.01	4.112	0.98	0.070	0.99	$31.10x10^{-4}$	0.55
CHR	2.70 ± 0.10	0.11 ± 0.004	95.81	3.472	0.97	0.056	0.99	$19.50x10^{-4}$	0.55
BbF	0.80 ± 0.03	0.03 ± 0.001	87.57	2.954	0.96	0.049	0.99	$17.30x10^{-4}$	0.55
BkF	0.80 ± 0.03	0.03 ± 0.001	93.84	2.747	0.98	0.048	0.99	$10.70x10^{-4}$	0.55
BaP	0.07 ± 0.003	0.003 ± $1.00x10^{-4}$	97.99	2.195	0.98	0.046	0.99	$7.10x10^{-4}$	0.55
IcdP	1.09 ± 0.04	0.04 ± 0.001	98.18	1.914	0.97	0.043	0.99	$6.20x10^{-4}$	0.55
DahA	4.60 ± 0.16	0.18 ± 0.006	96.94	1.421	0.97	0.037	0.99	$3.78x10^{-4}$	0.55
BghiP	0.51 ± 0.02	0.02 ± $7.00x10^{-4}$	96.80	1.326	0.98	0.034	0.99	$2.70x10^{-4}$	0.55

IPC $^{(A)}$: Initial PAH concentration (ng/ml), $^{(B)}$ Eff. = Effluent, $^{(C)}$ ZORKC: Zero order reaction kinetic constant (mg/l . h), $^{(D)}$ FORKC: First order reaction kinetic constant (1/h), $^{(E)}$ SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

At pH=7.0, the pseudo second order rate constants of less and more hydrophobic PAHs ranged at between $19.50x10^{-4}$ and $52.50x10^{-4}$ l/mg.h (R^2=0.54 - 0.64) and at betweeen $2.70x10^{-4}$ and $17.30x10^{-4}$ l/mg.h (R^2=0.55), respectively, after 150 min sonication time at 60°C (Table 5.116).

Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of less (ACL, FLN, PHE, FL, PY, CHR) and more (BaP, IcdP, DahA, BghiP) hydrophobic PAHs with the highest linear correlation coefficient of R^2=0.99 at pH=7.0 after 150 min sonication time at 60°C (Table 5.116). In this study, no significant difference in yields between less and more hydrophobic PAHs were observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times. A significant linear correlation between PAHs yields and pH value was observed (R^2=0.88, F=6.79, p=0.001).

The pseudo order reaction kinetic constans of raw ww at 25°C, 30°C and 60°C, HCO_3^{-1}=1.00 g/l at 60°C were given in Appendices (7.24), (7.25) and (7.26).

5.13 PAH Removal Mechanisms

5.13.1 Mechanisms of PAHs Sonication at 35 kHz Frequency and at 60°C in the Presence of 6.00 mg/l NaCl

Different suggestions were mentioned for the sonication mechanism of hydrophobic PAHs: Quesada-Penate et al. (2009) have observed that stronger hydrophobicity of organic solute increases the capacity for trapping $OH^\bullet$. $OH^\bullet$ suppression is due to the enrichment of hydrophobic substrates in the bubbles and at the interfacial area. Rather than the oxidation of the organic substrates by $OH^\bullet$ and/or H_2O_2, the pyrolysis of hydrophobic substrate in collapsing bubbles and/or at the interfacial area dominates the sonolytical decomposition. Most products stem from pyrolysis of the substrates during the collapse of cavitation bubbles.

When the sonolysis of H_2O occurs, it leads to the formation of the non-specific oxidative species $OH^{\bullet}$. The Ultrasonic degradation of less hydrophobic organic compounds in the aqueous phase is mainly the result of an oxidation process by means of $OH^{\bullet}$ which escapes from the bubble to the bulk solution. Hydrophobic compounds present in water are expected to penetrate the surrounding shell and/or the hot heart of the cavitation bubble in order to be pyrolyzed, burnt and/or ionized into the plasma core (Banjoo & Nelson, 2005). Some studies suggested that PAHs (for example, PHE) are degraded by a free radical mechanism with $OH^{\bullet}$, since hydroxylated compounds like phenanthrenediols have not been detected (Wu & Ondruschka, 2005). On the other hand, some recent research has shown that plasma allows the ionization of organics like PAHs (Rae et al., 2005).

In this study, the contribution of the oxidation pathway of PAHs through ultrasonic degradation was determined in a sonicator at a sonication intensity and frequency of 51 W/m^2 and 35 kHz, respectively. If we assume that $OH^{\bullet}$ is the main species leading to sonodegradation of PAHs, the oxidation rate $V_{PAH/OH}{}^{\bullet}$, the experimental rate of PAHs sonodegradation $V_{PAH\ /\ US}$ and the experimental pseudo first order reaction kinetic rate constant can be calculated using Eqs. (4.30), (4.31) and (4.32) in Section 4.6 at Chapter 4.

Physical and chemical properties of seven PAHs (PHE, ANT, PHE, CHR, PY, BbF, DahA and BghiP) as shown in Table 5.117. The second order reaction kinetic rate constants for seven PAHs were taken from the study performed by Lindsey & Tarr (2000a). A comparison of calculated oxidation rates of $OH^{\bullet}$ with Eq. (4.30) (See in Section 4.6 at Chapter 4) for the experimental sonodegradation rates is given in Table 5.118 at a frequency of 35 kHz for seven PAHs.

Table 5.117 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**CAS-No**	**MF**	**MW**	T_M	T_B	S_W	**V_P (25°C)**	**H (25°C)**	**log K_{OA} (25°C)**	**log K_{OW}**	**IPC**
PHE	85-01-8	$C_{14}H_{10}$	178	99	340	1.15	$1.21x10^{-4}$	$3.35x10^{-5}$	7.68	4.46	125.58
ANT	120-12-7	$C_{14}H_{10}$	178	215	340	$4.34x10^{-2}$	$2.67x10^{-6}$	$5.56x10^{-5}$	7.71	4.45	3.63
PY	129-00-0	$C_{16}H_{10}$	202	151	404	$1.35x10^{-1}$	$4.50x10^{-6}$	$1.19x10^{-5}$	8.81	4.88	14.49
CHR	218-01-9	$C_{18}H_{12}$	228	258	448	$2.00x10^{-3}$	$6.23x10^{-9}$	$5.23x10^{-6}$	10.30	5.81	2.32
BbF	205-99-2	$C_{20}H_{12}$	252	168	-	$1.50x10^{-3}$	$5.00x10^{-7}$	$6.57x10^{-7}$	11.34	5.78	0.23
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	$2.49x10^{-3}$	$1.00x10^{-10}$	$1.23x10^{-7}$	12.59	6.75	5.42
BghiP	191-24-2	$C_{22}H_{12}$	276	278	> 500	$2.60x10^{-4}$	$1.00x10^{-10}$	$3.31x10^{-7}$	12.55	6.63	0.58

phenanthrene (PHE), anthracene (ANT), pyrene (PY), chrysene (CHR), benz[*b*]fluoranthene (BbF), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g / mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg / l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 / mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng / ml).

Table 5.118 Calculated pseudo-first order reaction kinetics for seven PAHs in NaCl=6.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**Benzene Ring Number**	$\mathbf{k_{pf}}$ [a]
ANT	3.00	0.046
PHE	3.00	0.037
PY	4.00	0.025
CHR	4.00	0.019
BbF	5.00	0.011
DahA	5.00	0.009
BghiP	6.00	0.007

a: Experimental pseudo first order reaction of PAH, (1/min).

Since the sonooxidation of hydrophobic DahA and BghiP comprised 0.04% and 0.03% of the total sonodegradation process, $OH^{\bullet}$ is not the major process for complete degradation of these PAHs (Table 5.118). In other words, in this study, the contribution of $OH^{\bullet}$ is minor for the ultimate sonodegradation of more hydrophobic PAHs. This indicates the occupation of the heart and/or the surrounding shell of the bubble by hydrophobic PAH molecules, and limitation of the sonolysis of H_2O and the formation of $OH^{\bullet}$. This demonstrates that the main process for destruction of hydrophobic PAHs is pyrolysis.

The formation of by-products (hydroxylated compounds namely phenanthrenediols) for possible $OH^{\bullet}$ oxidation was not observed in HPLC. Similar results were obtained in the studies performed by Lindsey & Tarr (2000b), Wen et al. (2003) and Wu & Ondruschka (2005). Since the sonooxidation of less hydrophobic PHE, PY, CHR and ANT comprised 0.78%, 0.74% and 0.72%, 0.79% of the total sonodegradation process, $OH^{\bullet}$ is the major process for complete degradation of these PAHs. The contribution of the pyrolysis to the destruction of these PAHs is not significant.

H_2O_2 which is preferentially formed by the recombination of $OH^\bullet$ issue from the sonolysis of H_2O can be used as a good indicator of the $OH^\bullet$ production. The H_2O_2 measurement during acoustic cavitation, in absence and in the presence of PCI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the PAH treatment by sonication in PCI ww decreases with increasing sonication time at 60°C. In the absence of PCI ww (in deionized water) the H_2O_2 was accumulated and its concentration was measured as 185.00 mg/l, whereas this level was only 7.00 mg/l in PCI ww after 150 min sonication time in samples containing NaCl (Table 5.119). The $OH^\bullet$ ion concentrations also increased from $8.11x10^{-51}$ to $34.56x10^{-8}$ mg/l and from $9.93x10^{-61}$ to $7.52x10^{-13}$ after 150 min sonication time in PCI ww containing less (PHE, ANT, PY and CHR) and more (BbF, DahA and BghiP) hydrophobic PAHs, respectively. This showed that hydroxylation is the main mechanism for the removal of less hydrophobic PAHs. In other words, $OH^\bullet$ is the major process for complete degradation of less hydrophobic PAHs.

Table 5.119 Effect of NaCl=6.00 mg/l concentration on H_2O_2 production and $OH^\bullet$ ion concentrations in PCI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	185.00	0.00
H_2O_2 concentration (mg/l) for less hydrophobic PAHs (60°C) after 30 min sonication	196.00	$8.11x10^{-51}$
H_2O_2 concentration (mg/l) for more hydrophobic PAHs (60°C) after 30 min sonication	2.00	$9.93x10^{-61}$
H_2O_2 concentration (mg/l) for less hydrophobic PAHs (60°C) after 120 min sonication	106.00	$2.76x10^{-20}$
H_2O_2 concentration (mg/l) for more hydrophobic PAHs (60°C) after 120 min sonication	2.00	$2.48x10^{-34}$
H_2O_2 concentration (mg/l) for less hydrophobic PAHs (60°C) after 150 min sonication	7.00	$34.56x10^{-8}$
H_2O_2 concentration (mg/l) for more hydrophobic PAHs (60°C) after 150 min sonication	2.00	$7.52x10^{-13}$

In PCI ww the most sonogenerated OH$^{\bullet}$ reacted with 89.00-97.00% less hydrophobic PAH removals and radical recombination to produce H_2O_2 (Gogate et al., 2004). The OH$^{\bullet}$ ion concentrations remained constant around $7.52x10^{-13}$ mg/l after 150 min sonication time in PCI ww containing more hydrophobic BbF, DahA and BghiP (Table 5.119). No increase in OH$^{\bullet}$ ion concentrations was observed throughout sonication of more hydrophobic PAHs. This showed that hydroxylation is not the main mechanism for the removal of more hydrophobic PAHs. This indicates that the main process for the destruction of more hydrophobic PAHs is pyrolysis.

In order to determine the pyrolitic mechanism of PAH degradation a synthetic saturated solution of a mixture of seven PAHs (1.56 mg/l) was prepared to detect the gaseous by-products in the headspace of the sonication reactor (Figure 5.115). The theoretical total carbon amount of initial total PAHs for CH_4 and CO_2, shows that the carbon balance reaches about 11.13-15.28% and 38.40-45.26%, respectively (Figure 5.116).

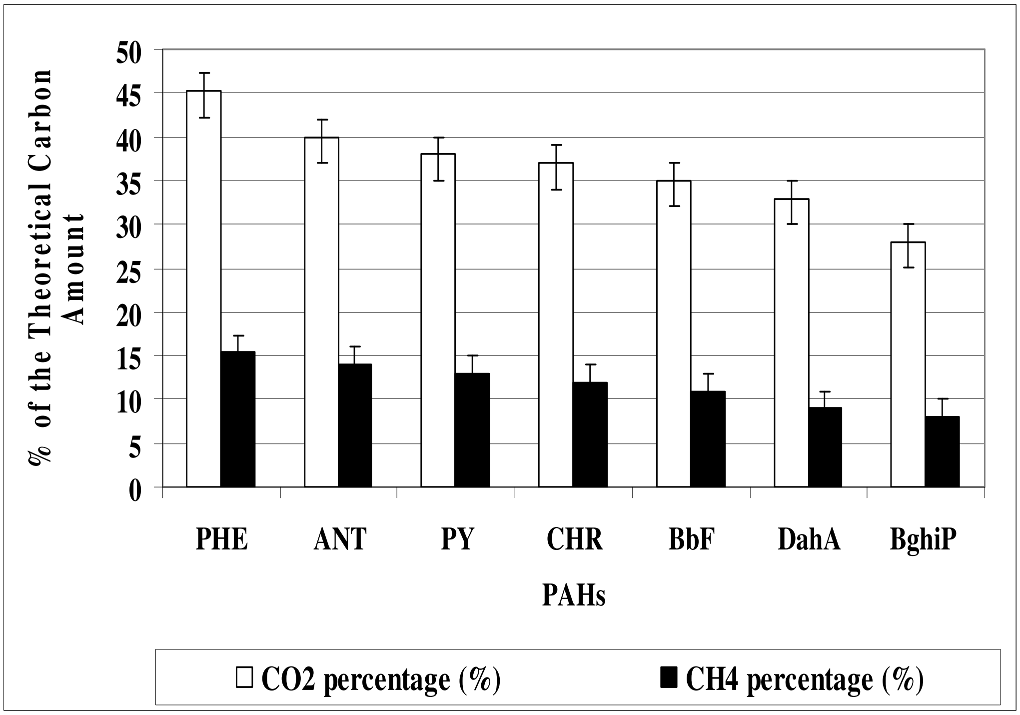


Figure 5.115 Theoretical carbon percentage based on CH_4(g) and CO_2(g) produced throughout sonication of PAHs (sonication power=640 W, sonication frequency=35 kHz).

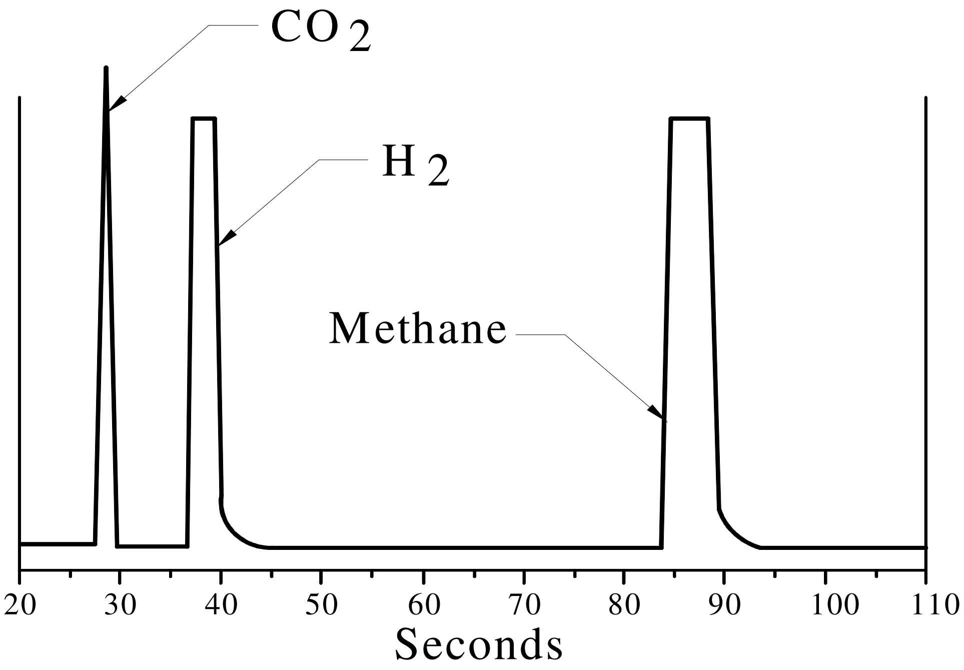


Figure 5.116 CH_4(g), H_2(g) and CO_2(g) spectra measured in the headspace of the sonicator by GC (sonication power=640 W, sonication frequency=35 kHz).

As mentioned previously the addition of 200 mg/l 1-butanol to the PAH mixture leads to a partial inhibition of the PAHs destruction and this is in agreement with the studies done by David (2009) and Psillakis et al. (2004) (See in section 5.9.12). About 15.21-35.46% inhibition was observed for less hydrophobic PAHs with the highest vapour pressure (PHE, ANT, CHR, PY and BbF) while all the other strong hydrophobic PAHs (DahA and BghiP) were not or very slightly affected by the $OH^{\bullet}$ scavenger. The oxidation of PAHs with $OH^{\bullet}$ appears to be of relatively minor importance, because of the low inhibition of the degradation by means of 1-butanol and since the steady-state $OH^{\bullet}$ concentration in the interfacial region of the cavitation bubble, where PAHs accumulate, is lower and not sufficient for a complete degradation of PAHs. Because of their properties, PAHs are then expected to be mainly localized in the heart and/or in the surrounding shell of the bubble, inhibiting the production of $OH^{\bullet}$ and hence the oxidation pathway.

5.13.2 PAHs Mechanisms at 35 kHz Frequency and 60^{o}C Temperature in the Presence of 6.00 mg/l Al_2O_3

In this study, physical and chemical properties of six PAHs (ACT, FL, BaA, BkF, BaP, IcdP) is given in Table 5.120. It is assumed that the sonication process is 100% controlled by oxidation of PAHs with [$OH^{\bullet}$] at a frequency of 35 kHz. [$OH^{\bullet}$]$_{ss}$ are the calculated steady-state concentrations of $OH^{\bullet}$ in PCI ww during sonication of six PAHs. The second order reaction kinetic rate constants for more and less hydrophobic PAHs were taken from the study performed by Lindsey & Tarr (2000a). A comparison of calculated oxidation rates of $OH^{\bullet}$ for the experimental sonodegradation rates is given in Table 5.121 at 35 kHz frequency for six PAHs.

Table 5.120 Physical and chemical properties of the PAHs studied in this work (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**CAS-No**	**MF**	**MW**	T_M	T_B	S_W **(25°C)**	V_P **(25°C)**	**H (25°C)**	**log** K_{OA} **(25°C)**	**log** K_{OW}	**IPC**
ACT	83-32-9	$C_{12}H_{10}$	154	93	279	3.90	$2.15x10^{-3}$	$1.84x10^{-4}$	6.52	3.92	66.82
FL	206-44-0	$C_{16}H_{10}$	202	108	384	$2.60x10^{-1}$	$9.22x10^{-6}$	$8.86x10^{-5}$	8.76	5.16	19.36
BaA	56-55-3	$C_{18}H_{12}$	228	84	438	$9.40x10^{-2}$	$2.10x10^{-7}$	$1.20x10^{-5}$	10.28	5.76	$5.50x10^{-1}$
BkF	207-08-9	$C_{20}H_{12}$	252	217	480	$8.00x10^{-3}$	$9.70x10^{-10}$	$5.84x10^{-6}$	11.37	6.11	$8.00x10^{-1}$
BaP	50-32-8	$C_{20}H_{12}$	252	177	495	$1.62x10^{-4}$	$5.49x10^{-9}$	$4.57x10^{-7}$	11.56	6.13	$7.50x10^{-2}$
IcdP	193-39-5	$C_{22}H_{12}$	276	164	536	$1.94x10^{-4}$	$1.25x10^{-10}$	$3.48x10^{-7}$	12.43	6.70	$10.93x10^{-2}$

acenaphthene (ACT), fluoranthene (FL), benz[*a*]anthracene (BaA), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP).

MF: Molecular formula, MW: Molecular weight (g/mol), T_M: Melting point (°C), T_B: Boiling point (°C), S_W: Solubility in water (mg/l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3/mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; IPC: Initial PAH concentration (mean, ng/ml)

Table 5.121 Calculated steady-state $[OH^{\bullet}]_{ss}$ concentrations for six PAHs, comparison of PAH oxidation rates of $OH^{\bullet}$ and experimental PAHs removal rates in Al_2O_3=6.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**Ring Num.**	$k_{PAH/OH^{\bullet}}$ [a]	k_{pf} [b]	$[OH^{\bullet}]_{ss}$ [c]	$V_{PAH/OH^{\bullet}}$ [d]	$V_{PAH/US}$ [e]	[f]	**InPC**
ACT	3.00	2.99×10^{10}	0.056	8.45×10^{-14}	8.77×10^{-5}	0.69×10^{-4}	0.98	6.68×10^{-5}
FL	4.00	2.78×10^{10}	0.047	6.26×10^{-14}	7.56×10^{-6}	0.51×10^{-5}	0.87	1.94×10^{-5}
BaA	4.00	2.04×10^{10}	0.038	3.55×10^{-14}	6.70×10^{-6}	0.40×10^{-5}	0.77	5.50×10^{-7}
BkF	5.00	1.85×10^{10}	0.029	2.09×10^{-15}	5.54×10^{-6}	0.39×10^{-5}	0.58	8.00×10^{-7}
BaP	5.00	1.07×10^{10}	0.019	1.98×10^{-16}	4.89×10^{-8}	0.23×10^{-7}	0.11	7.50×10^{-8}
IcdP	6.00	0.99×10^{10}	0.010	1.04×10^{-20}	1.99×10^{-10}	0.18×10^{-8}	0.10	1.09×10^{-7}

a: PAH oxidation rate constant (ng/ml.s); b: Experimental pseudo first order reaction of PAH, (1/min); c: Steady-state $[OH^{\bullet}]$ concentrations, (ng/ml); d: PAH oxidation rate (ng/ml.min); e: experimental rate of PAH sonodegradation (ng/ml.min); f: The percentage of PAH oxidation with $OH^{\bullet}$ ratio to conventional sonodegradation ratio ($V_{PAH/OH^{\bullet}}$ / $V_{PAH/US}$); InPC: Individual PAH concentration (ng/ml)

Since the sonooxidation of more hydrophobic BaP and IcdP comprised 0.11% and 0.10% of the total sonodegradation process, $OH^{\bullet}$ is not the major process for complete degradation of these PAHs (Table 5.121). In other words, in this study, the contribution of $OH^{\bullet}$ is minor for the ultimate sonodegradation of more hydrophobic PAHs. The formation of by-products (hydroxylated compounds namely phenanthrenediols) for possible $OH^{\bullet}$ oxidation was not observed in HPLC. Similar results were obtained in the studies performed by Lindsey & Tarr (2000b), Wen et al. (2003), Wu & Ondruschka (2005).

H_2O_2 which is preferentially formed by the recombination of $OH^{\bullet}$ issue from the sonolysis of H_2O can be used as a good indicator of the $OH^{\bullet}$ production. The H_2O_2 measurement during acoustic cavitation, in absence and in the presence of PCI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the PAHs treatment by sonication in PCI ww decreases with increasing sonication time at 60°C. In the absence of PCI ww (in deionized water) the H_2O_2 was accumulated and its concentration was measured as 184.00 mg/l, whereas this level was only 8.00 mg/l in PCI ww after 150 min sonication time in samples containing Al_2O_3 (Table 5.122). The $OH^\bullet$ ion concentrations also increased from 9.40×10^{-53} to 11.41×10^{-9} mg/l and from 8.51×10^{-62} to 2.57×10^{-12} mg/l after 150 min sonication time in PCI ww containing less (ACT, FL, BaA and BkF) and more (BaP and IcdP) hydrophobic PAHs, respectively. This showed that hydroxylation is the main mechanism for the removal of less hydrophobic PAHs. In other words, $OH^\bullet$ is the major process for complete degradation of less hydrophobic PAHs.

Table 5.122 Effect of Al_2O_3=6.00 mg/l concentration on H_2O_2 production and $OH^\bullet$ ion concentrations in PCI ww at 60°C after 30 min, 120 and 150 min sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

Conditions	**H_2O_2 Conc. (mg/l) (60°C)**	**$OH^\bullet$ ion Conc. (mg/l)**
H_2O_2 concentration (mg/l) in deionized water (60°C)	184.00	0.00
H_2O_2 concentration (mg/l) for less hydrophobic PAHs (60°C) after 30 min sonication	195.00	9.40×10^{-53}
H_2O_2 concentration (mg/l) for more hydrophobic PAHs (60°C) after 30 min sonication	3.00	8.51×10^{-62}
H_2O_2 concentration (mg/l) for less hydrophobic PAHs (60°C) after 120 min sonication	108.00	7.43×10^{-21}
H_2O_2 concentration (mg/l) for more hydrophobic PAHs (60°C) after 120 min sonication	3.00	4.13×10^{-32}
H_2O_2 concentration (mg/l) for less hydrophobic PAHs (60°C) after 150 min sonication	8.00	11.41×10^{-9}
H_2O_2 concentration (mg/l) for more hydrophobic PAHs (60°C) after 150 min sonication	3.00	2.57×10^{-12}

The OH$^{\bullet}$ ion concentrations remained constant around 2.57x10^{-12} mg/l after 150 min sonication time in PCI ww containing more hydrophobic BaP and IcdP. No increase in OH$^{\bullet}$ ion concentrations was observed throughout sonication of more hydrophobic PAHs. This showed that hydroxylation is not the main mechanism for the removal of more hydrophobic PAHs. This indicates that the main process for the destruction of more hydrophobic PAHs is pyrolysis.

Throughout the studies some gaseous by-products were observed in the headspace of the sonication reactor. 38.20-45.32% CO_2 and 11.10-15.03% CH_4 were measured after 10 min of sonication time in all the PAHs studied in the headspace of the sonicator reactor (Figure 5.117). The theoretical total carbon amount of initial total PAHs for $CH_4(g)$ and $CO_2(g)$, shows that the carbon balance reaches about 12.33-18.12% and 31.40-49.09%, respectively. It can be assumed that these gases are primarily formed as soon as PAHs penetrate the cavitation bubbles in order to be pyrolyzed.

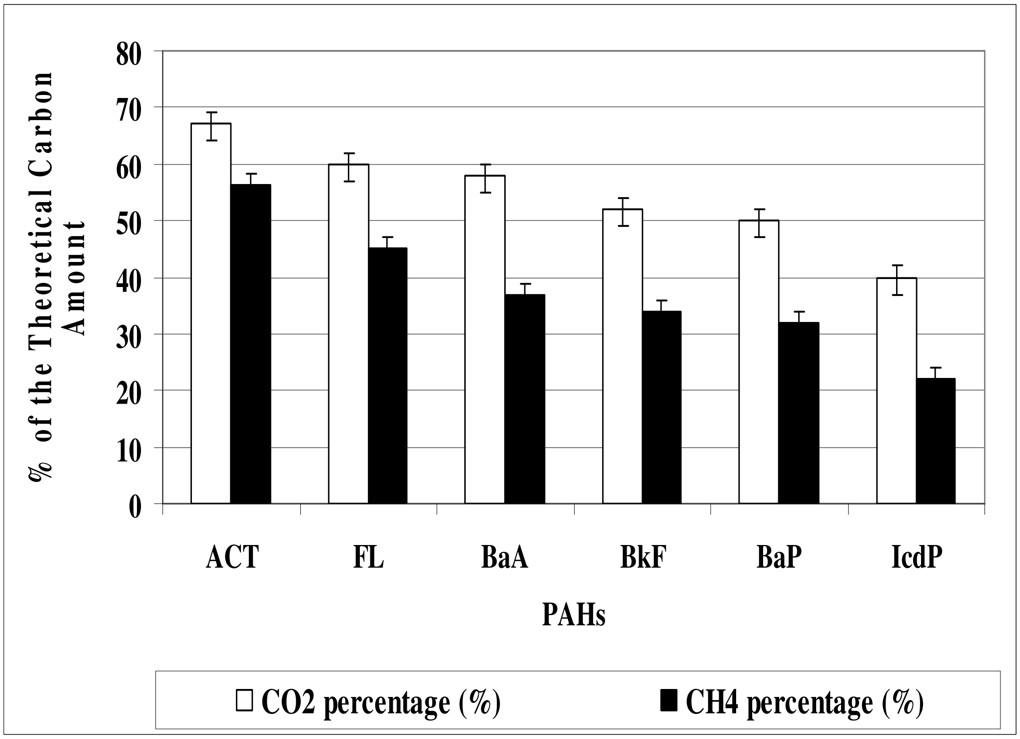


Figure 5.117 Theoretical carbon percentage based on $CH_4(g)$ and $CO_2(g)$ produced throughout sonication of PAHs (sonication power=640 W, sonication frequency=35 kHz).

5.13.3 Mechanisms of PAHs Sonication at 35 kHz Frequency and at 60^{o}C Temperature

Some studies suggested that PAHs (for example, PHE) are degraded by a free radical mechanism with $OH^\bullet$, since hydroxylated compounds like phenanthrenediols have been detected (David, 2009). On the other hand, some recent reserach has shown that plasma allows the formation of ionized organics like PAHs. This can lead to oxydized by-products (Sigman et al., 1998). The contribution of the oxidation pathway of PAHs through ultrasonic degradation can be determined. If we assume that $OH^\bullet$ is the main species leading to sonodegradation of PAHs, the oxidation rate $V_{PAH/OH}{}^\bullet$, the experimental rate of PAHs sonodegradation $V_{PAH\ /\ US}$ and, k_{pf} is the experimental pseudo first order reaction kinetic rate constant calculated in Eqs. (4.30), (4.31) and 4.32) (See in Section 4.6 at Chapter 4). Calculated steady-state $[OH^\bullet]_{ss}$ concentrations in PCI ww are shown during sonication of seven PAHs (FLN, FL, CHR, BbF, IcdP, DahA and BghiP) (Table 5.123). The second order reaction kinetic rate constants for seven PAHs were taken from the study performed by Lindsey & Tarr (2000a). The calculated values of $[OH^\bullet]_{ss}$ concentrations are in good agreement with the studies performed by David (2009), Destaillats et al. (2000), Lindsey & Tarr (2000a, 2000b) and Milkey et al. (2007). The comparison of calculated oxidation rates of $OH^\bullet$ with Eq. (4.30) (See in Section 4.6 at Chapter 4) for the experimental sonodegradation rates is given in Table 5.123 for a frequency of 35 kHz for seven PAHs.

Table 5.123 Calculated steady-state $[OH^{\bullet}]_{ss}$ concentrations for seven PAHs, comparison of PAH oxidation rates of $OH^{\bullet}$ and experimental PAHs removal rates after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**Ring Num.**	$k_{PAH/OH^{\bullet}}$ **a**	k_{pf} **b**	$[OH^{\bullet}]_{ss}$ **c**	$V_{PAH/OH^{\bullet}}$ **d**	$V_{PAH/US}$ **e**	**f**	**In PC**
FLN	3.00	2.30×10^{10}	0.016	4.34×10^{-21}	0.017	0.06	0.28	5.56×10^{-5}
FL	4.00	1.50×10^{10}	0.014	1.43×10^{-21}	0.014	0.04	0.35	1.94×10^{-5}
CHR	4.00	1.61×10^{10}	0.015	1.42×10^{-21}	0.011	0.04	0.27	2.68×10^{-7}
BbF	5.00	0.89×10^{10}	0.011	1.22×10^{-21}	0.009	0.03	0.30	7.90×10^{-7}
IcdP	6.00	0.75×10^{10}	0.009	1.13×10^{-21}	0.009	0.02	0.40	1.09×10^{-7}
DahA	6.00	0.74×10^{10}	0.008	1.12×10^{-21}	0.008	0.02	0.40	4.58×10^{-6}
BghiP	6.00	0.73×10^{10}	0.008	1.12×10^{-21}	0.007	0.01	0.40	5.13×10^{-4}

a: PAH oxidation rate constant (ng/ml.s); b: Experimental pseudo first order reaction of PAH, (1/min); c: Steady-state $[OH^{\bullet}]$ concentrations, (ng/ml); d: PAH oxidation rate (ng/ml.min); e: experimental rate of PAH sonodegradation (ng/ml.min); f: The percentage of PAH oxidation with $OH^{\bullet}$ ratio to conventional sonodegradation ratio ($V_{PAH/OH^{\bullet}}$ / $V_{PAH/US}$); In PC: Individual PAH concentration (ng/ml).

Since the sonooxidation of FLN, FL, CHR, BbF, IcdP, DahA and BghiP exhibited low percentages of the total sono-removal process, $OH^{\bullet}$ is not the major process for complete degradation of these PAHs (Table 5.123). In this study, the contribution of $OH^{\bullet}$ is minor for the ultimate sonodegradation of PAHs. The formation of by-products (hydroxylated compounds, namely phenanthrenediols) for possible $OH^{\bullet}$ oxydation was not observed on HPLC. Similar results were obtained in the studies performed by Lindsey & Tarr (2000b), Wen et al. (2003) and Wu & Ondruschka (2005).

In order to determine the pyrolitic mechanism of PAHs degradation a synthetic saturated solution (1.00 mg/l) was prepared with a mixture of seven PAHs to detect the gaseous by-products in the headspace of the sonication reactor (Figure 5.118).

44.12% CO_2(g) and 40.18% CH_4(g) were measured after 30 min of sonication time. It can be assumed that these gases are primarily formed as soon as PAHs penetrate the cavitation bubbles in order to be pyrolyzed as shown in Figure 5.118.

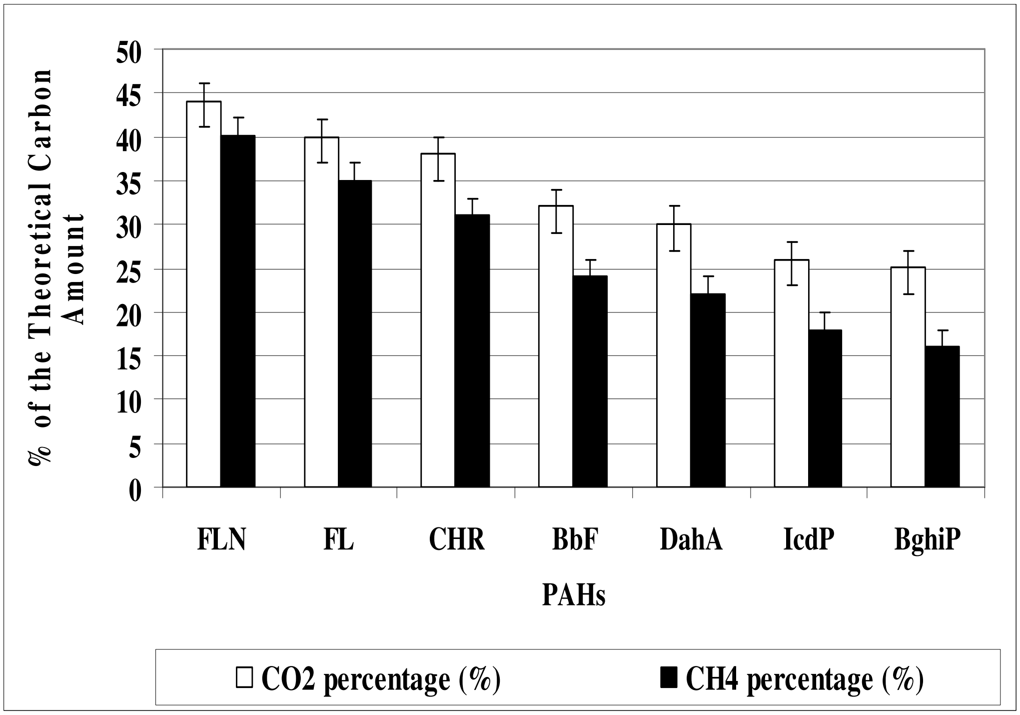


Figure 5.118 Theoretical carbon percentage based on CH_4 and CO_2 produced throughout sonication of seven PAHs (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

This could be explained by the rapid formation of the aforementioned two gases as FLN, FL, CHR, BbF, DahA, IcdP and BghiP penetrate the cavitation bubbles in order to be pyrolized as reported by David (2009) and Taylor Jr. et al. (1999) also mentioned that some carbonaceous gases were released through sonodegradation of PHE and $OH^{\bullet}$ oxidation was not observed. Furthermore, the pyrolysis of PHE was determined by the convertion of PHE to CH_4 and FL or to NAP (David, 2009). The preliminary studies showed that FL is an indication of a pyrolysis by-product formed by PHE due to high temperature reactions in or near a cavitation bubble (Park et al., 2000). Adewuyi (2001) also noted that pyrolysis in the interfacial region was predominant when the amount of PHE molecules migrating into the gaseous cavitation bubbles is expected to be small because of its low vapor pressure.

5.13.4 Mechanisms of PAHs Sonication at 35 kHz Frequency after 150 min Sonication in the Presence of 6.00 mg/l DO

Some studies suggested that PAHs for example (PHE are degraded by a free radical mechanism with $OH^{\bullet}$, since hydroxylated compounds like Phenanthrenediols have been detected (David, 2009). On the other hand, some recent research has shown that plasma allows the ionization of organics like PAHs. This can lead to oxidized by-products (Rae et al., 2005).

The contribution of the oxidation pathway of PAHs through ultrasonic degradation can be determined. If we assume that $OH^{\bullet}$ is the main species leading to sonodegradation of PAHs, the oxidation rate $V_{PAH/OH}{}^{\bullet}$, the experimental rate of PAHs sonodegradation $V_{PAH\ /\ US}$ and, k_{pf} is the experimental pseudo first order reaction kinetic rate constant calculated in the Eqs. (4.30), (4.31) and 4.32) (See in Section 4.6 at Chapter 4).

$[OH^{\bullet}]_{ss}$ is the calculated the steady-state concentrations in PCI ww during sonication of five PAHs (NAP, ACL, PHE, PY and BbF) (Table 5.124). The second order reaction kinetic rate constants for five PAHs were taken from the study performed by Lindsey & Tarr (2000a). The calculated values of $[OH^{\bullet}]_{ss}$ concentrations are in good agreement with the studies performed by Destaillats et al. (2000) and David (2009). A comparison of calculated oxidation rates of $OH^{\bullet}$ with Eq. (4.30) (See in Section 4.6 at Chapter 4) for the experimental sonodegradation rates is given in Table 5.124 at 35 kHz frequency for five PAHs.

Table 5.124 Calculated steady-state $[OH^\bullet]_{ss}$ concentrations for five PAHs, comparison of PAH oxidation rates of $OH^\bullet$ and experimental PAHs removal rates in DO=6.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values).

PAHs	**Ring Num.**	$\mathbf{k_{PAH/OH^\bullet}}$ a	$\mathbf{k_{pf}}$ b	$[OH^\bullet]_{ss}$ c	$\mathbf{V_{PAH/OH^\bullet}}$ d	$\mathbf{V_{PAH/US}}$ e	f	**InPC**
NAP	2.00	$2.80\text{x}10^{18}$	0.026	$9.28\text{x}10^{-21}$	0.029	0.52	0.05	$1.01\text{x}10^{-3}$
ACL	3.00	$2.60\text{x}10^{18}$	0.024	$9.23\text{x}10^{-21}$	0.023	0.48	0.04	$5.00\text{x}10^{-5}$
PHE	3.00	$2.30\text{x}10^{18}$	0.017	$4.34\text{x}10^{-21}$	0.009	0.06	0.15	$1.26\text{x}10^{-5}$
PY	4.00	$1.50\text{x}10^{18}$	0.015	$1.44\text{x}10^{-21}$	0.003	0,04	0.07	$1.55\text{x}10^{-5}$
BghiP	6.00	$0.90\text{x}10^{18}$	0.011	$1.22\text{x}10^{-21}$	0.001	0,04	0.02	$5.13\text{x}10^{-4}$

a: PAH oxidation rate constant (ng/ml.s); b: Experimental pseudo first order reaction of PAH, (1/min); c: Steady-state $[OH^\bullet]$ concentrations, (ng/ml); d: PAH oxidation rate (ng/ml.min); e: experimental rate of PAH sonodegradation (ng/ml.min); f: The percentage of PAH oxidation with $OH^\bullet$ ratio to conventional sonodegradation ratio ($V_{PAH/OH^\bullet}$ / $V_{PAH/US}$); InPC: Individual PAH concentration (ng/ml).

Since the sonooxidation of five PAHs (NAP, ACL, PHE, PY and BbF) comprised 0.05%, 0.04% and 0.15%, 0.07% and 0.02% of the total sonodegradation process, $OH^\bullet$ is not the major process for complete degradation of these PAHs (Table 5.124). In this study, the contribution of $OH^\bullet$ is minor for the ultimate sonodegradation of PAHs. The formation of by-products (hydroxylated compounds namely phenanthrenediols) for possible $OH^\bullet$ oxidation was not observed in HPLC (Table 5.125). Similar results were obtained in the studies performed by Lindsey & Tarr (2000a) and Wu & Ondruschka (2005).

In order to determine the pyrolitic mechanism of PAHs degradation a synthetic saturated solution of a mixture of five PAHs (1.00 mg/l) was prepared to detect the gaseous by products in the headspace of the sonication reactor. 67.11% CO_2(g) and 56.24% CH_4(g) were measured after 30 min of sonication time (Figure 5.119). This could be explained by the rapid formation of the aforementioned two gases as PAHs penetrate the cavitation bubbles in order to be pyrolized, as reported by David

(2009). The kinetic rate constants found in PCI ww throughout sonication were correlated with the recent studies in Table 5.126.

Table 5.125 Determined by-products of PCI ww after 120 min sonication time at 25°C with HPLC (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=1027.43 mg/l, initial TOC concentration=620.81 mg/l, initial total PAHs concentration=1378.77 ng/ml, n=3, mean values ± SD).

Time (min)	**By-Product Names**	**Values (ng/ml)**		
		Minimum	**Mean**	**Maximum**
120	1–methylnaphthalene	256.19±8.97	320.24±11.21	387.50±13.56
120	9–hydroxyfluorene	164.90±5.77	205.85±7.21	249.08±8.72
120	9,10–phenanthrenequione	62.53±2.19	78.16±2.74	94.57±3.31
120	benzoic acid	139.66±4.89	174.57±6.11	211.23±7.39
120	1,2,3–thiadiazole–4–carboxylic acid	62.06±2.17	77.58±2.72	93.87±3.29

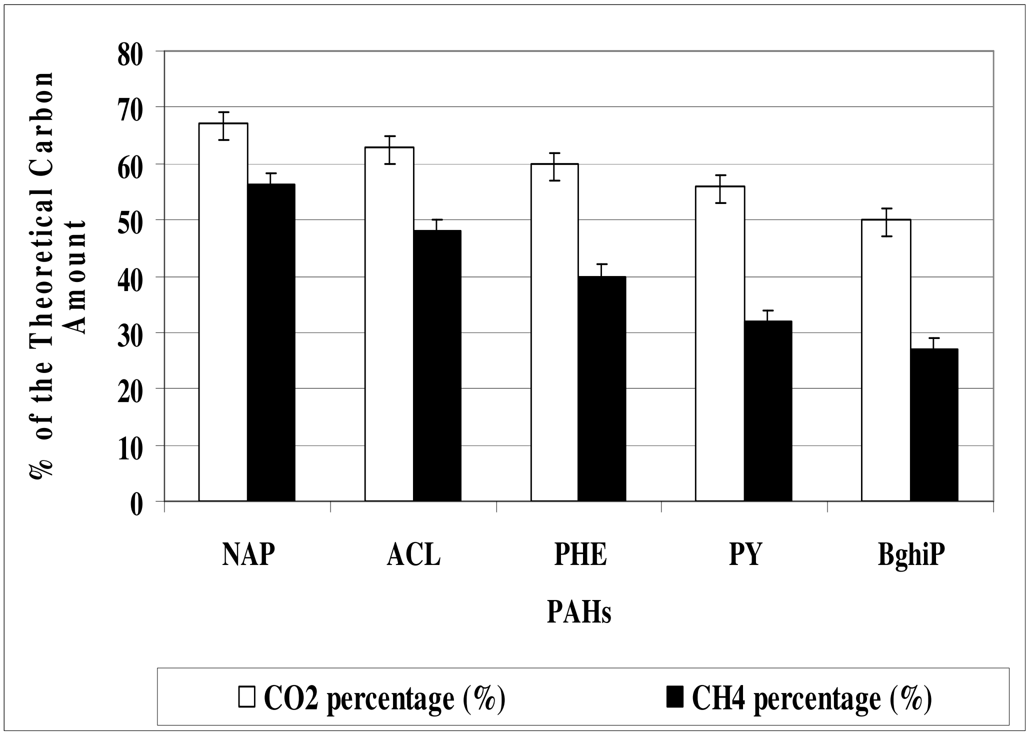


Figure 5.119 Theoretical carbon percentage based on CH_4 and CO_2 produced throughout sonication of seven PAHs (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

Table 5.126 The pseudo order reaction kinetic rate constants in PCI ww throughout sonication

ww Type	Sonication Frequency (kHz)	Sonication Power (W)	Sonication Time (min)	Pseudo Order Reaction Kinetic	Pseudo Order Reaction Kinetic Rate Constant (k=1/min)	Based on Removed Parameters	Chemicals and Doses	References
PCI ww	506	400	180	First	$4.67x10^{-2}$	PAHs	H_2O_2=100 mg/l	David & Riguier (2009)
	200	500	30	First	$4.50x10^{-2}$	PAHs	H_2O_2=300 mg/l	Yim et al. (2003)
	20	125	120	First	$9.50x10^{-1}$	PAHs	H_2O_2=300 mg/l	Abu-Hassan et al. (2006)
	520	14.60	140	First	$1.67x10^{-2}$	PAHs	H_2O_2=340 mg/l	De Visscher et al. (1996)
	25	50	60	First	$2.81x10^{-2}$	PAHs	H_2O_2=350 mg/l	Park et al. (2000)
	850	120	20	First	$5.00x10^{-2}$	PAHs	H_2O_2=1000 mg/l	Wu & Ondruschka (2005)
	506	400	90	First	$2.70x10^{-1}$	PAHs	H_2O_2=1000 g/l	David (2009)
	28	200	15	First	$2.20x10^{-3}$	PAHs	H_2O_2=1700 mg/l	Dai et al. (2008)
	35	640	150	First	$3.17x10^{-3}$	PAHs	H_2O_2=2000 mg/l	In this study *

Table 5.126 The pseudo order reaction kinetic rate constants in PCI ww throughout sonication (cont.).

ww Type	Sonication Frequency (kHz)	Sonication Power (W)	Sonication Time (min)	Pseudo Order Reaction Kinetic	Pseudo Order Reaction Kinetic Rate Constant (k=1/min)	Based on Removed Parameters	Chemicals and Doses	References
PCI ww	20	600	180	First	7.66x10^{-4}	PAHs	NaCl=16.00 g/l	Kim et al. (2001)
	80	150	240	First	2.80x10^{-2}	PAHs	NaCl=2.75 g/l	Psillakis et al. (2003)
	20	150	90	First	1.70x10^{-3}	PAHs	NaCl=5.85 g/l	de Lima Leite et al. (2002)
	80	150	60	First	1.22x10^{-2}	PAHs	NaCl=100 g/l	Psillakis et al. (2004)
	35	640	150	First	3.85x10^{-3}	PAHs	NaCl=15.00 g/l	In this study *
	20	300	140	First	1.16x10^{-5}	PAHs	Fe^{+2}=0.50 mg/l	Son et al. (2006)
	200	500	30	First	1.39x10^{-1}	PAHs	Fe^{+2}=25.00 mg/l	Yim et al. (2003)
	80	150	60	First	8.46x10^{-1}	PAHs	Fe^{+2}=75.00 mg/l	Psillakis et al. (2004)
	80	150	60	First	9.89x10^{-1}	PAHs	Fe^{+2}=100 mg/l	Psillakis et al. (2004)
	28	200	15	First	1.92x10^{-2}	PAHs	Fe^{+2}=2600 mg/l	Dai et al. (2008)
	35	640	150	First	2.38x10^{-3}	PAHs	Fe^{+2}=20.00 mg/l	In this study *

Table 5.126 The pseudo order reaction kinetic rate constants in PCI ww throughout sonication (cont.).

ww Type	**Sonication Frequency (kHz)**	**Sonication Power (W)**	**Sonication Time (min)**	**Pseudo Order Reaction Kinetic**	**Pseudo Order Reaction Kinetic Rate Constant (k=1/min)**	**Based on Removed Parameters**	**Chemicals and Doses**	**References**
PCI ww	200	500	30	First	$1.02x10^{-1}$	PAHs	Fe^{+3}=25.00 mg/l	Yim et al. (2003)
	35	640	150	First	$1.90x10^{-3}$	PAHs	Fe^{+3}=50.00 mg/l	In this study *
	80	150	60	First	$8.46x10^{-1}$	PAHs	C_4H_9OH=0.32 g/l	Psillakis et al. (2004)
	20	300	70	First	$8.50x10^{-3}$	PAHs	C_4H_9OH=3.00 g/l	Marvin et al. (2000)
	35	640	150	First	$1.75x10^{-3}$	PAHs	C_4H_9OH=2.00 g/l	In this study *
	200	500	30	First	$4.40x10^{-2}$	PAHs	air=0.05 ml/min	Yim et al. (2003)
	20	600	30	First	$4.35x10^{-4}$	PAHs	air=4.00 mg/l	Laughrey et al. (2001)
	35	640	150	First	$2.88x10^{-3}$	PAHs	1 h aeration	In this study *

Table 5.126 The pseudo order reaction kinetic rate constants in PCI ww throughout sonication (cont.).

ww Type	**Sonication Frequency (kHz)**	**Sonication Power (W)**	**Sonication Time (min)**	**Pseudo Order Reaction Kinetic**	**Pseudo Order Reaction Kinetic Rate Constant (k=1/min)**	**Based on Removed Parameters**	**Chemicals and Doses**	**References**
PCI ww	200	500	30	First	1.30x10^{-2}	PAHs	O_2=0.09 ml/min	Yim et al. (2003)
	20	600	30	First	8.17x10^{-4}	PAHs	O_2=4.00 mg/l	Laughrey et al. (2001)
	35	640	150	First	2.62x10^{-3}	PAHs	DO=10.00 mg/l	In this study *
	20	600	30	First	9.17x10^{-5}	PAHs	N_2=4.00 mg/l	Laughrey et al. (2001)
	35	640	150	First	2.17x10^{-3}	PAHs	N_2=6.00 mg/l	In this study *
	20	300	200	Zero	28.43x10^{-1} mg/l.h	PAHs	HCO_3=5000 mg/l	Son et al. (2006)
	35	640	150	First	47.10x10^{-4}	PAHs	HCO_3=1000 mg/l	In this study *

5.14 Removal Kinetic of OMI ww

5.14.1 Reaction Kinetic of OMI ww at 35 kHz and at 60^{o}C in the Presence of 10.00 mg/l DO

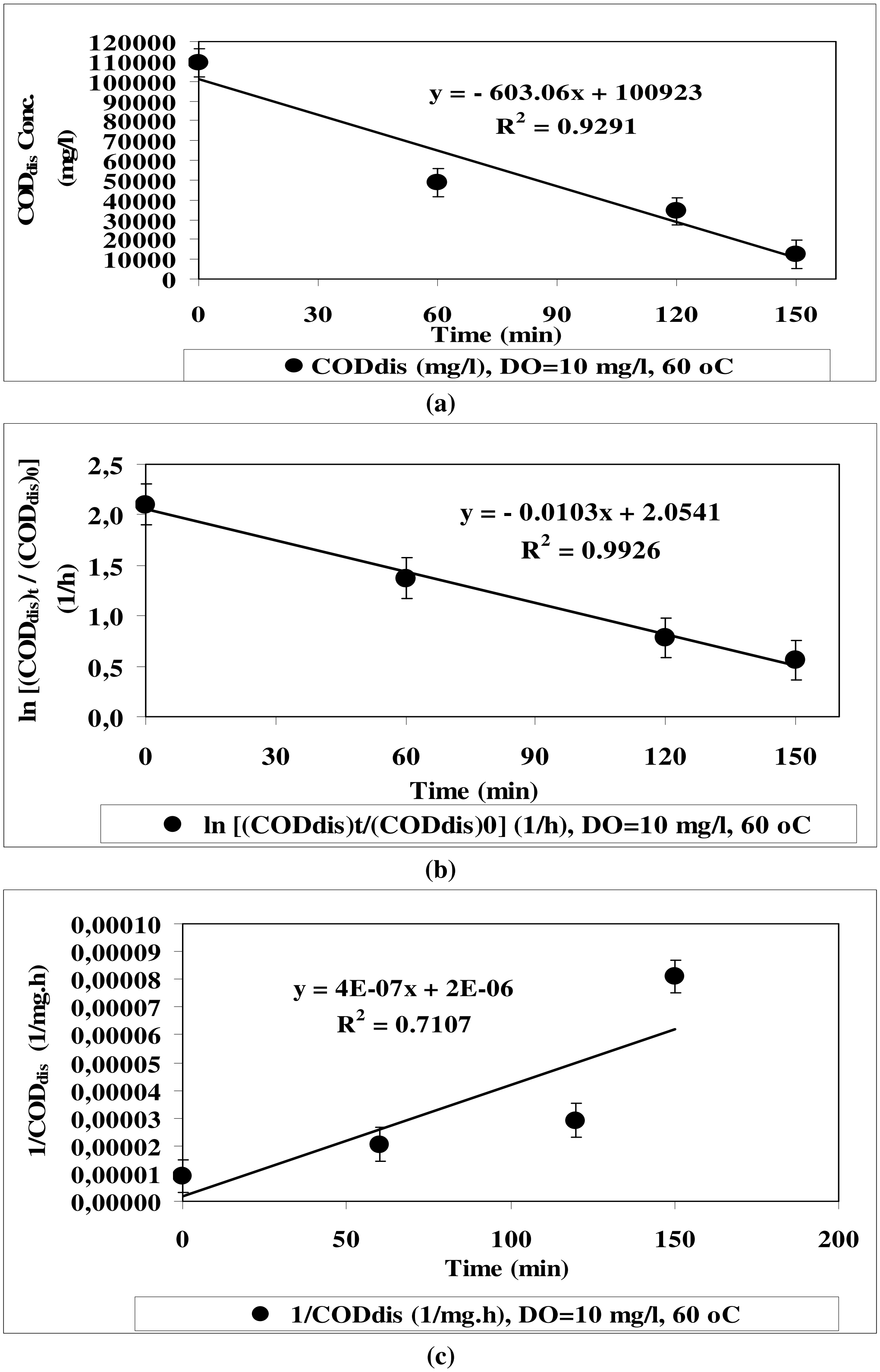
In this step of this study the COD$_{dis}$, TOC, color, total phenol, TAAs and TFAs removal kinetics were researched according to the pseudo zero, first and second order reaction kinetics in the presence of 10.00 mg/l DO in which the maximum COD$_{dis}$, TOC, color, total phenol, TAAs and TFAs removals were obtained in OMI ww.

The maximum yield in COD$_{dis}$ was 88.73% in DO=10.00 mg/l concentration after 150 min sonication time at 60^{o}C (Table 5.127). At a DO concentration of 10.00 mg/l, the pseudo zero order rate constant was 603.060 mg/l.h (R^2=0.92) after 150 min sonication time at 60^{o}C (Table 5.127; Figure 5.120a). At the same DO, the pseudo first order rate constant was 0.010 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.127; Figure 5.120b). At DO=10.00 mg/l, the pseudo second order rate constant was 4.03x10^{-7} l/mg.h (R^2=0.71) after 150 min sonication time at 60^{o}C (Table 5.127; Figure 5.120c). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of COD$_{dis}$ with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.127; Figure 5.120b).

Table 5.127 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of DO=10.00 mg/l concentration after 150 min sonication time at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	12334 ± 431.69	88.73	603.060	0.92	0.010	0.99	4.03x10^{-7}	0.71
TOC (E)	66488 ± 2327	8517 ± 298.10	87.19	361.710	0.93	0.012	0.99	5.82x10^{-7}	0.74
Color (F)	99.80 ± 3.493	6.20 ± 0.22	93.79	0.576	0.78	0.013	0.99	8.00x10^{-4}	0.77
Phenol (G)	4090 ± 143.15	352.48 ± 12.34	91.38	23.671	0.82	0.011	0.99	1.58x10^{-5}	0.90
TAAs (H)	3000 ± 105	252.48 ± 8.84	91.58	16.953	0.86	0.010	0.99	2.02x10^{-5}	0.71
TFAs (J)	5200 ± 182	1329.02 ± 46.52	74.44	25.468	0.98	0.008	0.99	3.54x10^{-6}	0.92

(A) ZORKC: Zero order reaction kinetic constant (mg/l.h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).



(a)

(b)

(c)

Figure 5.120 The pseudo zero (a), first (b) and second (c) order reaction kinetics of COD_{dis} in DO=10.00 mg/l concentrations at 60°C (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in TOC was 87.19% in DO=10.00 mg/l after 150 min sonication time at 60°C (Table 5.127). At DO=10.00 mg/l, the pseudo zero order rate constant was 361.710 mg/l.h (R^2=0.93) after 150 min sonication time at 60°C. At DO=10.00 mg/l, the pseudo first order rate constant was 0.012 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.127; Figure 5.121). At DO=10.00 mg/l, the pseudo second order rate constant was 5.82x10^{-7} l/mg.h (R^2=0.74) after 150 min sonication time at 60°C (Table 5.127). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TOC with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.127; Figure 5.121).

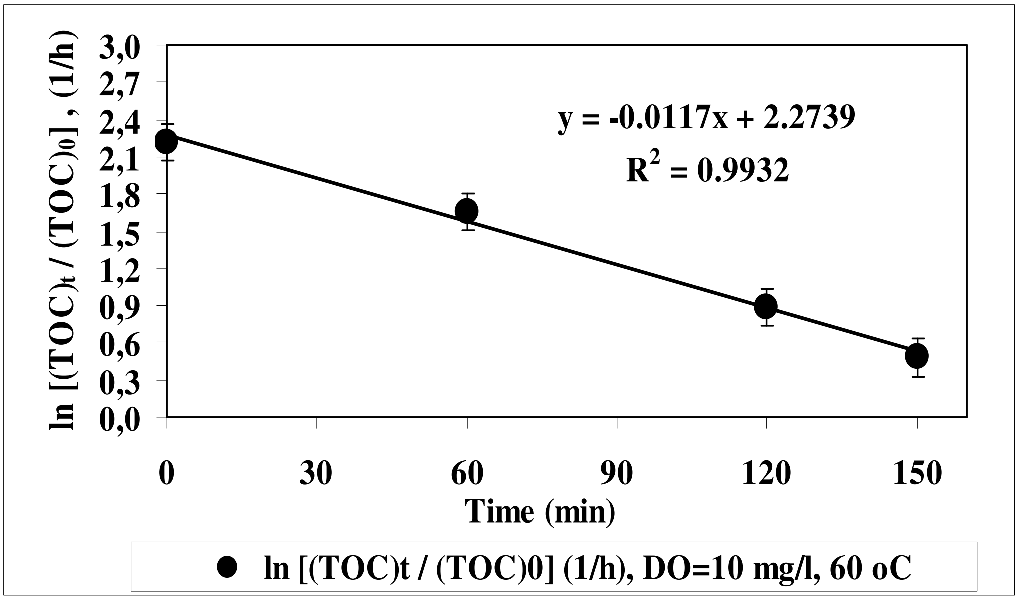


Figure 5.121 In the presence of DO=10.00 mg/l concentrations the removal kinetic of TOC according to pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in color was 93.79% in DO=10.00 mg/l after 150 min sonication time at 60°C (Table 5.127). At DO=10.00 mg/l the pseudo zero order rate constant was 0.576 mg/l.h (R^2=0.78) after 150 min sonication time at 60°C. At DO=10.00 mg/l, the pseudo first order rate constant was 0.013 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.127; Figure 5.122). At DO=10.00 mg/l, the pseudo second order rate constant was 8.00x10^{-4} l/mg.h (R^2=0.77) after 150 min sonication time at 60°C (Table 5.127). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of color with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.127; Figure 5.122). A significant linear correlation between color yields and DO concentrations was observed (R^2=0.83, F=5.12, p=0.001).

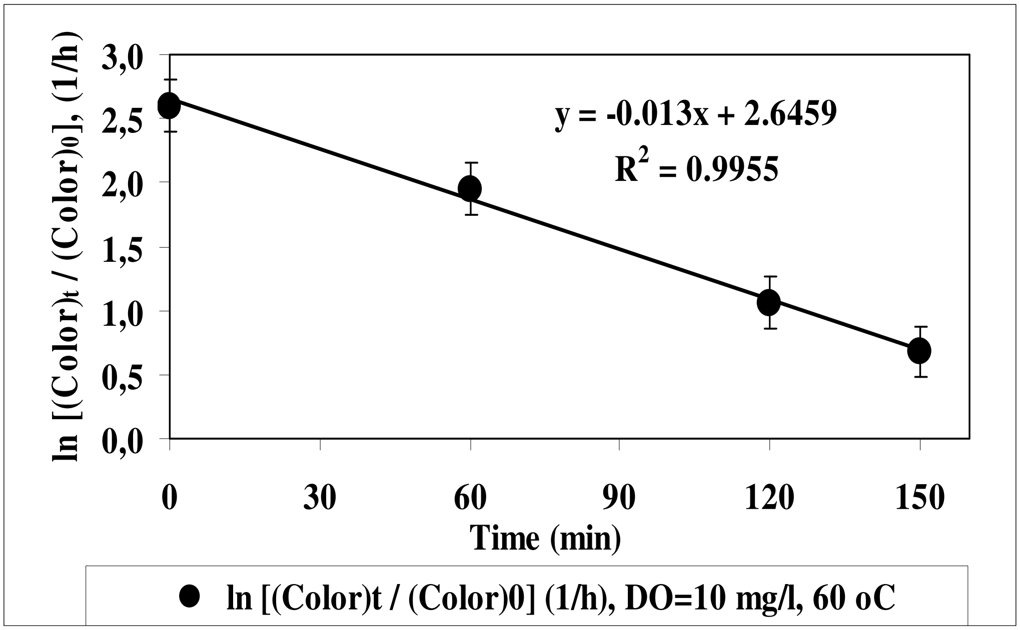


Figure 5.122 In the presence of DO=10.00 mg/l concentrations the removal kinetic of color according to pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in total phenol was 91.38% in DO=10.00 mg/l after 150 min sonication time at 60°C (Table 5.127). At DO=10.00 mg/l the pseudo zero order rate constant was 23.671 mg/l.h (R^2=0.82) after 150 min sonication time at 60°C. At DO=10.00 mg/l, the pseudo first order rate constant was 0.011 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.127; Figure 5.123). At DO=10.00 mg/l, the pseudo second order rate constant was $1.58 x 10^{-5}$ l/mg.h (R^2=0.90) after 150 min sonication time at 60°C (Table 5.127). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of total phenol with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.127; Figure 5.123).

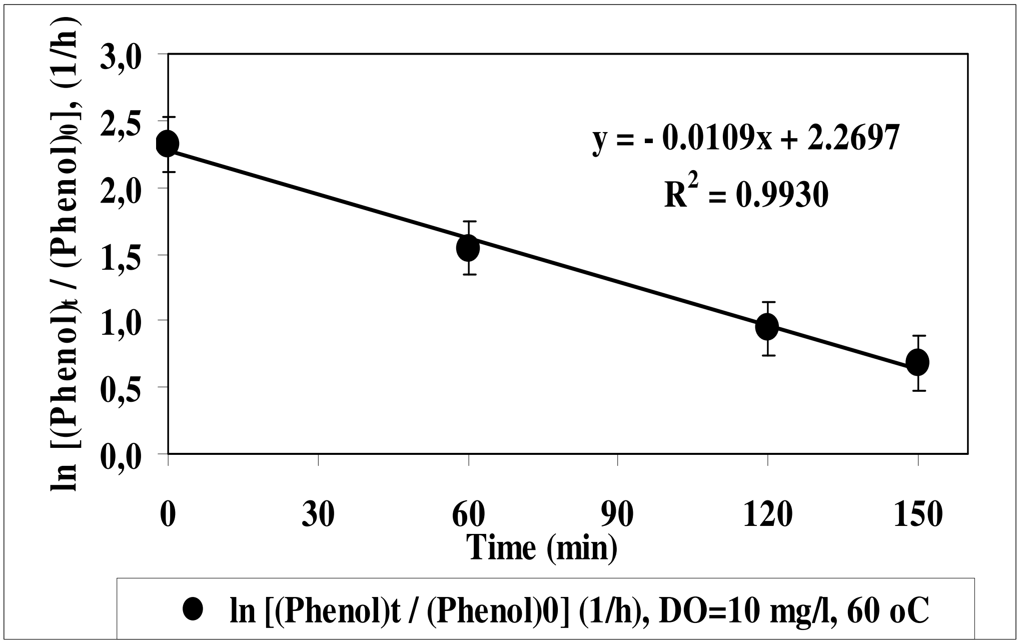


Figure 5.123 In the presence of DO=10.00 mg/l concentrations the removal kinetic of total phenol according to pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in TAAs was 91.58% in DO=10.00 mg/l after 150 min sonication time at 60°C (Table 5.127). At DO=10 mg/l the pseudo zero order rate constant was 16.953 mg/l.h (R^2=0.86) after 150 min sonication time at 60°C. At DO=10.00 mg/l, the pseudo first order rate constant was 0.010 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.127; Figure 5.124). At DO=10.00 mg/l, the pseudo second order rate constant was 2.02x10^{-5} l/mg.h (R^2=0.71) after 150 min sonication time at 60°C (Table 5.127). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TAAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.127; Figure 5.124).

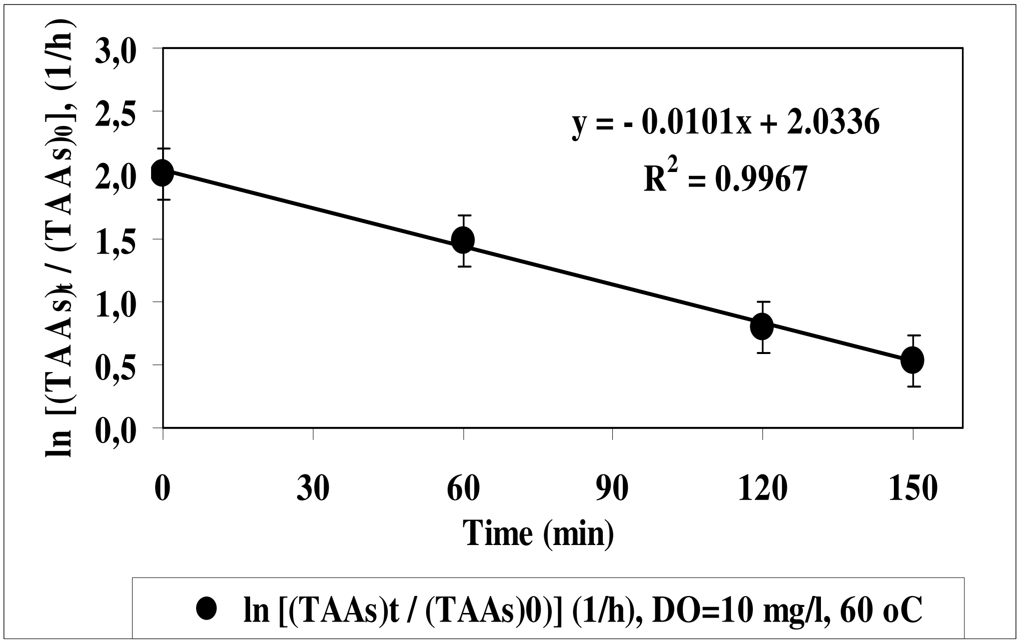


Figure 5.124 In the presence of DO=10.00 mg/l concentrations the removal kinetic of TAAs according to pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in TFAs was 74.44% in DO=10.00 mg/l after 150 min sonication time at 60°C (Table 5.127). At DO=10.00 mg/l the pseudo zero order rate constant was 25.468 mg/l.h (R^2=0.98) after 150 min sonication time at 60°C. At DO=10.00 mg/l, the pseudo first order rate constant was 0.008 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.127; Figure 5.125). At DO=10.00 mg/l, the pseudo second order rate constant was 3.54x10^{-6} l/mg.h (R^2=0.92) after 150 min sonication time at 60°C (Table 5.127). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TFAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.127; Figure 5.125).

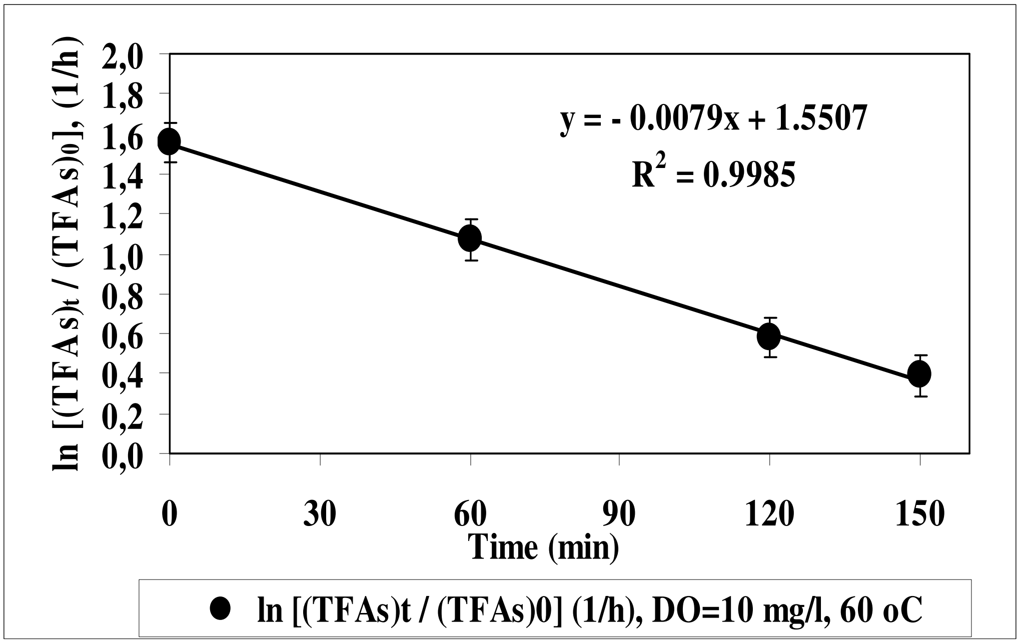


Figure 5.125 In the presence of DO=10.00 mg/l concentrations the removal kinetic of TFAs according to pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

In some previous studies, the sonochemical degradation of various classes of organics was found to obey a pseudo-first order or zero-order kinetics (Adewuyi, 2001; Gogate & Pandit, 2004a; 2004b; Yavuz et al., 2009) in OMI wws. The decolouration kinetic seems to fit reasonably well into simplified pseudo-first-order rate expression, for the concentration range used in the organics giving color in OMI ww (Vajnhandl & Le Marechal, 2007).

According to Psillakis et al. (2004) in certain reaction systems, for instance, the net effect of an increase in liquid bulk temperature and consequently in maximum collapse temperature is an increase in degradation rates. This occurs up to the point at which the cushioning effect of the vapor begins to dominate the system and further increases in liquid temperature result in reduced reaction rates. Additionally, the high vapor pressure in the bubble cushions the transfer of energy to the surroundings when bubble collapses. Therefore, if the main reaction mechanism is the pyrolysis in the bubble and around the interface, the reaction rate gets slower with the increase of temperature. However, the main reaction occurs at the aqueous phase, by radicals with the inorganic material, the reaction gets fast with the increase of temperature (Lim et al., 2007). Nevertheless, increase in the temperature resulted in increase in the reaction rate to some points depending on the frequency and power intensity and the effects of temperature to the sonolytic reaction and the relationship with other variables are stil not so clear as also reported by Lim et al. (2007). He et al. (2007) also demonstrated that the TOC degradation obeyed the pseudo-first-order rate law under all experimental conditions in OMI wws. It was found that the pseudo first order reaction rate constant was $9.00x10^{-4}$ 1/min in an OMI ww at a DO=0.10 ml/min, at 20 kHz frequency, at 800 W power, at pH=10.0, after 80 min sonication time at 60^oC. In this study, the pseudo first order rate constants were observed between $8.00x10^{-3}$ and $1.30x10^{-2}$ 1/min in DO=10.00 mg/l concentrations after 150 min sonication time at 60^oC. The pseudo first order rate constants in the present study at 60^oC is higher than the pseudo first order rate constants obtained by He et al. (2007) at 60^oC as mentioned above. This could be attributed to the differences in sonication powers, to the differences in DO concentrations and to the high frequency and to the long sonication time used throughout sonication.

In a study performed by Japon-Lujan et al. (2006) it was found that the pseudo first order reaction rate constants were $4.20x10^{-2}$ 1/min and $6.15x10^{-2}$ 1/min in an OMI ww at a DO=0.20 ml/min and at a DO=0.50 ml/min, at 20 kHz frequency, at 450 W power, at pH=8.0 and at pH=12.0, respectively, after 25 min sonication time at 60^oC. In this study, the pseudo first order rate constants were observed between $8.00x10^{-3}$ and $1.30x10^{-2}$ 1/min in DO=10.00 mg/l concentrations after 150 min sonication time at 60^oC. The pseudo first order rate constants in the present study at 60^oC is lower than the pseudo first order rate constants obtained by Japon-Lujan et al. (2006) at 60^oC as mentioned above. This could be attributed to the differences in pH values and to the differences in DO concentrations used throughout sonication.

5.14.2 Reaction Kinetic of OMI ww at 35 kHz and at 60^{o}C in the Presence of 2000 mg/l H_2O_2

In this step of this study the COD_{dis}, TOC, color, total phenol, TAAs and TFAs removal kinetics were researched according to the zero, first and second order reaction kinetics in the presence of 2000 mg/l H_2O_2 in which the maximum COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals were obtained in OMI ww.

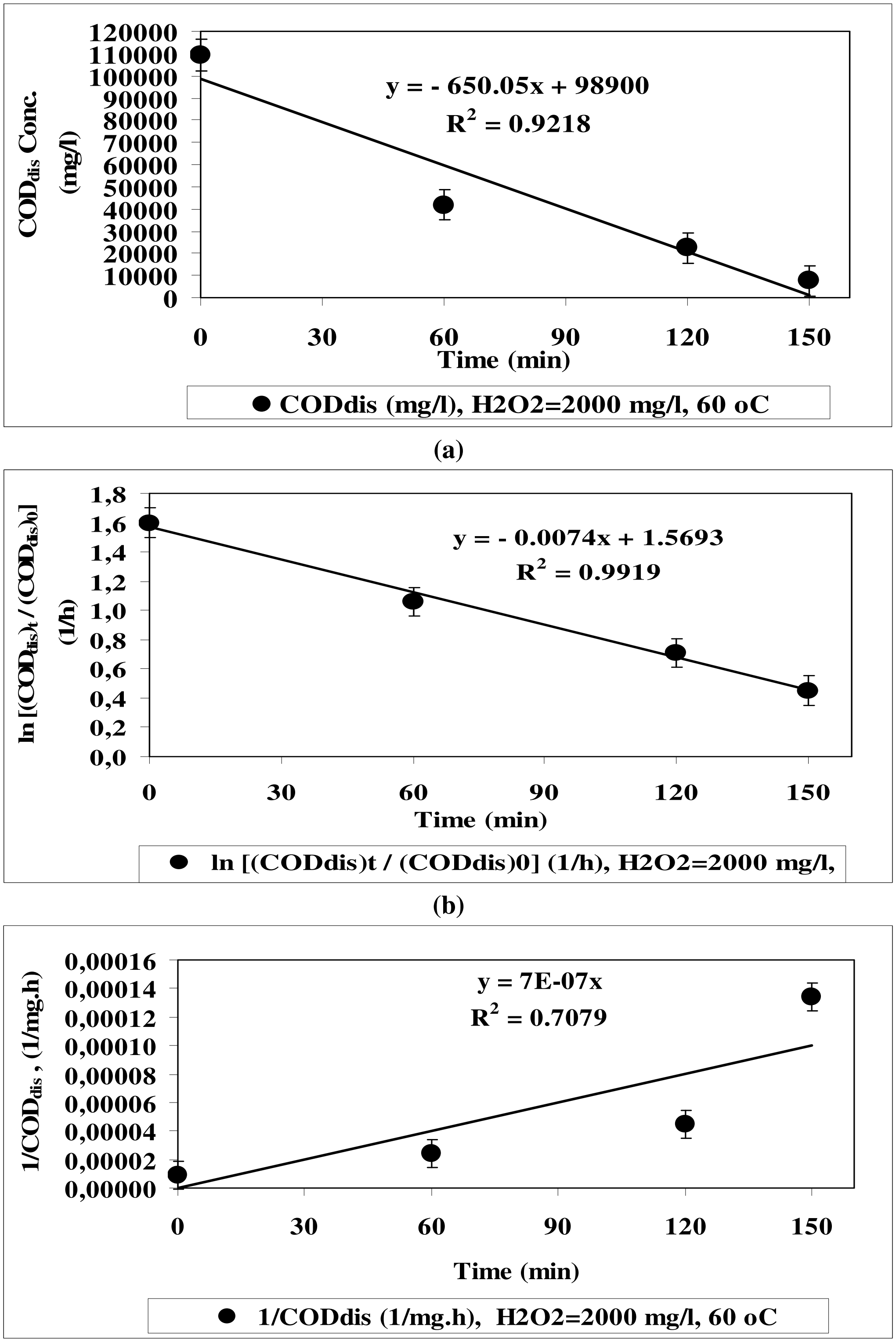
The maximum yield in COD_{dis} was 93.19% in H_2O_2=2000 mg/l after 150 min sonication time at 60^{o}C (Table 5.128). At H_2O_2=2000 mg/l the pseudo zero order rate constant was 650.050 mg/l.h (R^2=0.92) after 150 min sonication time at 60^{o}C (Table 5.128; Figure 5.126a). At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.007 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.128; Figure 5.126b). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 7.11x10^{-7} l/mg.h (R^2=0.70) after 150 min sonication time at 60^{o}C (Table 5.128; Figure 5.126c). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of COD_{dis} with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.128; Figure 5.126b). A significant linear correlation between COD_{dis} yields and H_2O_2 concentrations was observed (R^2=0.82, F=4.34, p=0.001).

The maximum yield in TOC was 92.14% in H_2O_2=2000 mg/l after 150 min sonication time at 60^{o}C (Table 5.128). At H_2O_2=2000 mg/l the pseudo zero order rate constant was 391.270 mg/l.h (R^2=0.92) after 150 min sonication time at 60^{o}C. At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.005 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.128). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 1.01x10^{-6} l/mg.h (R^2=0.93) after 150 min sonication time at 60^{o}C (Table 5.128). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TOC with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.128).

Table 5.128 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of H_2O_2=2000 mg/l concentrations after 150 min sonication time at $60^{o}C$ (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	7451.50 ± 260.80	93.19	650.050	0.92	0.007	0.99	$7.11x10^{-7}$	0.70
TOC (E)	66488 ± 2327	5224 ± 182.84	92.14	391.270	0.92	0.005	0.99	$1.01x10^{-6}$	0.93
Color (F)	99.80 ± 3.493	6.40 ± 0.23	93.59	0.595	0.84	0.015	0.99	$9.00\ x10^{-4}$	0.84
Phenol (G)	4090 ± 143.15	259.68 ± 9.09	93.65	24.228	0.83	0.006	0.99	$2.14x10^{-5}$	0.84
TAAs (H)	3000 ± 105	489.68 ± 17.14	83.68	15.890	0.86	0.011	0.99	$1.05x10^{-5}$	0.94
TFAs (J)	5200 ± 182	504.56 ± 17.66	90.30	32.146	0.96	0.016	0.99	$1.21x10^{-5}$	0.90

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total Phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).



(a)

(b)

(c)

Figure 5.126 The pseudo zero (a), first (b) and second (c) order reaction kinetics of COD_{dis} for H_2O_2=2000 mg/l concentration at 60°C (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in color was 93.59% in H_2O_2=2000 mg/l after 150 min sonication time at 60^{o}C (Table 5.128). At H_2O_2=2000 mg/l the pseudo zero order rate constant was 0.595 mg/l.h (R^2=0.84) after 150 min sonication time at 60^{o}C. At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.015 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.128). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 9.00x10^{-4} l/mg.h (R^2=0.84) after 150 min sonication time at 60^{o}C (Table 5.128). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of color with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.128).

The maximum yield in total phenol was 93.65% in H_2O_2=2000 mg/l after 150 min sonication time at 60^{o}C (Table 5.128). At H_2O_2=2000 mg/l the pseudo zero order rate constant was 24.228 mg/l.h (R^2=0.83) after 150 min sonication time at 60^{o}C. At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.006 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.128). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 2.14x10^{-5} l/mg.h (R^2=0.84) after 150 min sonication time at 60^{o}C (Table 5.128). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of total phenol with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.128).

The maximum yield in TAAs was 83.68% in H_2O_2=2000 mg/l after 150 min sonication time at 60^{o}C (Table 5.128). At H_2O_2=2000 mg/l the pseudo zero order rate constant was 15.890 mg/l.h (R^2=0.86) after 150 min sonication time at 60^{o}C. At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.011 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.128). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 1.05x10^{-5} l/mg.h (R^2=0.94) after 150 min sonication time at 60^{o}C (Table 5.128). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TAAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.128).

The maximum yield in TFAs was 90.30% in H_2O_2=2000 mg/l after 150 min sonication time at 60°C (Table 5.128). At H_2O_2=2000 mg/l the pseudo zero order rate constant was 32.146 mg/l.h (R^2=0.96) after 150 min sonication time at 60°C. At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.016 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.128). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 1.21×10^{-5} l/mg.h (R^2=0.90) after 150 min sonication time at 60°C (Table 5.128). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TFAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.128). A significant linear correlation between TFAs yields and H_2O_2 concentrations was observed (R^2=0.83, F=3.97, p=0.001).

In a study performed by Silva et al. (2007) it was observed that the pseudo zero order reaction rate constant was 4.20 mg/l.h in an OMI ww at a H_2O_2=4000 mg/l, at 80 kHz frequency, at 120 W power, at pH=7.0, after 180 min sonication time at 60°C. In this study, the pseudo first order rate constants were observed between 5.00×10^{-3} and 1.60×10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60°C for COD, TOC, color, total phenol, TAAs and TFAs sono-degradations. This could be attributed to the differences in sonication frequencies (higher sonication frequency) and to the differences in H_2O_2 concentrations (lower H_2O_2 concentrations) and to the short sonication time used throughout sonication.

In a study performed by Vassilakis et al. (2004) it was obtained that the pseudo first order reaction rate constant was 1.60×10^{-2} 1/min in an OMI ww at a H_2O_2=80.00 mg/l, at 80 kHz frequency, at 150 W power, at pH=7.0, after 240 min sonication time at 60°C. In this study, the pseudo first order rate constants were observed between 5.00×10^{-3} and 1.60×10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60°C for COD, TOC, color, total phenol, TAAs and TFAs sono-degradations. In the present study the kinetic constants exhibited similar data with the reaction kinetic obtained by Vassilakis et al. (2004) at 60°C as mentioned above. The similar kinetic rate constants could be attributed to similarities in the operational conditions such as sonication power, sonication frequency and sonication times throughout sonication.

5.14.3 Reaction Kinetic of OMI ww at 35 kHz and at 60^{o}C in the Presence of 20.00 mg/l TiO_2

In this step of this study the COD_{dis}, TOC, color, total phenol, TAAs and TFAs removal kinetics were researched according to the zero, first and second order reaction kinetics in the presence of 20.00 mg/l TiO_2 in which the maximum COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals were observed in OMI ww.

The maximum yield in COD_{dis} was 93.93% in TiO_2=20.00 mg/l after 150 min sonication time at 60^{o}C (Table 5.129). At TiO_2=20.00 mg/l the pseudo zero order rate constant was 659.520 mg/l.h (R^2=0.95) after 150 min sonication time at 60^{o}C. At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.010 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.129). At TiO_2=20.00 mg/l, the pseudo second order rate constant was 7.92x10^{-7} l/mg.h (R^2=0.65) after 150 min sonication time at 60^{o}C (Table 5.129). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of COD_{dis} with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.129).

The maximum yield in TOC was 93.35% in TiO_2=20.00 mg/l after 150 min sonication time at 60^{o}C (Table 5.129). At TiO_2=20.00 mg/l the pseudo zero order rate constant was 398.00 mg/l.h (R^2=0.95) after 150 min sonication time at 60^{o}C. At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.005 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.129). At TiO_2=20.00 mg/l, the pseudo second order rate constant was 1.18x10^{-6} l/mg.h (R^2=0.67) after 150 min sonication time at 60^{o}C (Table 5.129). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TOC with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.129).

Table 5.129 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of TiO_2=20.00 mg/l concentrations after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	6641 ± 232.44	93.93	659.520	0.95	0.010	0.99	$7.92x10^{-7}$	0.65
TOC (E)	66488 ± 2327	4419.50 ± 154.68	93.35	398.00	0.95	0.005	0.99	$1.18x10^{-6}$	0.67
Color (F)	99.80 ± 3.493	4.60 ± 0.16	95.39	0.603	0.84	0.008	0.99	$1.19x10^{-3}$	0.74
Phenol (G)	4090 ± 143.15	213.90 ± 7.50	94.77	26.472	0.96	0.010	0.99	$2.79x10^{-5}$	0.80
TAAs (H)	3000 ± 105	343.90 ± 12.04	88.54	16.608	0.83	0.010	0.99	$1.53x10^{-5}$	0.88
TFAs (J)	5200 ± 182	804.85 ± 28.17	84.52	29.896	0.98	0.007	0.99	$6.94x10^{-6}$	0.91

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total Phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

The maximum yield in color was 95.39% in TiO_2=20.00 mg/l after 150 min sonication time at 60°C (Table 5.129). At TiO_2=20.00 mg/l the pseudo zero order rate constant was 0.603 mg/l.h (R^2=0.84) after 150 min sonication time at 60°C. At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.008 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.129). At TiO_2=20.00 mg/l, the pseudo second order rate constant was $1.19x10^{-3}$ l/mg.h (R^2=0.74) after 150 min sonication time at 60°C (Table 5.129). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of color with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.129).

The maximum yield in total phenol was 94.77% in TiO_2=20.00 mg/l after 150 min sonication time at 60°C (Table 5.129). At TiO_2=20.00 mg/l the pseudo zero order rate constant was 26.472 mg/l.h (R^2=0.96) after 150 min sonication time at 60°C. At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.010 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.129). At TiO_2=20.00 mg/l, the pseudo second order rate constant was $2.79x10^{-5}$ l/mg.h (R^2=0.80) after 150 min sonication time at 60°C (Table 5.129). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of total phenol with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.129).

The maximum yield in TAAs was 88.54% in TiO_2=20.00 mg/l after 150 min sonication time at 60°C (Table 5.129). At TiO_2=20.00 mg/l the pseudo zero order rate constant was 16.608 mg/l.h (R^2=0.83) after 150 min sonication time at 60°C. At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.010 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.129). At TiO_2=20.00 mg/l, the pseudo second order rate constant was $1.53x10^{-5}$ l/mg.h (R^2=0.88) after 150 min sonication time at 60°C (Table 5.129). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TAAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.129).

The maximum yield in TFAs was 84.52% in TiO_2=20.00 mg/l after 150 min sonication time at 60°C (Table 5.129). At TiO_2=20.00 mg/l the pseudo zero order rate constant was 29.896 mg/l.h (R^2=0.98) after 150 min sonication time at 60°C. At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.007 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.129). At TiO_2=20.00 mg/l, the pseudo second order rate constant was $6.94x10^{-6}$ l/mg.h (R^2=0.91) after 150 min sonication time at 60°C (Table 5.129). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TFAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.129). A significant linear correlation between TFAs yields and TiO_2 concentrations was observed (R^2=0.92, F=5.16, p=0.001).

In a study performed by Vassilakis et al. (2004) it was found that the pseudo first order reaction rate constant was $1.46x10^{-2}$ 1/min in an OMI ww at a TiO_2=10.00 mg/l, at 80 kHz frequency, at 150 W power, at pH=7.0, after 240 min sonication time at 60°C. In this study, the pseudo first order rate constants were observed between $5.00x10^{-3}$ and $1.00x10^{-2}$ 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60°C for COD, TOC, color, total phenol, TAAs and TFAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is lower than the pseudo first order rate constants obtained by Vassilakis et al. (2004) at 60°C. This could be attributed to the lower sonication frequency and to the high TiO_2 concentrations and to the lower sonication time used throughout sonication.

In this study, the high TAAs yield was observed in TiO_2=20.00 mg/l. In a study performed by Canizares-Macias et al. (2004) it was observed that the pseudo first order reaction rate constant was $1.69x10^{-2}$ 1/min in an OMI ww at a TiO_2=20.00 mg/l, at 20 kHz frequency, at 400 W power, at pH=7.0, after 20 min sonication time at 60°C. In this study, the pseudo first order rate constants were observed between $5.00x10^{-3}$ and $1.00x10^{-2}$ 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60°C for COD, TOC, color, total phenol, TAAs and TFAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is lower than the pseudo first order rate constants obtained by Canizares-Macias et al. (2004) at 60°C as mentioned above. This could be attributed to the differences in the composition of OMI ww, to the higher sonication frequency, to the higher sonication power and to the long sonication time used throughout sonication.

5.14.4 Reaction Kinetic of OMI ww at 35 kHz and at 60^{o}C in the Presence of 15.00 mg/l NaCl

In this step of this study the COD_{dis}, TOC, color, total phenol, TAAs and TFAs removal kinetics were researched according to the pseudo zero, first and second order reaction kinetics in the presence of 15.00 g/l NaCl in which the maximum COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals were obtained in OMI ww.

The maximum yield in COD_{dis} was 93.15% in NaCl=15.00 g/l after 150 min sonication time at 60^{o}C (Table 5.130). At NaCl=15.00 g/l, the pseudo zero order rate constant was 633.230 mg/l.h (R^2=0.85) after 150 min sonication time at 60^{o}C. At NaCl=15.00 g/l, the pseudo first order rate constant was 0.010 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.130). At NaCl=15.00 g/l, the pseudo second order rate constant was 6.94x10^{-7} l/mg.h (R^2=0.71) after 150 min sonication time at 60^{o}C (Table 5.130). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of COD_{dis} with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.130).

Table 5.130 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of NaCl=15.00 g/l concentrations after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	7500.50 ± 262.52	93.15	633.230	0.85	0.010	0.99	6.94x10^{-7}	0.71
TOC (E)	66488 ± 2327	5110.50 ± 178.87	92.31	381.850	0.86	0.012	0.99	1.02x10^{-6}	0.73
Color (F)	99.80 ± 3.493	3.90 ± 0.14	96.09	0.597	0.84	0.014	0.99	1.34x10^{-3}	0.62
Phenol (G)	4090 ± 143.15	256.68 ± 8.98	93.72	25.467	0.97	0.009	0.99	2.14x10^{-5}	0.71
TAAs (H)	3000 ± 105	257 ± 9.00	91.44	17.166	0.89	0.011	0.99	2.01x10^{-5}	0.72
TFAs (J)	5200 ± 182	1496.19 ± 52.37	71.23	24.059	0.98	0.012	0.99	2.97x10^{-6}	0.92

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

The maximum yield in TOC was 92.31% in NaCl=15.00 g/l after 150 min sonication time at 60°C (Table 5.130). At NaCl=15.00 g/l, the pseudo zero order rate constant was 381.850 mg/l.h (R^2=0.86) after 150 min sonication time at 60°C. At NaCl=15.00 g/l, the pseudo first order rate constant was 0.012 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.130). At NaCl=15.00 g/l, the pseudo second order rate constant was 1.02×10^{-6} l/mg.h (R^2=0.73) after 150 min sonication time at 60°C (Table 5.130). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TOC with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.130).

The maximum yield in color was 96.09% in NaCl=15.00 g/l after 150 min sonication time at 60°C (Table 5.130). At NaCl=15.00 g/l, the pseudo zero order rate constant was 0.597 mg/l.h (R^2=0.84) after 150 min sonication time at 60°C. At NaCl=15.00 g/l, the pseudo first order rate constant was 0.014 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.130). At NaCl=15.00 g/l, the pseudo second order rate constant was 1.34×10^{-3} l/mg.h (R^2=0.62) after 150 min sonication time at 60°C (Table 5.130). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of color with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.130).

The maximum yield in total phenol was 93.72% in NaCl=15.00 g/l after 150 min sonication time at 60°C (Table 5.130). At NaCl=15.00 g/l, the pseudo zero order rate constant was 25.467 mg/l.h (R^2=0.97) after 150 min sonication time at 60°C. At NaCl=15.00 g/l, the pseudo first order rate constant was 0.009 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.130). At NaCl=15.00 g/l, the pseudo second order rate constant was 2.14×10^{-5} l/mg.h (R^2=0.71) after 150 min sonication time at 60°C (Table 5.130). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of total phenol with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.130).

The maximum yield in TAAs was 91.44% in NaCl=15.00 g/l after 150 min sonication time at 60^{o}C (Table 5.130). At NaCl=15.00 g/l, the pseudo zero order rate constant was 17.166 mg/l.h (R^2=0.89) after 150 min sonication time at 60^{o}C. At NaCl=15.00 g/l, the pseudo first order rate constant was 0.011 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.130). At NaCl=15.00 g/l, the pseudo second order rate constant was 2.01x10^{-5} l/mg.h (R^2=0.72) after 150 min sonication time at 60^{o}C (Table 5.130). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TAAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.130).

The maximum yield in TFAs was 71.23% in NaCl=15.00 g/l after 150 min sonication time at 60^{o}C (Table 5.130). At NaCl=15.00 g/l, the pseudo zero order rate constant was 24.059 mg/l.h (R^2=0.98) after 150 min sonication time at 60^{o}C. At NaCl=15.00 g/l, the pseudo first order rate constant was 0.012 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.130). At NaCl=15.00 g/l, the pseudo second order rate constant was 2.97x10^{-6} l/mg.h (R^2=0.92) after 150 min sonication time at 60^{o}C (Table 5.130). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TFAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.130).

In a study performed by Vassilakis et al. (2004) it was obtained that the pseudo first order reaction rate constant was 1.35x10^{-2} 1/min in an OMI ww at a NaCl=15.00 g/l, at 80 kHz frequency, at 150 W power, at pH=7.0, after 240 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants were observed between 9.00x10^{-3} and 1.40x10^{-2} 1/min in NaCl=15.00 g/l, after 150 min sonication time at 60^{o}C for COD, TOC, color, total phenol, TAAs and TFAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is higher than the pseudo first order rate constant obtained by Vassilakis et al. (2004) at 60^{o}C. This could be attributed to the lower sonication frequency, to the short sonication time and to the higher sonication power used throughout sonication.

In the present study, the high color yield was found in NaCl=15.00 g/l. In a study performed by De Visscher et al. (1996) it was found that the pseudo first order reaction rate constant was 1.67x10^{-2} 1/min in an OMI ww at a NaCl=12.00 g/l, at 520 kHz frequency, at 14.60 W power, at pH=7.0, after 140 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants were observed between 9.00x10^{-3} and 1.40x10^{-2} 1/min in NaCl=15.00 g/l, after 150 min sonication time at 60^{o}C for COD, TOC, color, total phenol, TAAs and TFAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is lower than the pseudo first order rate constant obtained by De Visscher et al. (1996) at 60^{o}C as mentioned above. This could be attributed to the higher NaCl concentration and to the lower sonication frequency used throughout sonication.

The kinetic rate constants found in OMI ww throughout sonication were correlated with the recent studies as shown in Table 5.131.

The kinetic rate constants calculated based on COD_{dis}, TOC, color, total phenol, TAAs and TFAs in the presence of 25^{o}C, 30^{o}C, 60^{o}C, 1 h aeration, 30 min N_2(g) (6.00 mg/l N_2) sparging, pH=10.0, Fe^{+2}=20.00 mg/l, Fe^{+3}=50.00 mg/l, HCO_3^{-1}=5.00 g/l and C_4H_9OH=2.00 g/l, were illustrated in Appendices 7.27, 7.28, 7.29, 7.30, 7.31, 7.32, 7.32, 7.34, 7.35 and 7.36, respectively.

Table 5.131 The pseudo order reaction kinetic rate constants in OMI ww throughout sonication.

ww Type	Sonication Frequency (kHz)	Sonication Power (W)	Sonication Time (min)	Pseudo Order Reaction Kinetic	Pseudo Order Reaction Kinetic Constant (k=1/min)	Based on Removed Parameters	Chemicals and Doses	References
OMI ww	80	150	240	First	$1.60x10^{-2}$	COD	H_2O_2=80.00 mg/l	Vassilakis et al. (2004)
	80	120	180	Zero	4.2 mg/l.h	color	H_2O_2=4000 mg/l	Silva et al. (2007)
	35	640	150	First	$7.00x10^{-3}$	COD	H_2O_2=2000 mg/l	In this study *
	35	640	150	First	$1.50x10^{-2}$	color	H_2O_2=2000 mg/l	In this study *
	80	150	240	First	$1.46x10^{-2}$	color	TiO_2=10.00 mg/l	Vassilakis et al. (2004)
	20	400	20	First	$1.69x10^{-2}$	TOC	TiO_2=20.00 mg/l	Canizares-Macias et al. (2004)
	35	640	150	First	$5.00x10^{-3}$	TOC	TiO_2=20.00 mg/l	In this study *
	35	640	150	First	$8.00x10^{-3}$	color	TiO_2=20.00 mg/l	In this study *
	520	14.60	140	First	$1.67x10^{-2}$	TAAs	NaCl=10.00 g/l	De Visscher et al. (1996)
	80	150	240	First	$1.35x10^{-2}$	COD	NaCl=15.00 g/l	Vassilakis et al. (2004)
	35	640	150	First	$1.00x10^{-2}$	COD	NaCl=15.00 g/l	In this study *
	35	640	150	First	$1.10x10^{-2}$	TAAs	NaCl=15.00 g/l	In this study *

* In this study the kinetic rate constants were calculated based on COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals throughout sono-degradation of OMI ww for different additives.

Table 5.131 The pseudo order reaction kinetic rate constants in OMI ww throughout sonication (cont.).

ww Type	**Sonication Frequency (kHz)**	**Sonication Power (W)**	**Sonication Time (min)**	**Pseudo Order Reaction Kinetic**	**Pseudo Order Reaction Kinetic Constant (k=1/min)**	**Based on Removed Parameters**	**Chemicals and Doses**	**References**
OMI ww	80	150	240	First	$2.11x10^{-2}$	COD	Fe^{+2}=30.00mg/l	Vassilakis et al. (2004)
	35	640	150	First	$1.50x10^{-2}$	COD	Fe^{+2}=20.00 mg/l	In this study *
	20	450	25	First	$4.20x10^{-2}$	color	DO=0.20 ml/min	Japon-Lujan et al. (2006)
	20	450	25	First	$6.15x10^{-2}$	TAAs	DO=0.50 ml/min	Japon-Lujan et al. (2006)
	20	800	80	First	$9.00x10^{-4}$	total phenol	DO=0.10 ml/min	He et al. (2007)
	35	640	150	First	$1.30x10^{-2}$	color	DO=10.00 mg/l	In this study *
	35	640	150	First	$1.10x10^{-2}$	total phenol	DO=10.00 mg/l	In this study *
	35	640	150	First	$1.10x10^{-2}$	TAAs	DO=10.00 mg/l	In this study *

* In this study the kinetic rate constants were calculated based on COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals throughout sono-degradation of OMI ww for different additives.

5.15 Removal Kinetic of TI ww

5.15.1 Reaction Kinetic of TI ww at 35 kHz and at 60^{o}C in the Presence of 2000 mg/l H_2O_2

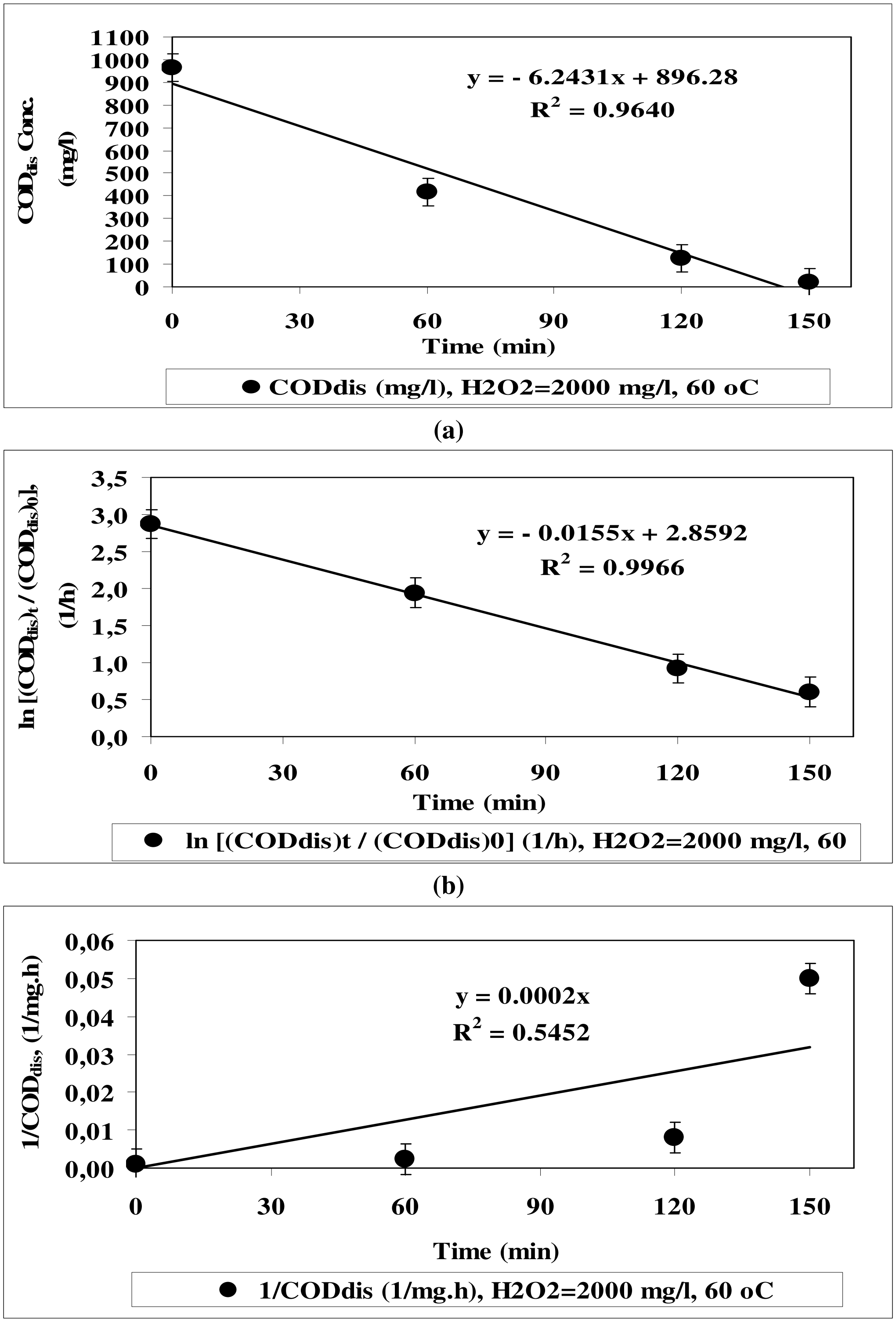
In this step of this study the COD_{dis}, TOC, color and TAAs removal kinetics were researched according to the pseudo zero, first and second order reaction kinetics in the presence of 2000 mg/l H_2O_2 in which the maximum COD_{dis}, TOC, color and TAAs removals were obtained in TI ww.

The maximum yield in COD_{dis} was 97.92% in H_2O_2=2000 mg/l after 150 min sonication time at 60^{o}C (Table 5.132). At H_2O_2=2000 mg/l, the pseudo zero order rate constant was 6.243 mg/l.h (R^2=0.96) after 150 min sonication time at 60^{o}C (Table 5.132; Figure 5.127a). At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.016 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.132; Figure 5.127b). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 2.66x10^{-4} l/mg.h (R^2=0.54) after 150 min sonication time at 60^{o}C (Table 5.132; Figure 5.127c). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of COD_{dis} with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.132; Figure 5.127b).

Table 5.132 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of H_2O_2=2000 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC** [(A)]	**ZORKC (R^2)**	**FORKC** [(B)]	**FORKC (R^2)**	**SORKC** [(C)]	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	20.02 ± 0.70	97.92	6.243	0.96	0.016	0.99	2.66×10^{-4}	0.54
TOC (E)	587.84 ± 20.57	23.63 ± 0.83	95.98	3.726	0.95	0.013	0.99	2.31×10^{-4}	0.65
Color (F)	88.56 ± 3.10	4.20 ± 0.15	95.06	0.526	0.74	0.012	0.99	1.35×10^{-3}	0.91
TAAs (G)	1620 ± 56.70	321.39 ± 11.25	80.16	8.391	0.95	0.017	0.99	1.42×10^{-5}	0.67

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).



(a)

(b)

(c)

Figure 5.127 The pseudo zero (a), first (b) and second (c) order reaction kinetics of COD_{dis} for H_2O_2=2000 mg/l concentration at 60°C (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in TOC was 95.98% in H_2O_2=2000 mg/l after 150 min sonication time at 60°C (Table 5.132). At H_2O_2=2000 mg/l, the pseudo zero order rate constant was 3.726 mg/l.h (R^2=0.95) after 150 min sonication time at 60°C (Table 5.132). At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.013 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.132; Figure 5.128). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 2.31×10^{-4} l/mg.h (R^2=0.65) after 150 min sonication time at 60°C (Table 5.132). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TOC with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.132; Figure 5.128).

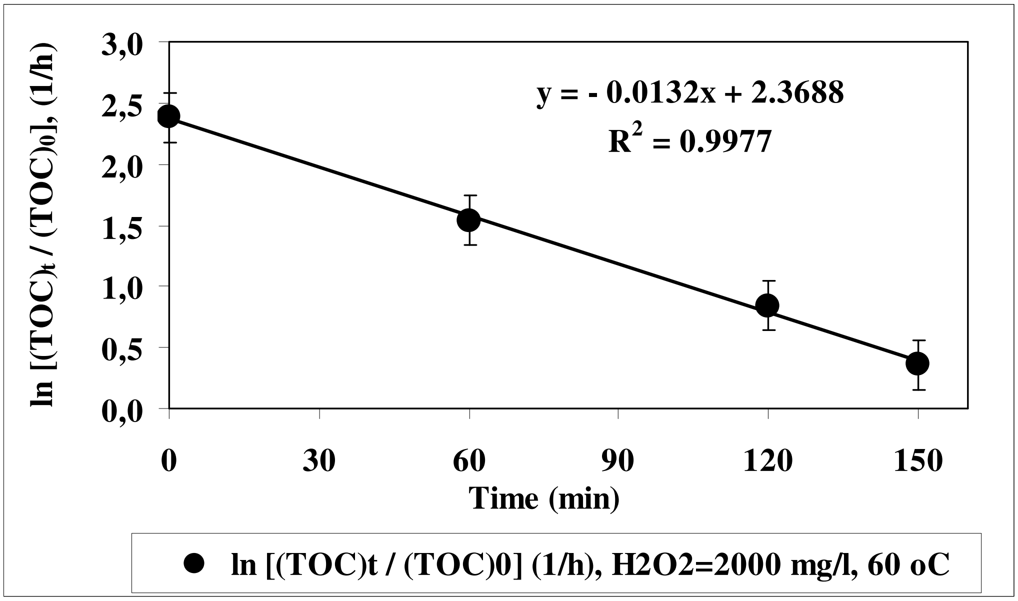


Figure 5.128 In the presence of H_2O_2=2000 mg/l concentrations the removal kinetic of TOC according to the pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in color was 95.06% in H_2O_2=2000 mg/l after 150 min sonication time at 60°C (Table 5.132). At H_2O_2=2000 mg/l, the pseudo zero order rate constant was 0.526 mg/l.h (R^2=0.74) after 150 min sonication time at 60°C (Table 5.132). At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.012 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.132; Figure 5.129). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 1.35×10^{-3} l/mg.h

(R^2=0.91) after 150 min sonication time at 60°C (Table 5.132). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of color with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.132; Figure 5.129).

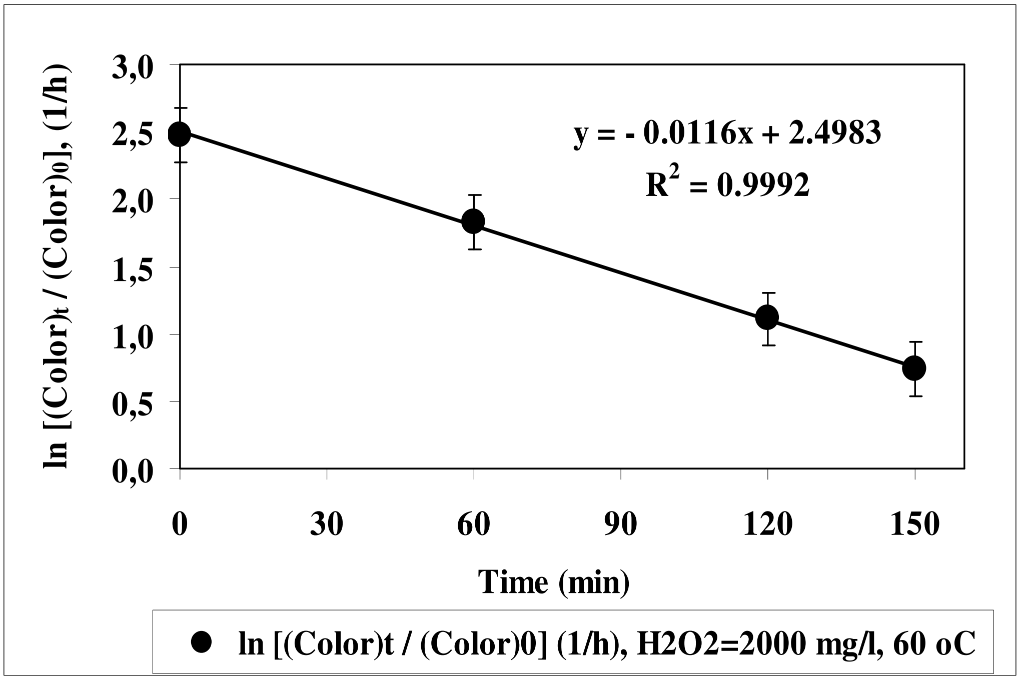


Figure 5.129 In the presence of H_2O_2=2000 mg/l concentrations the removal kinetic of color according to the pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in TAAs was 80.16% in H_2O_2=2000 mg/l after 150 min sonication time at 60°C (Table 5.132). At H_2O_2=2000 mg/l, the pseudo zero order rate constant was 8.391 mg/l.h (R^2=0.95) after 150 min sonication time at 60°C (Table 5.132). At H_2O_2=2000 mg/l, the pseudo first order rate constant was 0.017 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.132; Figure 5.4). At H_2O_2=2000 mg/l, the pseudo second order rate constant was 1.42x10^{-5} l/mg.h (R^2=0.67) after 150 min sonication time at 60°C (Table 5.132). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TAAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.132; Figure 5.130).

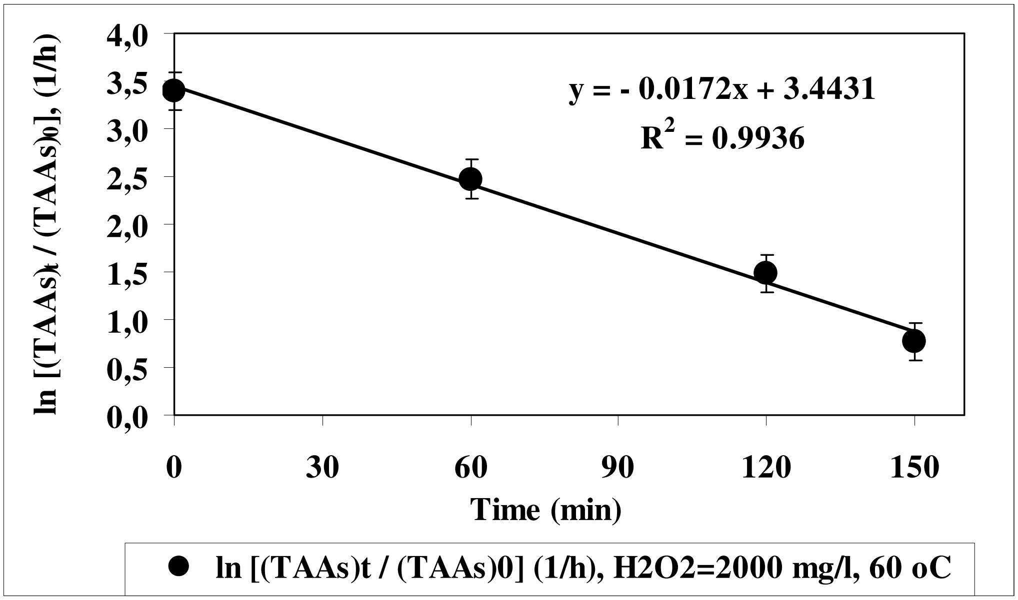


Figure 5.130 In the presence of H_2O_2=2000 mg/l concentrations the removal kinetic of TAAs according to the pseudo first order reaction kinetic (sonication power=640 W, sonication frequency=35 kHz).

The results performed by Entezari et al. (2007), Kruus et al. (1997) and Abbasi & Asl (2008) showed that the COD and TAAs in TI ww were removed according to pseudo first order reaction kinetic.

In a study performed by Abbasi & Asl (2008) it was found that the pseudo first order reaction rate constant was 9.90x10^{-3} 1/min in a TI ww, at a H_2O_2=1000 mg/l, at 35 kHz frequency, at 160 W power, at pH=7.0, after 180 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants varied between 1.20x10^{-2} and 1.70x10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is higher than the pseudo first order rate constants obtained by Abbasi & Asl (2008) at 60^{o}C. This could be attributed to the higher sonication power used throughout sonication.

Inoue, M. et al. (2006) reported a higher first order degradation rate constant for Rhodamine B than that for Orange II in TI ww. The degradation mechanism was basically explained with $OH^{\bullet}$ reactions. The pseudo first order reaction constants of Rhodamine B ranged between $1.20x10^{-4}$ and $3.12x10^{-4}$ 1/min in a TI ww, at a H_2O_2=20000 mg/l, at 35.40 mg/l initial TOC concentration, at 651 kHz frequency, at 11.40 W and at 41.50 W powers, respectively, after 600 min sonication time at 25^{o}C. The pseudo first order reaction constants of Orange II varied between $1.30x10^{-4}$ and $7.40x10^{-4}$ 1/min in H_2O_2=25000 mg/l, at 35.40 mg/l initial TOC concentration, at 651 kHz frequency, at 11.40-41.50 W powers, after 600 min sonication time at 25^{o}C. In this study, the pseudo first order kinetic constant was $1.30x10^{-2}$ 1/min in H_2O_2=2000 mg/l at 587.84 mg/l TOC concentration, after 150 min sonication time at 60^{o}C. In the present study the pseudo first order reaction constants are higher than the pseudo first order kinetic constants observed by Inoue, M. et al. (2006) at 25^{o}C. This could be attributed to the higher sonication power used throughout sonication.

In a study performed by Behnajady et al. (2008a) it was found that the pseudo first order reaction rate constant was $9.00x10^{-3}$ 1/min in a TI ww, at a H_2O_2=10.00 mg/l, at 35 kHz frequency, at 170 W power, at pH=7.0, after 80 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants ranged between $1.20x10^{-2}$ and $1.70x10^{-2}$ 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is higher than the pseudo first order rate constants obtained by Behnajady et al. (2008a) at 60^{o}C as mentioned above. This could be attributed to the long sonication time and to the higher H_2O_2 concentrations used throughout sonication.

In a study performed by Mehrdad & Hashemzadeh (2010) it was found that the pseudo first order reaction rate constants were $1.87x10^{-3}$ 1/min, $5.40x10^{-3}$ 1/min, $5.91x10^{-3}$ 1/min and $6.35x10^{-3}$ 1/min in a TI ww, at a H_2O_2=200 mg/l, at 24 kHz frequency, at 160 W, at 240 W, at 320 W and at 400 W powers, respectively, at pH=7.0, after 10000 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants varied between $1.20x10^{-2}$ and $1.70x10^{-2}$ 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is higher than the pseudo first order rate constants obtained by Mehrdad & Hashemzadeh (2010) at 60°C as mentioned above. This could be attributed to the higher sonication power and to the higher sonication frequency and to the higher H_2O_2 concentrations used throughout sonication.

In a study performed by Wang, J. et al. (2008) it was found that the pseudo first order reaction rate constant was 1.52×10^{-3} 1/min in a TI ww, at a H_2O_2=650 mg/l, at 20 kHz frequency, at 150 W power, at pH=7.0, after 240 min sonication time at 60°C. In this study, the pseudo first order rate constants varied between 1.20×10^{-2} and 1.70×10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is higher than the pseudo first order rate constants obtained by Wang, J. et al. (2008) at 60°C as mentioned above. This could be attributed to the higher sonication power, to the higher sonication frequency and to the higher H_2O_2 concentrations used throughout sonication.

In a study performed by Wang, J. et al. (2011) it was found that the pseudo first order reaction rate constant was 1.25×10^{-2} 1/min in a TI ww, at a H_2O_2=300 mg/l, at 20 kHz frequency, at 90 W power, at pH=7.0, after 120 min sonication time at 60°C. In this study, the pseudo first order rate constants ranged between 1.20×10^{-2} and 1.70×10^{-2} 1/min in H_2O_2=2000 mg/l after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. In the present study the kinetic constants exhibited similar data with the reaction kinetic obtained by Wang, J. et al. (2011) at 60°C as mentioned above. The similar kinetic rate constants could be attributed to similarities in the operational conditions such as sonication power, sonication frequency and sonication times throughout sonication.

In a study performed by Wang & Zhu (2004) it was found that the pseudo first order reaction rate constant was 5.66×10^{-1} 1/min in a TI ww, at a H_2O_2=100 mg/l, at 20 kHz frequency, at 2500 W power, at pH=7.0, after 180 min sonication time at

60^{o}C. In this study, the pseudo first order rate constants observed between 1.20x10^{-2} and 1.70x10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is lower than the pseudo first order rate constants obtained by Wang & Zhu (2004) at 60^{o}C as mentioned above. This could be attributed to the lower sonication power and to the short sonication time used throughout sonication.

In a study performed by Destaillats et al. (2000a) it was found that the pseudo first order reaction rate constant was 4.20x10^{-2} 1/min in a TI ww, at a H_2O_2=400 mg/l, at 500 kHz frequency, at 50 W power, at pH=7.0, after 300 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants ranged between 1.20x10^{-2} and 1.70x10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is lower than the pseudo first order rate constants observed by Destaillats et al. (2000a) at 60^{o}C as mentioned above. This could be attributed to the short sonication time used throughout sonication.

In a study performed by Tauber et al. (2005) it was found that the pseudo first order reaction rate constant was 1.66x10^{-1} 1/min in a TI ww, at a H_2O_2=1000 mg/l, at 850 kHz frequency, at 120 W power, at pH=7.0, after 80 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants ranged between 1.20x10^{-2} and 1.70x10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is lower than the pseudo first order rate constants obtained by Tauber et al. (2005) at 60^{o}C as mentioned above. This could be attributed to the lower sonication frequency used throughout sonication.

In a study performed by Yavuz et al. (2009) it was found that the pseudo first order reaction rate constant was 1.21x10^{-1} 1/min in a TI ww, at a H_2O_2=1000 mg/l, at 40 kHz frequency, at 25 W power, at pH=7.0, after 30 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants varied between 1.20x10^{-2} and

1.70×10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is lower than the pseudo first order rate constants obtained by Yavuz et al. (2009) at 60°C. This could be attributed to the lower sonication frequency and to the differences in the dyestuffs composition of TI ww used throughout sonication.

In a study performed by Rehorek et al. (2004) it was found that 3.10×10^{-2} 1/min, 1.21×10^{-2} and 6.21×10^{-2} 1/min pseudo first order reaction rate constants were observed in a TI ww in H_2O_2=6800 mg/l, at 850 kHz frequency, at 60 W, at 90 W and at 120 W powers, respectively, at pH=7.0, after 150 min sonication time at 60°C. In this study, the pseudo first order rate constants varied between 1.20×10^{-2} and 1.70×10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is lower than the pseudo first order rate constants obtained by Rehorek et al. (2004) at 60°C as mentioned above. This could be attributed to the lower sonication frequency and to the differences in the dyestuffs properties of TI ww used throughout sonication.

In a study performed by Zhang, H. et al. (2006) it was found that pseudo first order reaction rate constant was 5.17×10^{-1} 1/min in a TI ww, at a H_2O_2=170 mg/l, at 20 kHz frequency, at 250 W power, at pH=7.0, after 30 min sonication time at 60°C. In this study, the pseudo first order rate constants ranged between 1.20×10^{-2} and 1.70×10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is lower than the pseudo first order rate constants obtained by Zhang, H. et al. (2006) at 60°C as mentioned above. This could be attributed to the dyestuffs properties of TI ww used throughout sonication.

In a study performed by Gültekin et al. (2009) it was found that pseudo first order reaction rate constant was 6.48×10^{-2} 1/min in a TI ww, at a H_2O_2=120 mg/l, at 300 kHz frequency, at 25 W power, at pH=7.0, after 30 min sonication time at 60°C. In this study, the pseudo first order rate constants varied between 1.20x10^{-2} and 1.70x10^{-2} 1/min in H_2O_2=2000 mg/l, after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is lower than the pseudo first order rate constants obtained by Gültekin et al. (2009) at 60°C as mentioned above. This could be attributed to the lower sonication frequency and to the dyestuffs properties of TI ww used throughout sonication.

5.15.2 Reaction Kinetic of TI ww at 35 kHz and at 60°C in the Presence of 20.00 mg/l TiO_2

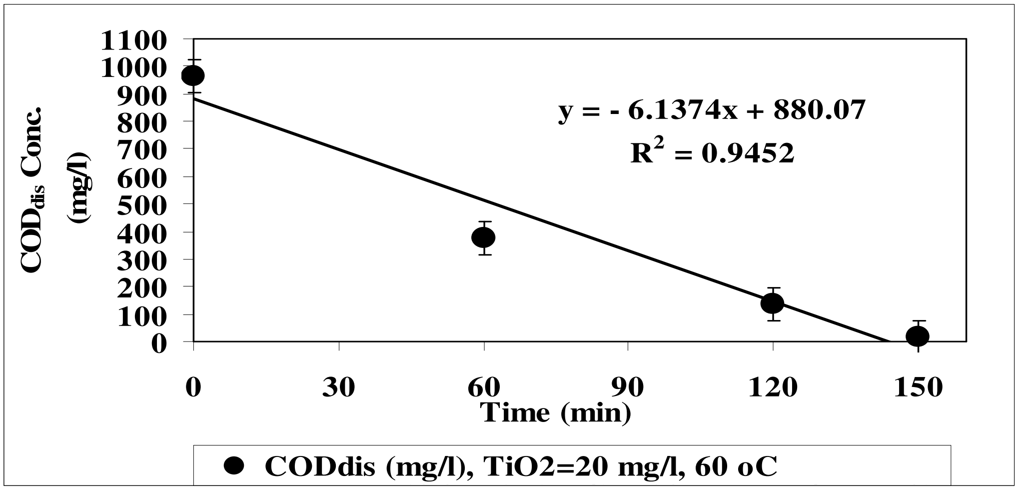
In this step of this study the COD_{dis}, TOC, color and TAAs removal kinetics were researched according to the pseudo zero, first and second order reaction kinetics in the presence of 20.00 mg/l TiO_2 in which the maximum COD_{dis}, TOC, color and TAAs removals were observed in TI ww.

The maximum yield in COD_{dis} was 98.13% in TiO_2=20.00 mg/l after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo zero order rate constant was 6.137 mg/l.h (R^2=0.94) after 150 min sonication time at 60°C (Table 5.133; Figure 5.131a). At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.015 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.133; Figure 5.131b). At TiO_2=20.00 mg/l, the pseudo second order rate constant was 2.92x10^{-4} l/mg.h (R^2=0.51) after 150 min sonication time at 60°C (Table 5.133; Figure 5.131c). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of COD_{dis} with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.133; Figure 5.131b).

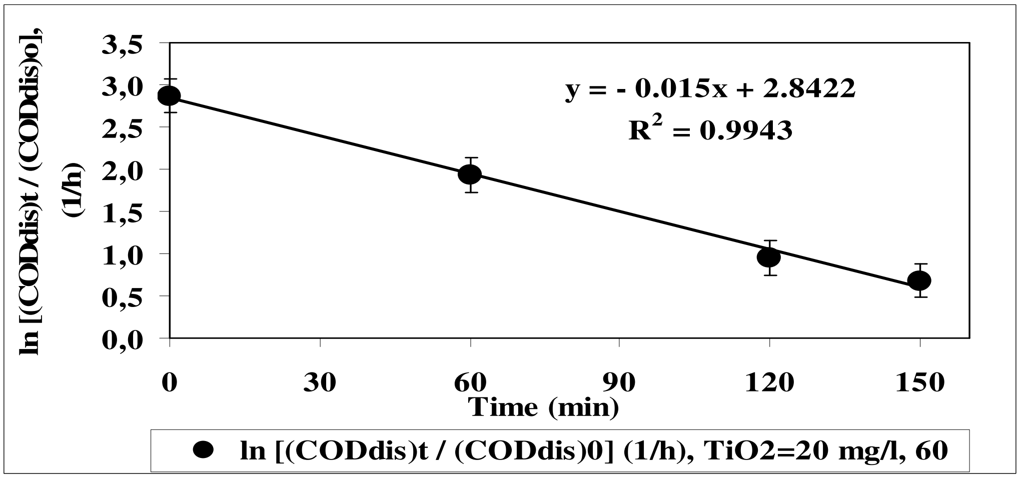
Table 5.133 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of TiO_2=20.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	18.02 ± 0.63	98.13	6.137	0.94	0.015	0.99	$2.92x10^{-4}$	0.51
TOC (E)	587.84 ± 20.57	10.68 ± 0.37	98.18	3.745	0.94	0.015	0.99	$4.92x10^{-4}$	0.51
Color (F)	88.56 ± 3.10	3.20 ± 0.11	96.24	0.539	0.79	0.011	0.99	$1.77x10^{-3}$	0.79
TAAs (G)	1620 ± 56.70	372.27 ± 13.03	77.02	8.449	0.97	0.019	0.99	$1.26x10^{-5}$	0.78

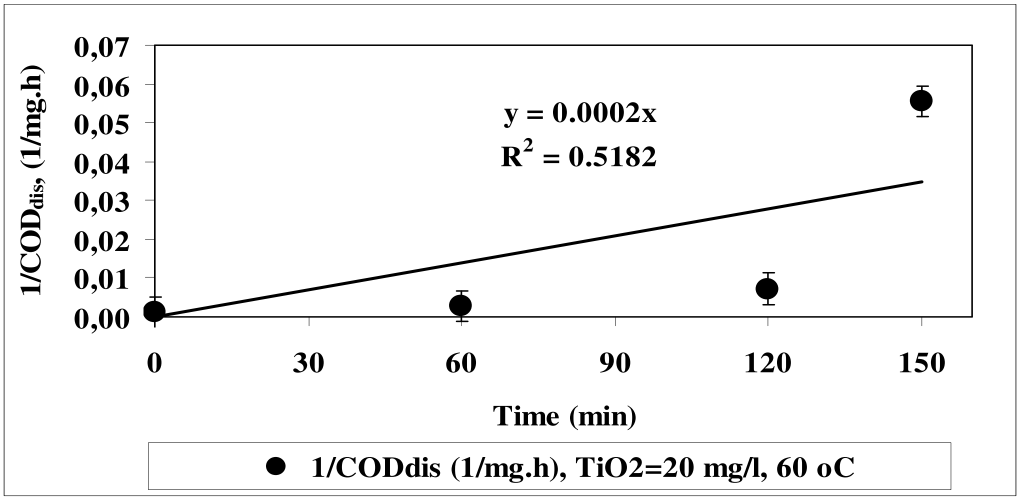
(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).



(a)



(b)



(c)

Figure 5.131 The pseudo zero (a), first (b) and second (c) order reaction kinetics of COD_{dis} for TiO_2=20.00 mg/l concentration at 60°C (sonication power=640 W, sonication frequency=35 kHz).

The maximum yield in TOC was 98.18% in TiO_2=20.00 mg/l after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo zero order rate constant was 3.745 mg/l.h (R^2=0.94) after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.015 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo second order rate constant was 4.92×10^{-4} l/mg.h (R^2=0.51) after 150 min sonication time at 60°C (Table 5.133). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TOC with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.133).

The maximum yield in color was 96.24% in TiO_2=20.00 mg/l after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo zero order rate constant was 0.539 mg/l.h (R^2=0.79) after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.011 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo second order rate constant was 1.77×10^{-3} l/mg.h (R^2=0.79) after 150 min sonication time at 60°C (Table 5.133). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of color with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.133).

The maximum yield in TAAs was 77.02% in TiO_2=20.00 mg/l after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo zero order rate constant was 8.449 mg/l.h (R^2=0.97) after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo first order rate constant was 0.019 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.133). At TiO_2=20.00 mg/l, the pseudo second order rate constant was 1.26×10^{-5} l/mg.h (R^2=0.78) after 150 min sonication time at 60°C (Table 5.133). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TAAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.133).

Various studies have demonstrated that decolorization rates fit a pseudo-first-order reaction model in TI ww (Song et al., 2007; Mrowetz et al., 2003; Kritikos et al., 2007; Wu, C.-H., 2008; Wu & Yu, 2009).

In a study performed by Yuan et al. (2009) it was found that pseudo first order reaction rate constants were 3.30×10^{-4} 1/min, 3.60×10^{-4} 1/min, 2.01×10^{-5} 1/min, 2.33×10^{-5} and 1.90×10^{-4} 1/min in a TI ww, at a TiO_2=100 mg/l, at 18 kHz, at 20 kHz, at 24 kHz, at 27 kHz and at 30 kHz frequency, respectively, at 24 W power, at pH=7.0, after 195 min sonication time at 60°C. In this study, the pseudo first order rate constants varied between 1.10×10^{-2} and 1.90×10^{-2} 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is higher than the pseudo first order rate constants obtained by Yuan et al. (2009) at 60°C as mentioned above. This could be attributed to the higher sonication frequency and to the higher sonication power used throughout sonication.

In a study performed by Abbasi & Asl (2008) it was found that the pseudo first order reaction rate constant was 9.00×10^{-4} 1/min in a TI ww, at a TiO_2=100 mg/l, at 35 kHz frequency, at 160 W power, at pH=7.0, after 180 min sonication time at 60°C. In this study, the pseudo first order rate constants ranged between 1.10×10^{-2} and 1.90×10^{-2} 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is higher than the pseudo first order rate constants obtained by Abbasi & Asl (2008) at 60°C as mentioned above. This could be attributed to the higher sonication power used throughout sonication.

In a study performed by Wang, J. et al. (2009) it was found that the pseudo first order reaction rate constant was 4.40×10^{-3} 1/min in a TI ww, at a TiO_2=20.00 mg/l, at 40 kHz frequency, at 50 W power, at pH=7.0, after 100 min sonication time at 60°C. In this study, the pseudo first order rate constants varied between 1.10×10^{-2} and 1.90×10^{-2} 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is higher than the pseudo first order rate constants obtained by Wang, J. et al. (2009) at 60^{o}C as mentioned above. This could be attributed to the higher sonication power and to the long sonication time used throughout sonication.

In a study performed by Mrowetz et al. (2003) it was found that pseudo first order reaction rate constants were 9.90x10^{-3} and 1.00x10^{-2} 1/min in a TI ww, at 100 and 280 mg/l TiO_2, respectively, at 20 kHz frequency, at 15 W power, at pH=7.0, after 330 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants varied between 1.10x10^{-2} and 1.90x10^{-2} 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is higher than the pseudo first order rate constants obtained by Mrowetz et al. (2003) at 60^{o}C as mentioned above. This could be attributed to the higher sonication frequency and to the higher sonication power used throughout sonication.

In a study performed by Madhavan et al. (2010) it was found that the pseudo first order reaction rate constant was 5.00x10^{-7} 1/min in a TI ww, at a TiO_2=1000 mg/l, at 213 kHz frequency, at 20 W power, at pH=7.0, after 60 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants ranged between 1.10x10^{-2} and 1.90x10^{-2} 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is higher than the pseudo first order rate constants obtained by Madhavan et al. (2010) at 60^{o}C as mentioned above. This could be attributed to the higher sonication power and to the long sonication time used throughout sonication.

In a study performed by Gonzalez & Martinez (2008) it was found that the pseudo first order reaction rate constant was 9.67x10^{-4} 1/min in a TI ww, at a TiO_2=100 mg/l, at 20 kHz frequency, at 15 W power, at pH=7.0, after 60 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants varied between 1.10x10^{-2} and 1.90x10^{-2} 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is higher than the pseudo first order rate constants obtained by Gonzalez & Martinez (2008) at 60^{o}C as mentioned above. This could be attributed to the higher sonication frequency, to the higher sonication power and to the long sonication time used throughout sonication.

In a study performed by Tangestaninejad et al. (2008) it was found that pseudo first order reaction rate constants were 9.20x10^{-2} 1/min, 9.50x10^{-2} 1/min, 1.40x10^{-1} and 1.08x10^{-1} 1/min in a TI ww, at a TiO_2=50.00 mg/l, at 24 kHz frequency, at 400 W power, at pH=7.0, after 15 min, 20 min, 25 and 30 min sonication times, respectively, at 60^{o}C. In this study, the pseudo first order rate constants ranged between 1.10x10^{-2} and 1.90x10^{-2} 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is lower than the pseudo first order rate constants obtained by Tangestaninejad et al. (2008) at 60^{o}C as mentioned above. This could be attributed to the differences in the dyestuffs properties of TI ww used throughout sonication.

In a study performed by Wu, C.-H. (2009) and Wu & Yu (2009) it was found that pseudo first order reaction rate constants were 3.10x10^{-1} 1/min and 9.40x10^{-1} 1/min in a TI ww, at a TiO_2=2000 mg/l, at 40 kHz frequency, at 400 W power, at pH=7.0, after 120 and 240 min sonication times, respectively, at 60^{o}C. In this study, the pseudo first order rate constants ranged between 1.10x10^{-2} and 1.90x10^{-2} 1/min in TiO_2=20 mg/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is lower than the pseudo first order rate constants obtained by Wu, C.-H. (2009) and Wu & Yu (2009) at 60^{o}C as mentioned above. This could be attributed to the different dyestuff properties of TI ww and to the short sonication time used throughout sonication.

In a study performed by Eren & Ince (2010) it was found that the pseudo first order reaction rate constant was 2.53x10^{-2} 1/min in a TI ww, at a TiO_2=4400 mg/l, at 20 kHz frequency, at 180 W power, at pH=7.0, after 30 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants varied between 1.10x10^{-2} and

$1.90x10^{-2}$ 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60^oC for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^oC is lower than the pseudo first order rate constants obtained by Eren & Ince (2010) at 60^oC as mentioned above. This could be attributed to the different dyestuff properties of TI ww used throughout sonication.

In a study performed by Byun & Kwak (2005) it was found that the pseudo first order reaction rate constant was $8.25x10^{-2}$ 1/min in a TI ww, at a TiO_2=7600 mg/l, at 20 kHz frequency, at 165 W power, at pH=7.0, after 60 min sonication time at 60^oC. In this study, the pseudo first order rate constants varied between $1.10x10^{-2}$ and $1.90x10^{-2}$ 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60^oC for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^oC is lower than the pseudo first order rate constants obtained by Byun & Kwak (2005) at 60^oC as mentioned above. This could be attributed to the different dyestuff properties of TI ww used throughout sonication.

In a study performed by Jamalluddin & Abdullah (2010) it was found that the pseudo first order reaction rate constant was $6.10x10^{-2}$ 1/min in a TI ww, at a TiO_2=76.00 mg/l, at 35 kHz frequency, at 60 W power, at pH=7.0, after 60 min sonication time at 60^oC. In this study, the pseudo first order rate constants varied between $1.10x10^{-2}$ and $1.90x10^{-2}$ 1/min in TiO_2=20.00 mg/l, after 150 min sonication time at 60^oC for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^oC is lower than the pseudo first order rate constants obtained by Jamalluddin & Abdullah (2010) at 60^oC as mentioned above. This could be attributed to the different dyestuff properties of TI ww used throughout sonication.

5.15.3 Reaction Kinetic of TI ww at 35 kHz and at 60^{o}C in the Presence of 15.00 g/l NaCl

In this step of this study the COD$_{dis}$, TOC, color and TAAs removal kinetics were researched according to the pseudo zero, first and second order reaction kinetics in the presence of 15.00 g/l NaCl in which the maximum COD$_{dis}$, TOC, color and TAAs removals were obtained in TI ww.

The maximum yield in COD$_{dis}$ was 97.32% in NaCl=15.00 g/l after 150 min sonication time at 60^{o}C (Table 5.134). At NaCl=15.00 g/l, the pseudo zero order rate constant was 5.960 mg/l.h (R^2=0.91) after 150 min sonication time at 60^{o}C (Table 5.134). At NaCl=15.00 g/l, the pseudo first order rate constant was 0.016 1/h (R^2=0.99) after 150 min sonication time at 60^{o}C (Table 5.134). At NaCl=15.00 g/l, the pseudo second order rate constant was 2.03x10^{-4} l/mg.h (R^2=0.54) after 150 min sonication time at 60^{o}C (Table 5.134). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of COD$_{dis}$ with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^{o}C (Table 5.134).

Table 5.134 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of NaCl=15.00 g/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC** (A)	**ZORKC (R^2)**	**FORKC** (B)	**FORKC (R^2)**	**SORKC** (C)	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	25.80 ± 0.90	97.32	5.960	0.91	0.016	0.99	$2.03x10^{-4}$	0.54
TOC (E)	587.84 ± 20.57	18.64 ± 0.65	96.83	3.633	0.92	0.017	0.99	$2.82x10^{-4}$	0.57
Color (F)	88.56 ± 3.10	2.10 ± 0.07	97.53	0.543	0.72	0.026	0.99	$3.16x10^{-3}$	0.98
TAAs (G)	1620 ± 56.70	561.59 ± 19.66	65.33	6.918	0.98	0.023	0.99	$7.11x10^{-6}$	0.83

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

The maximum yield in TOC was 96.83% in NaCl=15.00 g/l after 150 min sonication time at 60°C (Table 5.134). At NaCl=15.00 g/l, the pseudo zero order rate constant was 3.633 mg/l.h (R^2=0.92) after 150 min sonication time at 60°C (Table 5.134). At NaCl=15.00 g/l, the pseudo first order rate constant was 0.017 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.134). At NaCl=15.00 g/l, the pseudo second order rate constant was 2.82×10^{-4} l/mg.h (R^2=0.57) after 150 min sonication time at 60°C (Table 5.134). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TOC with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.134).

The maximum yield in color was 97.53% in NaCl=15.00 g/l after 150 min sonication time at 60°C (Table 5.134). At NaCl=15.00 g/l, the pseudo zero order rate constant was 0.543 mg/l.h (R^2=0.72) after 150 min sonication time at 60°C (Table 5.134). At NaCl=15.00 g/l, the pseudo first order rate constant was 0.026 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.134). At NaCl=15.00 g/l, the pseudo second order rate constant was 3.16×10^{-3} l/mg.h (R^2=0.98) after 150 min sonication time at 60°C (Table 5.134). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of color with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.134).

The maximum yield in TAAs was 65.33% in NaCl=15.00 g/l after 150 min sonication time at 60°C (Table 5.134). At NaCl=15.00 g/l, the pseudo zero order rate constant was 6.918 mg/l.h (R^2=0.98) after 150 min sonication time at 60°C (Table 5.134). At NaCl=15.00 g/l, the pseudo first order rate constant was 0.023 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.134). At NaCl=15.00 g/l, the pseudo second order rate constant was 7.11×10^{-6} l/mg.h (R^2=0.83) after 150 min sonication time at 60°C (Table 5.134). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TAAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.134).

The sonochemical degradation of non-volatile pollutants in aqueous solution takes place in the bubble-bulk interface area due to the exposure to free radicals and high temperature and pressure (Fındık & Gündüz, 2007; Nam et al., 2003; Sayan & Edecan, 2008). Addition of NaCl can increase the hydrophilicity, the surface tension and ionic strength of the aqueous phase and decrease the vapor pressure (Seymour & Gupta, 1997). All these factors help in collapsing of the bubbles more violently, and resulting in high degradation degrees of COD, TOC and color in TI ww (Wang, J. et al., 2007; Wang, J.- P. et al., 2007).

Gultekin & Ince (2006) studied the degradation of aryl-azo-naphthol dyes (C.I. Reactive Orange 16 and C.I. Acid Orange 7) by sonication and found that the rate of bleaching was decelerated by increasing concentrations of the dye in a TI ww. The pseudo first order reaction kinetic was suitable for these decolorization. The pseudo first order rate constants were found as $42.90\text{x}10^{-3}$ 1/min and $16.90\text{x}10^{-3}$ 1/min for C.I. Reactive Orange 16 and C.I. Acid Orange 7 dyes, respectively at a frequency of 40 kHz, 400 W power after 60 min sonication time at pH=3.0-9.0 and at 30^{o}C. In this study, the pseudo first order rate constants varied between $1.60\text{x}10^{-2}$ and $2.60\text{x}10^{-2}$ 1/min in NaCl=15.00 g/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is higher than the pseudo first order rate constants obtained by Gultekin & Ince (2006) at 60^{o}C as mentioned above. This could be attributed to the long sonication time and to the higher sonication power used throughout sonication.

In a study performed by Behnajady et al. (2008b) it was found that the pseudo first order reaction rate constant was $8.00\text{x}10^{-3}$ 1/min in a TI ww, at NaCl=2.50 g/l, at 35 kHz frequency, at 170 W power, at pH=7.0, after 180 min sonication time at 60^{o}C. In this study, the pseudo first order rate constants ranged between $1.60\text{x}10^{-2}$ and $2.60\text{x}10^{-2}$ 1/min in NaCl=15.00 g/l, after 150 min sonication time at 60^{o}C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^{o}C is higher than the pseudo first order rate constants obtained by Behnajady et al. (2008b) at 60^{o}C as mentioned above. This could be attributed to the higher sonication power and to the higher NaCl concentrations used throughout sonication.

In a study performed by Wu, C.-H. (2008) and Wu & Yu (2009) it was found that pseudo first order reaction rate constants were $1.21x10^{-3}$ 1/min and $2.20x10^{-3}$ 1/min in a TI ww, at 5.00 and 7.50 g/l NaCl concentrations, respectively, at 40 kHz frequency, at 400 W power, at pH=7.0, after 120 min sonication time at 60^oC. In this study, the pseudo first order rate constants varied between $1.60x10^{-2}$ and $2.60x10^{-2}$ 1/min in NaCl=15.00 g/l after 150 min sonication time at 60^oC for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^oC is higher than the pseudo first order rate constants obtained by Wu, C.-H. (2008) and Wu & Yu (2009) at 60^oC as mentioned above. This could be attributed to the higher sonication power, to the higher NaCl concentrations and to the long sonication time used throughout sonication.

In a study performed by Wang, X. et al. (2008) it was found that pseudo first order reaction rate constants were $1.24x10^{-3}$ 1/min, $1.44x10^{-3}$ 1/min $1.74x10^{-3}$ 1/min in a TI ww, at 3.00, 6.00 and 9.00 g/l NaCl concentrations, respectively, at 20 kHz frequency, at 150 W power, at pH=7.0, after 240 min sonication time at 60^oC. In this study, the pseudo first order rate constants varied between $1.60x10^{-2}$ and $2.60x10^{-2}$ 1/min in NaCl=15.00 g/l after 150 min sonication time at 60^oC for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^oC is higher than the pseudo first order rate constants obtained by Wang, X. et al. (2008) at 60^oC as mentioned above. This could be attributed to the higher sonication frequency, to the higher sonication power, to the higher NaCl concentrations and to the long sonication time used throughout sonication.

5.15.4 Reaction Kinetic of TI ww at 35 kHz and at 60°C in the Presence of 20.00 mg/l Fe^{+2}

In this step of this study the COD_{dis}, TOC, color and TAAs removal kinetics were researched according to the pseudo zero, first and second order reaction kinetics in the presence of 20.00 mg/l Fe^{+2} in which the maximum COD_{dis}, TOC, color and TAAs removals were observed in TI ww.

The maximum yield in COD_{dis} was 99.26% in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60°C (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo zero order rate constant was 6.181 mg/l.h (R^2=0.91) after 150 min sonication time at 60°C (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo first order rate constant was 0.015 1/h (R^2=0.99) after 150 min sonication time at 60°C (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo second order rate constant was 7.26×10^{-4} l/mg.h (R^2=0.46) after 150 min sonication time at 60°C (Table 5.135). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of COD_{dis} with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.135).

Table 5.135 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of Fe^{+2}=20.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	7.14 ± 0.25	99.26	6.181	0.91	0.015	0.99	7.26x10^{-4}	0.46
TOC (E)	587.84 ± 20.57	4.51 ± 0.16	99.23	3.773	0.92	0.018	0.99	1.15x10^{-3}	0.46
Color (F)	88.56 ± 3.10	2.90 ± 0.11	96.59	0.532	0.74	0.017	0.99	1.92x10^{-3}	0.82
TAAs (G)	1620 ± 56.70	374.05 ± 13.09	76.91	8.176	0.96	0.024	0.99	1.20x10^{-5}	0.73

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

The maximum yield in TOC was 99.23% in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60^oC (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo zero order rate constant was 3.773 mg/l.h (R^2=0.92) after 150 min sonication time at 60^oC (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo first order rate constant was 0.018 1/h (R^2=0.99) after 150 min sonication time at 60^oC (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo second order rate constant was $1.15x10^{-3}$ l/mg.h (R^2=0.46) after 150 min sonication time at 60^oC (Table 5.135). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of TOC with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^oC (Table 5.135).

The maximum yield in color was 96.59% in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60^oC (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo zero order rate constant was 0.532 mg/l.h (R^2=0.74) after 150 min sonication time at 60^oC (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo first order rate constant was 0.017 1/h (R^2=0.99) after 150 min sonication time at 60^oC (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo second order rate constant was $1.92x10^{-3}$ l/mg.h (R^2=0.82) after 150 min sonication time at 60^oC (Table 5.135). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of color with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60^oC (Table 5.135). A significant linear correlation between color yields and Fe^{+2} concentrations was observed (R^2=0.85, F=4.56, p=0.001).

The maximum yield in TAAs was 76.91% in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60^oC (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo zero order rate constant was 8.176 mg/l.h (R^2=0.96) after 150 min sonication time at 60^oC (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo first order rate constant was 0.024 1/h (R^2=0.99) after 150 min sonication time at 60^oC (Table 5.135). At Fe^{+2}=20.00 mg/l, the pseudo second order rate constant was $1.20x10^{-5}$ l/mg.h (R^2=0.73) after 150 min sonication time at 60^oC (Table 5.135). Among the reaction kinetics used it was found that the pseudo first order reaction kinetic was suitable for the sonodegradation of

TAAs with the highest linear correlation coefficient of R^2=0.99 after 150 min sonication time at 60°C (Table 5.135).

Okitsu et al. (2005) proposed a kinetic model for ultrasonic degradation of azo dye in TI ww. The proposed kinetics model is based on the local reaction site at the interface region of the cavitation bubbles, where azo dye molecules are quickly decomposed because an extremely high concentration of $OH^\bullet$ exists in this region. They also proposed the applicability of their model for various sonochemical reactions occurring in an aqueous medium in TI ww. The obtained data were then roughly analyzed to obey a pseudo-first order kinetics.

In a study performed by Gopinath et al. (2010) it was found that the pseudo first order reaction rate constant was $6.85x10^{-3}$ 1/min in a TI ww, at a Fe^{+2}=30.00 mg/l, at 30 kHz frequency, at 150 W power, at pH=7.0, after 60 min sonication time at 60°C. In this study, the pseudo first order rate constants varied between $1.50x10^{-2}$ and $2.40x10^{-2}$ 1/min in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is higher than the pseudo first order rate constants obtained by Gopinath et al. (2010) at 60°C as mentioned above. This could be attributed to the higher sonication frequency, to the higher sonication power, to the long sonication time used throughout sonication.

In a study performed by Mrowetz et al. (2003) it was found that the pseudo first order reaction rate constant was $1.20x10^{-3}$ 1/min in a TI ww, at a Fe^{+2}=1040 mg/l, at 20 kHz frequency, at 15 W power, at pH=7.0, after 130 min sonication time at 60°C. In this study, the pseudo first order rate constants ranged between $1.50x10^{-2}$ and $2.40x10^{-2}$ 1/min in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is higher than the pseudo first order rate constants obtained by Mrowetz et al. (2003) at 60°C as mentioned above. This could be attributed to the higher sonication frequency, to the higher sonication power, to the long sonication time used throughout sonication.

In a study performed by Wang, J. et al. (2008) it was found that the pseudo first order reaction rate constant was $6.10x10^{-3}$ 1/min in a TI ww, at a Fe^{+2}=260 mg/l, at 20 kHz frequency, at 150 W power, at pH=7.0, after 240 min sonication time at 60^oC. In this study, the pseudo first order rate constants ranged between $1.50x10^{-2}$ and $2.40x10^{-2}$ 1/min in Fe^{+2}=20.00 mg/l after 150 min sonication at 60^oC for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^oC is higher than the pseudo first order rate constants obtained by Wang, J. et al. (2008) at 60^oC as mentioned above. This could be attributed to the higher sonication frequency and to the higher sonication power used throughout sonication.

In a study performed by Mehrdad & Hashemzadeh (2010) it was found that pseudo first order reaction rate constants were $7.39x10^{-3}$ 1/min, $1.28x10^{-2}$ 1/min, $1.49x10^{-2}$ and $1.85x10^{-2}$ 1/min in a TI ww, at a Fe^{+2}=2000 mg/l, at 24 kHz frequency, at 160 W, at 240 W, at 320 W and at 400 W powers, respectively, at pH=7.0, after 10000 min sonication time at 60^oC. In this study, the pseudo first order rate constants varied between $1.50x10^{-2}$ and $2.40x10^{-2}$ 1/min in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60^oC for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^oC is higher than the pseudo first order rate constants obtained by Mehrdad & Hashemzadeh (2010) at 60^oC as mentioned above. This could be attributed to the higher sonication frequency and to the higher sonication power used throughout sonication.

In a study performed by Vajnhandl & Le Marechal (2007) it was found that the pseudo first order reaction rate constant was $3.23x10^{-2}$ 1/min in a TI ww, at a Fe^{+2}=20.00 mg/l, at 817 kHz frequency, at 150 W power, at pH=7.0, after 80 min sonication time at 60^oC. In this study, the pseudo first order rate constants varied between $1.50x10^{-2}$ and $2.40x10^{-2}$ 1/min in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60^oC for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60^oC is higher than the pseudo first order rate constants obtained by Vajnhandl & Le Marechal (2007) at 60^oC as mentioned above. This could be attributed to the higher sonication power and to the long sonication time used throughout sonication.

In a study performed by Zhang, J. et al. (2009) it was found that the pseudo first order reaction rate constant was 2.58×10^{-1} 1/min in a TI ww, at a Fe^{+2}=500 mg/l, at 20 kHz frequency, at 250 W power, at pH=7.0, after 30 min sonication time at 60°C. In this study, the pseudo first order rate constants ranged between 1.50×10^{-2} and 2.40×10^{-2} 1/min in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is lower than the pseudo first order rate constants obtained by Zhang, J. et al. (2009) at 60°C as mentioned above. This could be attributed to the different dyestuff concentrations in the composition of TI ww used throughout sonication.

In a study performed by Jamalluddin & Abdullah (2010) it was found that the pseudo first order reaction rate constant was 5.00×10^{-2} 1/min in a TI ww, at a Fe^{+2}=52.00 mg/l, at 35 kHz frequency, at 50 W power, at pH=7.0, after 60 min sonication time at 60°C. In this study, the pseudo first order rate constants varied between 1.50×10^{-2} and 2.40×10^{-2} 1/min in Fe^{+2}=20.00 mg/l after 150 min sonication time at 60°C for COD, TOC, color and TAAs sono-degradations. The pseudo first order rate constants in the present study at 60°C is lower than the pseudo first order rate constants obtained by Jamalluddin & Abdullah (2010) at 60°C as mentioned above. This could be attributed to the different dyestuff concentrations used throughout sonication.

The kinetic rate constants found in TI ww throughout sonication were correlated with the recent studies as shown in Table 5.136.

The kinetic rate constants calculated based on COD_{dis}, TOC, color and TAAs in the presence of 25^oC, 30^oC, 60^oC, 1 h aeration, 30 min $N_2(g)$ (6.00 mg/l N_2) sparging, pH=10.0, DO=10.00 mg/l, Fe^{+3}=50.00 mg/l, HCO_3^{-1}=5.00 g/l and C_4H_9OH=2.00 g/l, were illustrated in Appendices 7.37, 7.38, 7.39, 7.40, 7.41, 7.42, 7.43, 7.44, 7.45 and 7.46, respectively.

Table 5.136 The pseudo order reaction kinetic rate constants in TI ww throughout sonication.

ww Type	Sonication Frequency (kHz)	Sonication Power (W)	Sonication Time (min)	Pseudo Order Reaction Kinetic	Pseudo Order Reaction Kinetic Constant (k=1/min)	Based on Removed Parameters	Chemicals and Doses	References
TI ww	35	170	80	First	$9.00x10^{-3}$	COD	H_2O_2=10.00 mg/l	Behnajady et al. (2008b)
	50	2500	180	First	$5.66x10^{-1}$	COD	H_2O_2=100 mg/l	Wang, X. et al. (2009)
	300	25	30	First	$6.48x10^{-2}$	color	H_2O_2=120 mg/l	Gültekin et al. (2009)
	20	250	30	First	$5.17x10^{-1}$	COD	H_2O_2=170 mg/l	Zhang, J. et al. (2009)
	24	160	10000	First	$1.87x10^{-3}$	color	H_2O_2=200 mg/l	Mehrdad & Hashemzadeh (2010)
	24	240	10000	First	$5.40x10^{-3}$	color	H_2O_2=200 mg/l	Mehrdad & Hashemzadeh (2010)
	24	320	10000	First	$5.91x10^{-3}$	color	H_2O_2=200 mg/l	Mehrdad & Hashemzadeh (2010)
	24	400	10000	First	$6.35x10^{-3}$	color	H_2O_2=200 mg/l	Mehrdad & Hashemzadeh (2010)
	20	90	120	First	$1.25x10^{-2}$	COD	H_2O_2=300 mg/l	Wang, J. et al. (2011)
	500	50	300	First	$4.20x10^{-2}$	TOC	H_2O_2=400 mg/l	Destaillats et al. (2000)
	20	150	240	First	$1.52x10^{-3}$	COD	H_2O_2=650 mg/l	Wang, X. et al. (2008)
	35	640	150	First	$1.60x10^{-2}$	COD	H_2O_2=2000 mg/l	In this study *
	35	640	150	First	$1.20x10^{-2}$	color	H_2O_2=2000 mg/l	In this study *
	35	640	150	First	$1.30x10^{-2}$	TOC	H_2O_2=2000 mg/l	In this study *

* In this study the pseudo order reaction kinetic rate constants were calculated based on COD_{dis}, TOC, color and TAAs removals throughout sono-degradation of TI ww for different additives.

Table 5.136 The pseudo order reaction kinetic rate constants in TI ww throughout sonication (cont.).

ww Type	Sonication Frequency (kHz)	Sonication Power (W)	Sonication Time (min)	Pseudo Order Reaction Kinetic	Pseudo Order Reaction Kinetic Constant (k=1/min)	Based on Removed Parameters	Chemicals and Doses	References
TI ww	850	120	80	First	$1.66x10^{-1}$	COD	H_2O_2=1000 mg/l	Tauber et al. (2005)
	40	25	30	First	$1.21x10^{-1}$	TOC	H_2O_2=1000 mg/l	Yavuz et al. (2009)
	35	160	180	First	$9.90x10^{-3}$	TAAs	H_2O_2=1000 mg/l	Abbasi & Asl (2008)
	850	60	150	First	$3.10x10^{-2}$	color	H_2O_2=6800 mg/l	Rehorek et al. (2004)
	850	90	150	First	$1.21x10^{-2}$	color	H_2O_2=6800 mg/l	Rehorek et al. (2004)
	850	120	150	First	$6.21x10^{-2}$	color	H_2O_2=6800 mg/l	Rehorek et al. (2004)
	651	11.40	600	First	$1.20x10^{-4}$	COD	H_2O_2=20000 mg/l	Inoue, M. et al. (2006)
	651	29	600	First	$3.70x10^{-4}$	COD	H_2O_2=20000 mg/l	Inoue, M. et al. (2006)
	651	41.50	600	First	$5.20x10^{-4}$	COD	H_2O_2=20000 mg/l	Inoue, M. et al. (2006)
	651	11.40	600	First	$1.30x10^{-4}$	COD	H_2O_2=25000 mg/l	Inoue, M. et al. (2006)
	651	29	600	First	$4.00x10^{-4}$	COD	H_2O_2=25000 mg/l	Inoue, M. et al. (2006)
	651	41.50	600	First	$7.40x10^{-4}$	COD	H_2O_2=25000 mg/l	Inoue, M. et al. (2006)
	35	640	150	First	$1.60x10^{-2}$	COD	H_2O_2=2000 mg/l	In this study *
	35	640	150	First	$1.20x10^{-2}$	color	H_2O_2=2000 mg/l	In this study *
	35	640	150	First	$1.30x10^{-2}$	TOC	H_2O_2=2000 mg/l	In this study *
	35	640	150	First	$1.70x10^{-2}$	TAAs	H_2O_2=2000 mg/l	In this study *

* In this study the pseudo order reaction kinetic rate constants were calculated based on COD_{dis}, TOC, color and TAAs removals throughout sono-degradation of TI ww for different additives.

Table 5.136 The pseudo order reaction kinetic rate constants in TI ww throughout sonication (cont.).

ww Type	Sonication Frequency (kHz)	Sonication Power (W)	Sonication Time (min)	Pseudo Order Reaction Kinetic	Pseudo Order Reaction Kinetic Constant (k=1/min)	Based on Removed Parameters	Chemicals and Doses	References
TI ww	40	50	100	First	4.40×10^{-3}	COD	TiO_2=20.00 mg/l	Wang, J. et al. (2009)
	24	400	15	First	9.20×10^{-2}	color	TiO_2=50.00 mg/l	Tangestaninejad et al. (2008)
	24	400	20	First	9.50×10^{-2}	color	TiO_2=50.00 mg/l	Tangestaninejad et al. (2008)
	24	400	25	First	1.40×10^{-1}	color	TiO_2=50.00 mg/l	Tangestaninejad et al. (2008)
	24	400	30	First	1.08×10^{-1}	color	TiO_2=50.00 mg/l	Tangestaninejad et al. (2008)
	35	50	60	First	6.10×10^{-2}	COD	TiO_2=76.00 mg/l	Jamalluddin & Abdullah (2010)
	20	15	60	First	9.67×10^{-4}	COD	TiO_2=100 mg/l	Gonzalez & Martinez (2008)
	18	24	195	First	3.30×10^{-4}	COD	TiO_2=100 mg/l	Yuan et al. (2009)
	20	24	195	First	3.60×10^{-4}	COD	TiO_2=100 mg/l	Yuan et al. (2009)
	24	24	195	First	2.01×10^{-5}	COD	TiO_2=100 mg/l	Yuan et al. (2009)
	27	24	195	First	2.33×10^{-5}	COD	TiO_2=100 mg/l	Yuan et al. (2009)
	30	24	195	First	1.90×10^{-4}	COD	TiO_2=100 mg/l	Yuan et al. (2009)
	35	640	150	First	1.50×10^{-2}	COD	TiO_2=20.00 mg/l	In this study *
	35	640	150	First	1.50×10^{-2}	color	TiO_2=20.00 mg/l	In this study *

* In this study the kinetic rate constants were calculated based on COD_{dis}, TOC, color and TAAs removals throughout sono-degradation of TI ww for different additives.

Table 5.136 The pseudo order reaction kinetic rate constants in TI ww throughout sonication (cont.).

ww Type	Sonication Frequency (kHz)	Sonication Power (W)	Sonication Time (min)	Pseudo Order Reaction Kinetic	Pseudo Order Reaction Kinetic Constant (k=1/min)	Based on Removed Parameters	Chemicals and Doses	References
TI ww	35	160	180	First	$9.00x10^{-4}$	TAAs	TiO_2=100 mg/l	Abbasi & Asl (2008)
	20	15	330	First	$9.90x10^{-3}$	TOC	TiO_2=100 mg/l	Mrowetz et al. (2003)
	20	15	330	First	$1.00x10^{-2}$	TOC	TiO_2=280 mg/l	Mrowetz et al. (2003)
	213	20	60	First	$5.00x10^{-7}$	COD	TiO_2=1000 mg/l	Madhavan et al. (2010)
	40	400	120	First	$9.40x10^{-1}$	COD	TiO_2=3000 mg/l	Wu & Yu (2009)
	40	400	120	First	$3.10x10^{-1}$	COD	TiO_2=2000 mg/l	Wu, C.-H. (2009)
	20	180	30	First	$2.53x10^{-2}$	color	TiO_2=4400 mg/l	Eren & Ince (2010)
	20	165	60	First	$8.25x10^{-2}$	color	TiO_2=7600 mg/l	Byun & Kwak (2005)
	35	640	150	First	$1.50x10^{-2}$	COD	TiO_2=20.00 mg/l	In this study *
	35	640	150	First	$1.50x10^{-2}$	color	TiO_2=20.00 mg/l	In this study *
	35	640	150	First	$1.10x10^{-2}$	TOC	TiO_2=20.00 mg/l	In this study *
	35	640	150	First	$1.90x10^{-2}$	TAAs	TiO_2=20.00 mg/l	In this study *

* In this study the pseudo order reaction kinetic rate constants were calculated based on COD_{dis}, TOC, color and TAAs removals throughout sono-degradation of TI ww for different additives.

Table 5.136 The pseudo order reaction kinetic rate constants in TI ww throughout sonication (cont.).

ww Type	Sonication Frequency (kHz)	Sonication Power (W)	Sonication Time (min)	Pseudo Order Reaction Kinetic	Pseudo Order Reaction Kinetic Constant (k=1/min)	Based on Removed Parameters	Chemicals and Doses	References
TI ww	35	170	180	First	8.00x10^{-3}	COD	NaCl=2.50 g/l	Behnajady et al. (2008b)
	20	150	240	First	1.24x10^{-3}	COD	NaCl=3.00 g/l	Wang, X. et al. (2008)
	40	400	120	First	1.21x10^{-3}	color	NaCl=5.00 g/l	Wu, C.-H. (2009)
	20	150	240	First	1.44x10^{-3}	COD	NaCl=6.00 g/l	Wang, X. et al. (2008)
	40	400	120	First	2.20x10^{-3}	COD	NaCl=7.50 g/l	Wu, C.-H. (2008)
	20	150	240	First	1.74x10^{-3}	COD	NaCl=9.00 g/l	Wang, X. et al. (2008)
	35	640	150	First	1.60x10^{-2}	COD	NaCl=15.00 g/l	In this study *
	35	640	150	First	2.60x10^{-2}	color	NaCl=15.00 g/l	In this study *
	817	150	80	First	3.23x10^{-2}	COD	Fe^{+2}=20.00 mg/l	Vajnhandl & Le Marechal (2007)
	30	150	60	First	6.85x10^{-3}	color	Fe^{+2}=30.00 mg/l	Gopinath et al. (2010)
	35	50	60	First	5.00x10^{-2}	color	Fe^{+2}=52.00 mg/l	Jamalluddin & Abdullah (2010)
	20	150	240	First	6.01x10^{-3}	COD	Fe^{+2}=260 mg/l	Wang, X. et al. (2008)
	20	250	30	First	2.58x10^{-1}	color	Fe^{+2}=500 mg/l	Zhang, H. et al. (2009)
	20	15	130	First	1.20x10^{-3}	color	Fe^{+2}=1040 mg/l	Mrowetz et al. (2003)
	35	640	150	First	1.50x10^{-2}	COD	Fe^{+2}=20.00 mg/l	In this study *
	35	640	150	First	1.70x10^{-2}	color	Fe^{+2}=20.00 mg/l	In this study *

* In this study the pseudo order reaction kinetic rate constants were calculated based on COD$_{dis}$, TOC, color and TAAs removals throughout sono-degradation of TI ww for different additives.

Table 5.136 The pseudo order reaction kinetic rate constants in TI ww throughout sonication (cont.).

ww Type	**Sonication Frequency (kHz)**	**Sonication Power (W)**	**Sonication Time (min)**	**Pseudo Order Reaction Kinetic**	**Pseudo Order Reaction Kinetic Constant (k=1/min)**	**Based on Removed Parameters**	**Chemicals and Doses**	**References**
TI ww	24	160	10000	First	$7.39x10^{-3}$	color	Fe^{+2}=2000 mg/l	Mehrdad & Hashemzadeh (2010)
	24	240	10000	First	$1.28x10^{-2}$	color	Fe^{+2}=2000 mg/l	Mehrdad & Hashemzadeh (2010)
	24	320	10000	First	$1.49x10^{-2}$	color	Fe^{+2}=2000 mg/l	Mehrdad & Hashemzadeh (2010)
	24	400	10000	First	$1.85x10^{-2}$	color	Fe^{+2}=2000 mg/l	Mehrdad & Hashemzadeh (2010)
	35	640	150	First	$1.70x10^{-2}$	color	Fe^{+2}=20.00 mg/l	In this study *
	1700	14	35	Zero	1.274 mg/l.min	color	C_4H_9OH=1.57 mg/l	Ghodbane & Hamdaoui (2009b)
	1700	14	35	Zero	6.524 mg/l.min	color	C_4H_9OH=3.99 mg/l	Ghodbane & Hamdaoui (2009b)
	1700	14	35	Zero	1.780 mg/l.min	color	C_4H_9OH=7.98 mg/l	Ghodbane & Hamdaoui (2009b)
	300	25	30	First	$2.78x10^{-2}$	color	C_4H_9OH=31.50 mg/l	Gültekin et al. (2009)
	35	170	200	First	$1.48x10^{-2}$	COD	C_4H_9OH=1000 mg/l	Behnajady et al. (2008b)
	35	170	210	First	$7.00x10^{-3}$	COD	C_4H_9OH=1000 mg/l	Behnajady et al., (2008b)
	40	400	120	First	$6.30x10^{-3}$	COD	C_4H_9OH=1200 mg/l	Wu, C.-H. (2008)
	40	400	120	First	$9.40x10^{-1}$	COD	C_4H_9OH=1200 mg/l	Wu, C.-H. (2009)
	35	640	150	First	$1.20x10^{-2}$	COD	C_4H_9OH=2000 mg/l	In this study *
	35	640	150	First	$1.80x10^{-2}$	color	C_4H_9OH=2000 mg/l	In this study *

* In this study the pseudo order reaction kinetic rate constants were calculated based on COD_{dis}, TOC, color and TAAs removals throughout sono-degradation of TI ww for different additives.

Table 5.136 The pseudo order reaction kinetic rate constants in TI ww throughout sonication (cont.).

ww Type	Sonication Frequency (kHz)	Sonication Power (W)	Sonication Time (min)	Pseudo Order Reaction Kinetic	Pseudo Order Reaction Kinetic Constant (k=1/min)	Based on Removed Parameters	Chemicals and Doses	References
TI ww	354.50	35	20	First	1.15x10^{-4}	color	HCO_3=2100 mg/l	Minero et al. (2004)
	354.50	35	30	First	2.35x10^{-1}	color	HCO_3=6100 mg/l	Minero et al. (2004)
	35	640	150	First	2.00x10^{-2}	color	HCO_3=5000 mg/l	In this study *
	300	400	60	First	4.29x10^{-4}	color	pH=3.0	Ince & Tezcanli-Güyer (2004)
	40	400	120	First	2.90x10^{-1}	color	pH=4.0	Destaillats et al. (2000a)
	40	400	120	First	7.00x10^{-4}	color	pH=4.0	Wu, C.-H. (2008)
	22.50	600	30	First	1.47x10^{-6}	color	pH=6.0	Sivakumar & Pandit (2001)
	40	400	120	First	2.50x10^{-1}	color	pH=7.0	Wu & Yu (2009)
	40	400	120	First	1.30x10^{-3}	color	pH=7.0	Wu, C.-H. (2008)
	22.50	240	30	First	4.67x10^{-5}	color	pH=7.0	Sivakumar & Pandit (2001)
	22.50	240	30	First	7.67x10^{-5}	color	pH=8.0	Sivakumar & Pandit (2001)
	20	400	120	First	8.20x10^{-3}	color	pH=8.0	He et al. (2008)
	300	400	60	First	1.69x10^{-4}	color	pH=9.0	Ince & Tezcanli-Güyer (2004)
	40	400	120	First	1.90x10^{-1}	color	pH=10.0	Wu & Yu (2009)
	35	640	150	First	1.80x10^{-2}	color	pH=10.00	In this study *

* In this study the pseudo order reaction kinetic rate constants were calculated based on COD_{dis}, TOC, color and TAAs removals throughout sono-degradation of TI ww for different additives.

Table 5.136 The pseudo order reaction kinetic rate constants in TI ww throughout sonication (cont.).

ww Type	**Sonication Frequency (kHz)**	**Sonication Power (W)**	**Sonication Time (min)**	**Pseudo Order Reaction Kinetic**	**Pseudo Order Reaction Kinetic Constant (k=1/min)**	**Based on Removed Parameters**	**Chemicals and Doses**	**References**
TI ww	40	400	120	First	3.60×10^{-3}	color	pH=10.0	Wu, C.-H. (2008)
	20	800	80	First	9.00×10^{-4}	color	pH=10.0	He et al. (2007)
	20	400	120	First	8.00×10^{-3}	color	pH=10.0	He et al. (2008)
	35	640	150	First	1.80×10^{-2}	color	pH=10.00	In this study *
	35	50	60	First	4.00×10^{-3}	color	air=1.00 ml/min	Jamalluddin & Abdullah (2010)
	520	40	20	First	7.00×10^{-2}	color	air=10.00 ml/min	Ince & Tezcanli (2001)
	35	640	150	First	1.60×10^{-2}	color	1 h aeration (60°C)	In this study *
	20	165	60	First	2.19×10^{-2}	color	O_2=5.00 mg/l	Byun & Kwak (2005)
	24	400	15	First	7.90×10^{-2}	color	O_2=5.00 ml/min	Tangestaninejad et al. (2008)
	24	400	20	First	3.20×10^{-1}	color	O_2=5.00 ml/min	Tangestaninejad et al. (2008)
	500	50	300	First	4.20×10^{-2}	color	O_2=50.00 ml/min	Destaillats et al. (2000a)
	20	175	20	First	2.30×10^{-1}	color	O_2=100 ml/min	Zhang, H. et al. (2006)
	35	640	150	First	2.40×10^{-2}	color	DO=10.00 mg/l	In this study *
	20	300	30	Second	1.30×10^{-1} 1/mg.h	color	Raw ww (60°C)	Entezari et al. (2008)
	500	300	30	Second	3.80×10^{-1} 1/mg.h	color	Raw ww (60°C)	Entezari et al. (2008)
	35	640	150	First	1.30×10^{-2} 1/min	color	Raw ww (60°C)	In this study *

* In this study the pseudo order reaction kinetic rate constants were calculated based on COD_{dis}, TOC, color and TAAs removals throughout sono-degradation of TI ww for different additives.

5.16 Acute Toxicity Evaluations in PCI ww

5.16.1 Effect of Increasing Sonication Time on the Acute Toxicity Removal Efficiencies in PCI ww at Ambient Conditions

5.16.1.1 Effect of Increasing Sonication Time on the Microtox Acute Toxicity Removal Efficiencies in PCI ww at Ambient Conditions

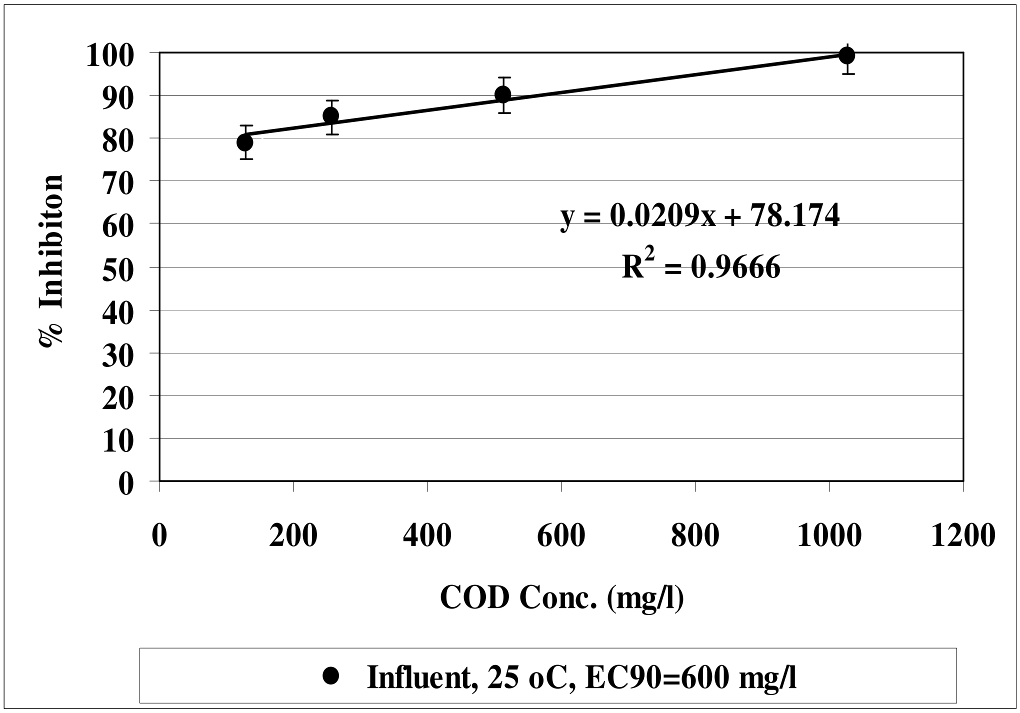
Microtox test is an acute toxicity test. Toxicity was estimated in terms of EC_{50}, defined as the concentration of the toxicant causing 50.00% reduction in activity of the *Photobacterium phosphoreum*. Figure 5.132 was shown the acute toxicity test results obtained from the Microtox acute toxicity test through sonication with increasing sonication time (60 min, 120 and 150 min) at pH=7.0 and at 25^{o}C ambient conditions.

All PCI ww samples were serially diluted in 2.00% NaCI (w/v) and each assay was performed at pH=7.0 and a temperature of 15°C. NaCl (2.00%) was used as the control. The initial EC_{90} value at pH=7.0 was found as 600 mg/l at 25^{o}C ambient conditions (Table 5.137; Figure 5.132a). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{80}=610 mg/l to EC_{60}=510 mg/l and to EC_{50}=525 mg/l, respectively, at 25^{o}C (Table 5.137; Figure 5.132b-c-d). The toxicity removal efficiencies were 11.11%, 33.33% and 44.44% after 60 min, 120 and 150 min sonication times, respectively, at 25^{o}C. 44.44% maximum Microtox acute toxicity removal was found after 150 min sonication time at 25^{o}C (Table 5.137; Figure 5.132d).

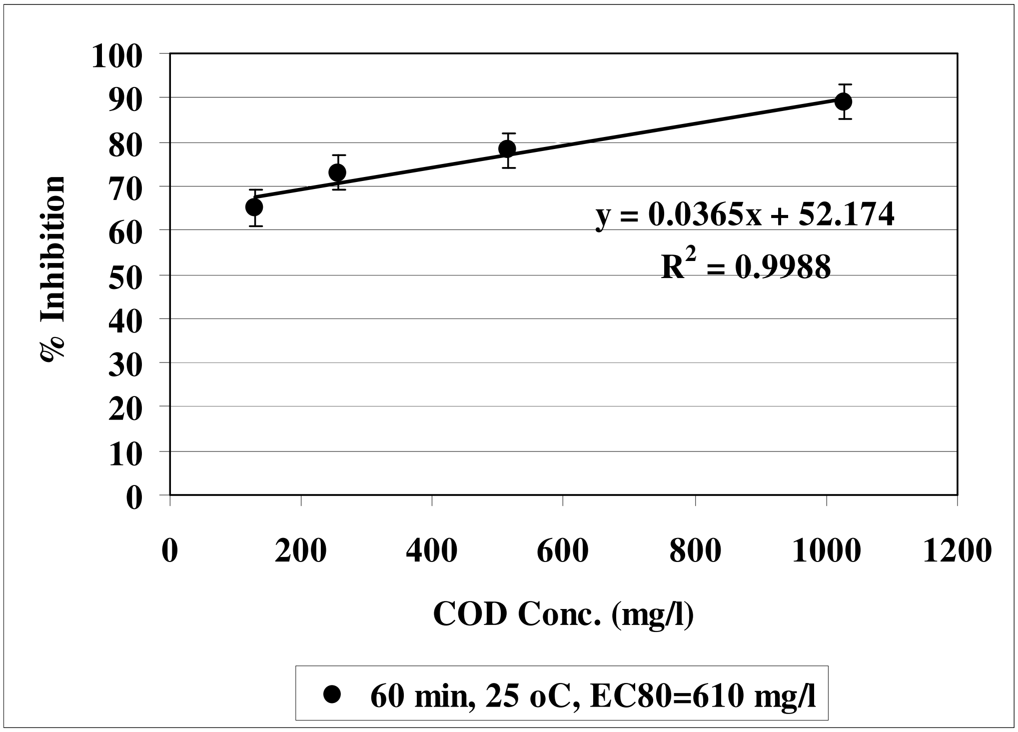
Table 5.137 Effect of increasing sonication time on Microtox acute toxicity in PCI ww at 25^{o}C ambient conditions (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, *EC (mg/l)**			
		25^{o}C			
		0. min	**60. min**	**120. min**	**150. min**
		***EC$_{90}$**	***EC**	***EC**	***EC**
1	Raw ww, control	600	EC$_{80}$=610	EC$_{60}$=510	EC$_{50}$=525

* EC values were calculated based on COD$_{dis}$ (mg/l).

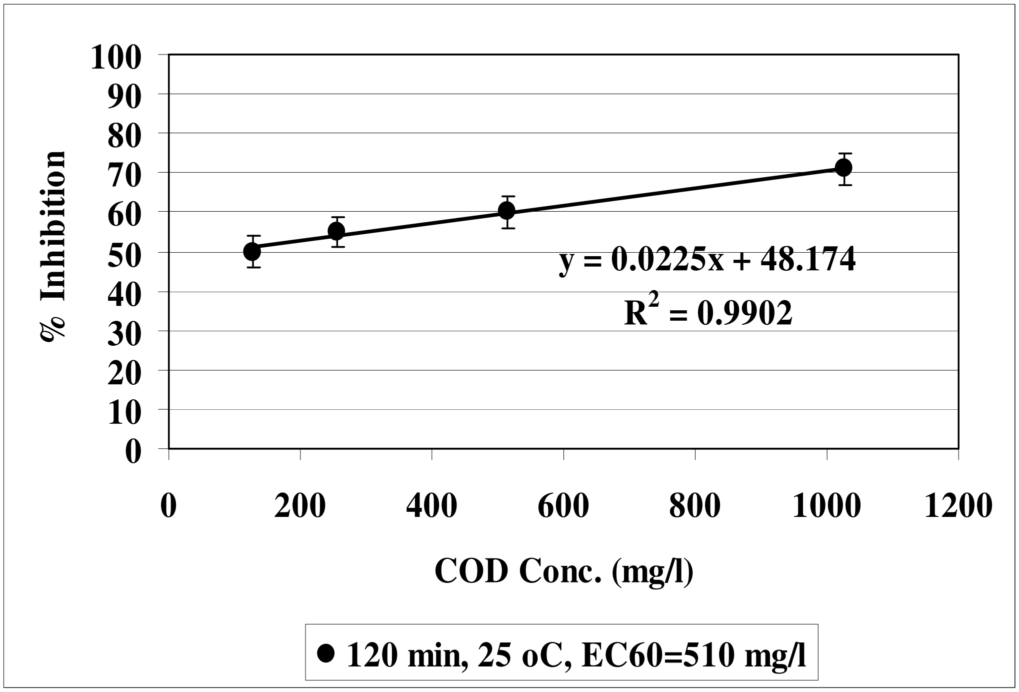


(a)

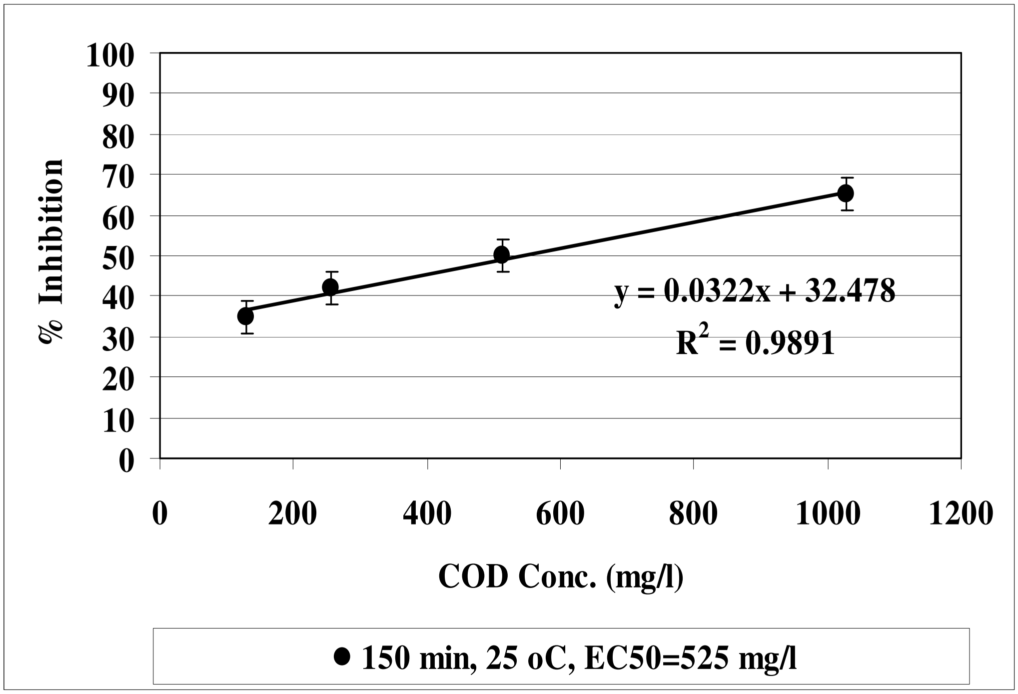


(b)

Figure 5.132 Effect of increasing sonication time on Microtox acute toxicity in PCI ww for (a) influent at 25°C and (b) after 60 min sonication time at 25°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.132 Effect of increasing sonication time on Microtox acute toxicity in PCI ww for (c) after 120 min sonication time at 25°C and (d) after 150 min sonication time at 25°C (640 W power, 35 kHz frequency).

5.16.1.2 Effect of Increasing Sonication Time on Daphnia magna Acute Toxicity Removal Efficiencies in PCI ww at Ambient Conditions

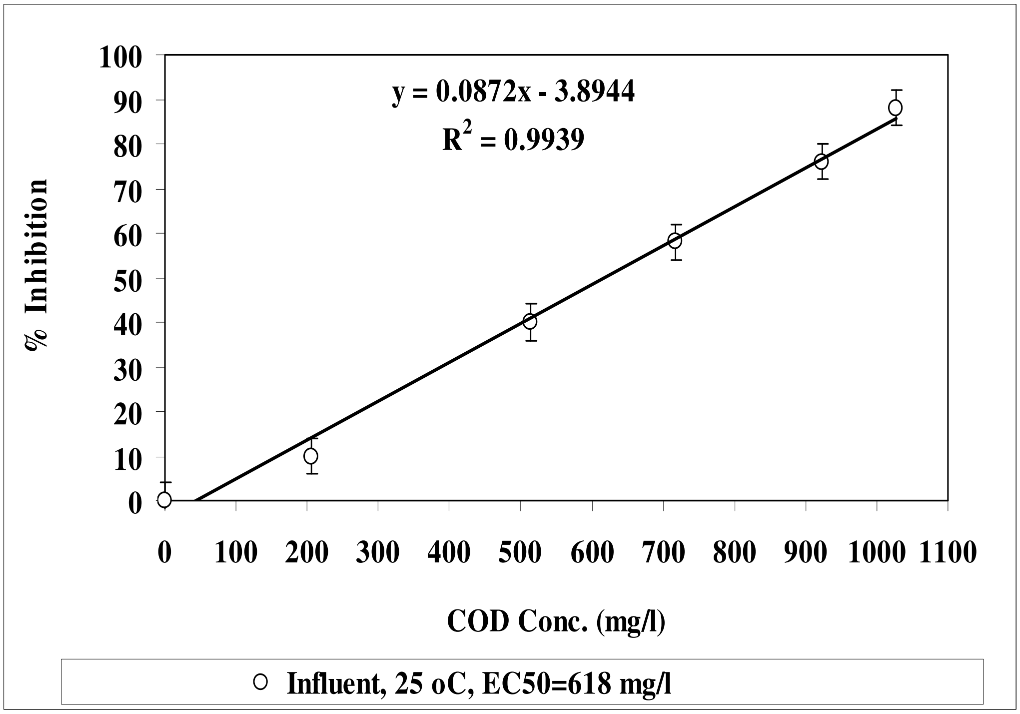
The *Daphnia magna* test is accepted as an acute toxicity test. Toxicity was estimated in terms of EC_{50}, defined as the concentration of the toxicant causing 50.00% reduction in activity of the water flea. The effective PAHs concentrations caused 50.00% mortality in *Daphnia magna* cells (EC_{50}- mg/l) in raw and sonicated wastewater samples were monitored based on COD (mg/l) concentrations. The EC_{50} values and the other EC values were calculated by taking into consideration the dilution ratios and the inhibitory concentrations. Figure 5.133 was shown the acute toxicity test results obtained from the *Daphnia magna* test through sonication with increasing sonication time (60 min, 120 and 150 min) at pH=7.0 and at 25^{o}C.

The test samples containing an initial total PAHs concentration of 1378.77 ng/ml were diluted at 1/1, 1/2, 1/8, 1/16 and 1/24 ratios after sonication experiments. The young 10 *Daphnids* (< 24 h old) were added to each test vessel at the initiation time (t=0). After 24 h of exposure, the EC values of total PAHs concentrations were calculated. As seen in Table 5.138 (SET 1) and Figure 5.133a the initial EC_{50} values were obtained as 618 mg/l at 25^{o}C. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{45}=425 mg/l to EC_{40}=325 mg/l and to EC_{35}=182 mg/l, respectively, at 25^{o}C (Table 5.138, SET 1; Figure 5.133b-c-d). 10.00%, 20.00% and 30.00% toxicity removals were found after 60 min, 120 and 150 min sonication time, respectively, at 25^{o}C. 30.00% maximum *Daphnia magna* acute toxicity removal was found after 150 min sonication time at 25^{o}C (Table 5.138, SET 1; Figure 5.133d).

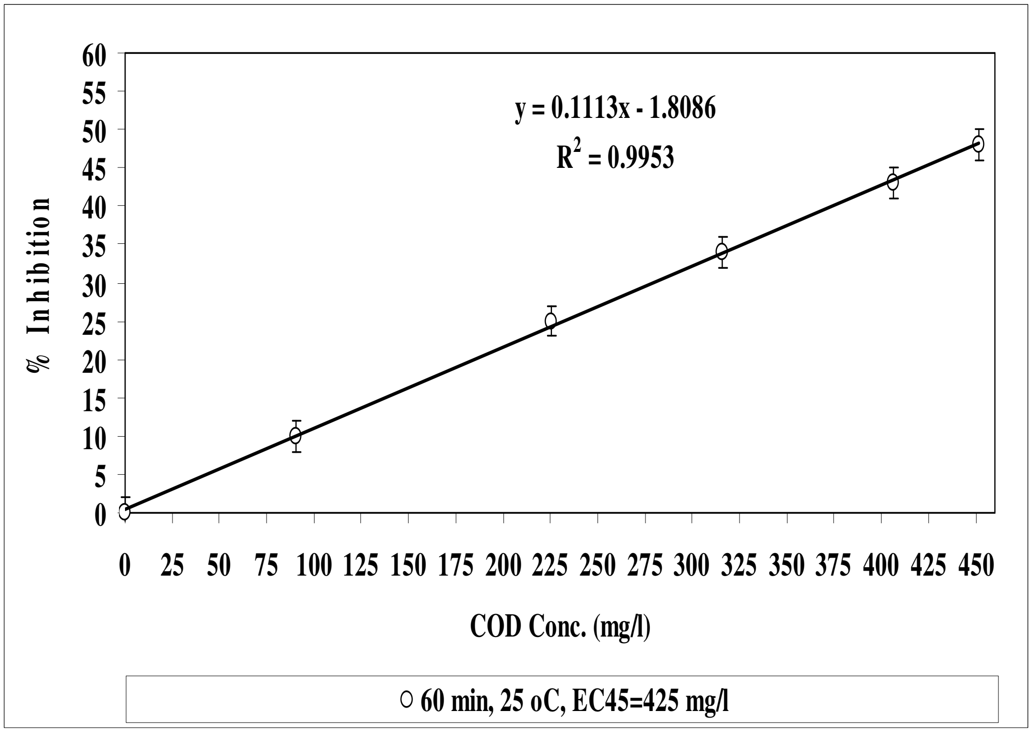
Table 5.138 Effect of increasing sonication time on *Daphnia magna* acute toxicity in PCI ww at 25^{o}C ambient conditions (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, *EC (mg/l)**			
		25^{o}C			
		0. min	**60. min**	**120. min**	**150. min**
		***EC$_{50}$**	***EC**	***EC**	***EC**
1	Raw ww, control	618	EC$_{45}$=425	EC$_{40}$=325	EC$_{35}$=182

* EC values were calculated based on COD (mg/l).

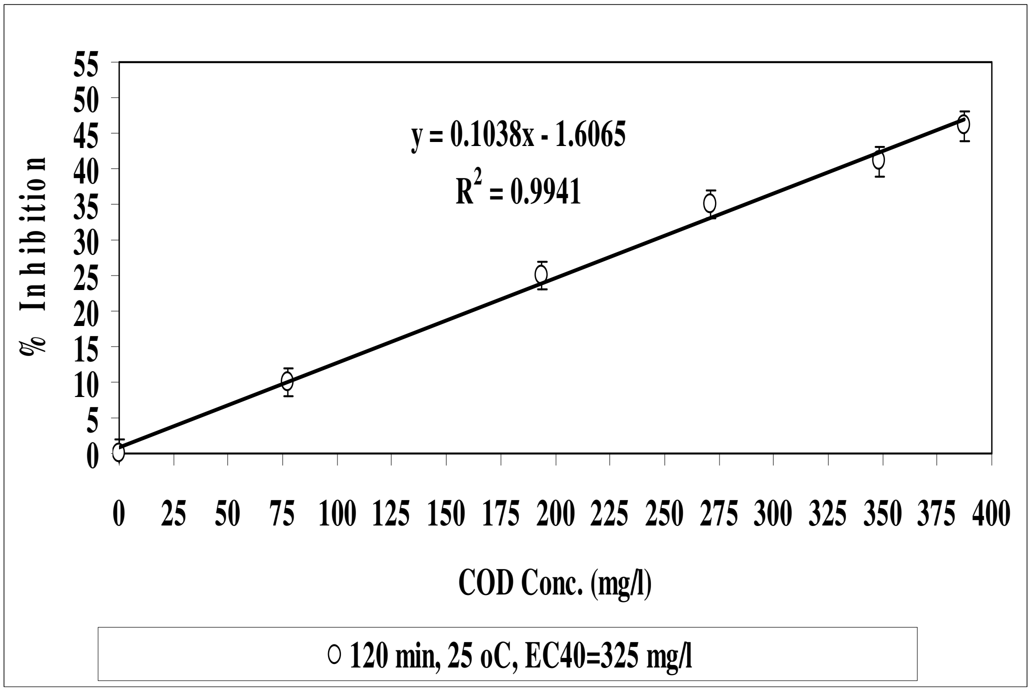


(a)

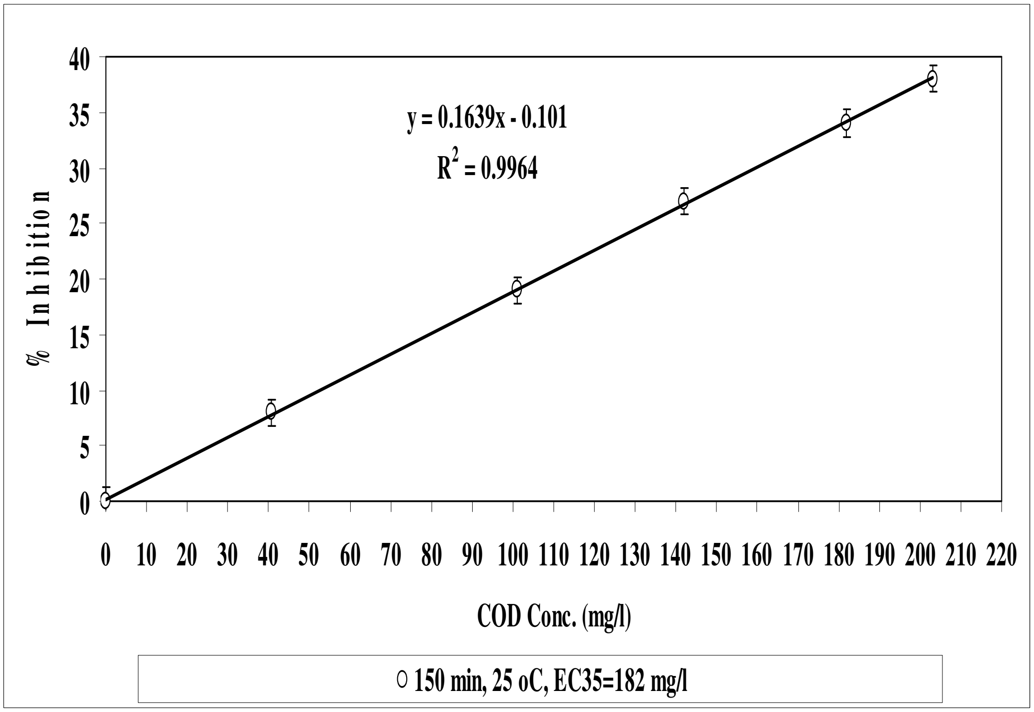


(b)

Figure 5.133 Effect of increasing sonication time on *Daphnia magna* acute toxicity in PCI ww for (a) influent at 25°C and (b) after 60 min sonication time at 25°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.133 Effect of increasing sonication time on *Daphnia magna* acute toxicity in PCI ww for (c) after 120 min sonication time at 25°C and (d) after 150 min sonication time at 25°C (640 W power, 35 kHz frequency).

5.16.2 Effect of Increasing Temperature on the Removal of Acute Toxicity in PCI ww at Increasing Sonication Time

5.16.2.1 Effect of Increasing Temperature on the Removal of Microtox Acute Toxicity in PCI ww at Increasing Sonication Time

The initial EC_{90} values at pH=7.0 was found as 600 mg/l at 25°C (Table 5.139, SET 1; Figure 5.134a). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{70}, to EC_{50} and to EC_{40} at 30°C. The EC_{70}, the EC_{50} and the EC_{40} values were measured as 610 mg/l, 590 and 680 mg/l, respectively, at 30°C (Table 5.139, SET 2). The toxicity removal efficiencies were 22.22%, 44.44% and 55.56% after 60 min, 120 and 150 min sonication times, respectively, at 30°C (Table 5.139, SET 2).

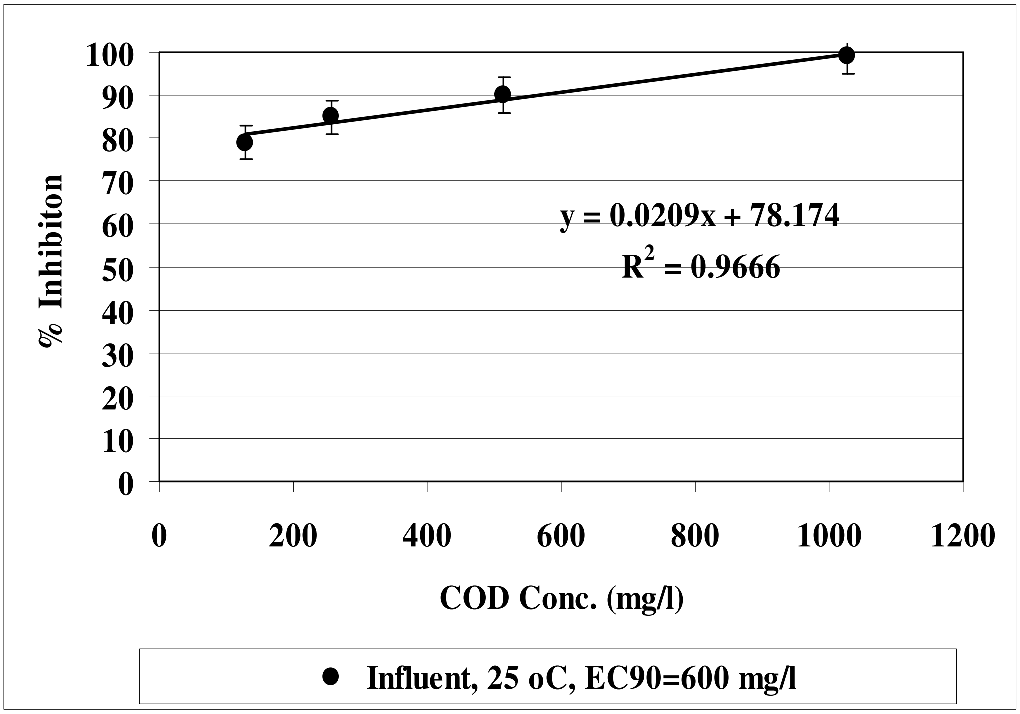
The EC_{90} values decreased to EC_{60}, to EC_{40} and to EC_{30} after 60 min, 120 and 150 min of sonication, respectively, at 60°C (Table 5.139, SET 2; Figure 5.134b-c-d). The EC_{60}, the EC_{40} and the EC_{30} values were measured as 680 mg/l, 810 and 410 mg/l, respectively, at 60°C. The toxicity removal efficiencies were 33.33%, 55.56% and 66.67% after 60 min, 120 and 150 min sonication times, respectively, at 60°C (Table 5.139, SET 2; Figure 5.134b-c-d). 66.67% maximum acute toxicity removal was observed in Microtox test at 60°C after 150 min sonication (Table 5.139, SET 2; Figure 5.134d).

The results of the study showed that as the sonication temperature and sonication time increased from 25 to 30 and 60°C; from 60 to 150 min, respectively, the acute toxicity decreased.

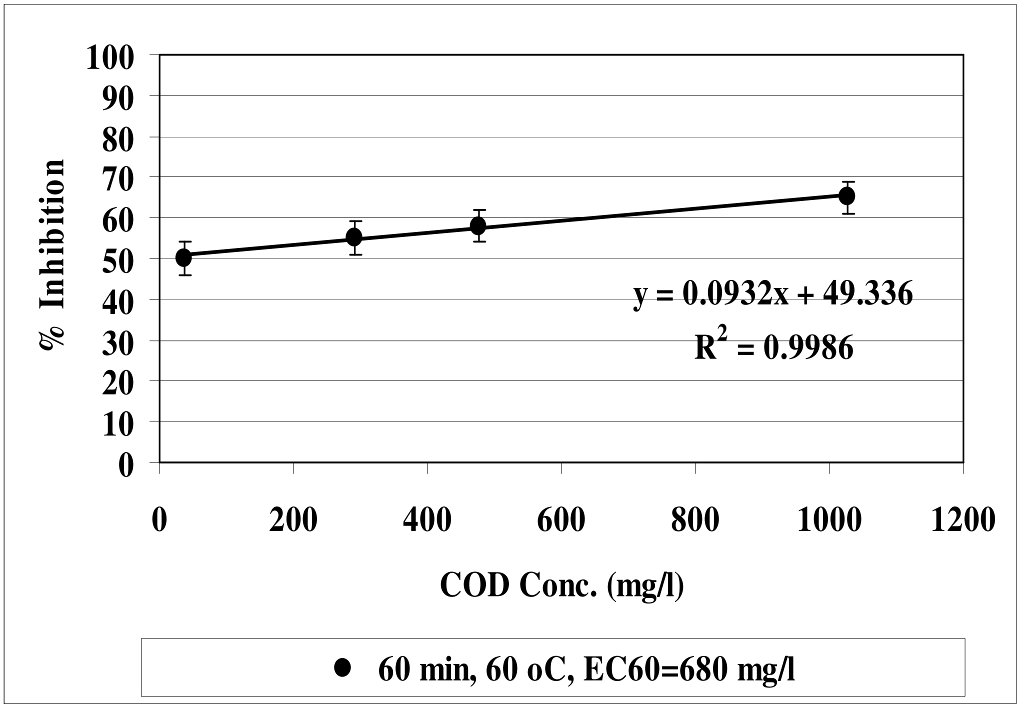
Table 5.139 Effect of increasing sonication temperature on Microtox acute toxicity in PCI ww at 30^{o}C and at 60^{o}C (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25^{o}C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC$_{90}$**		***EC**		***EC**		***EC**	
1	Raw ww, control	600		EC$_{80}$=610		EC$_{60}$=510		EC$_{50}$=525	
		30^{o}C				**60^{o}C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC$_{90}$**	***EC**	***EC**	***EC**	***EC$_{90}$**	***EC**	***EC**	***EC**
2	Raw ww, control	600	EC$_{70}$= 610	EC$_{50}$= 590	EC$_{40}$= 680	600	EC$_{60}$= 680	EC$_{40}$= 410	EC$_{30}$= 410

* EC values were calculated based on COD$_{dis}$ (mg/l).

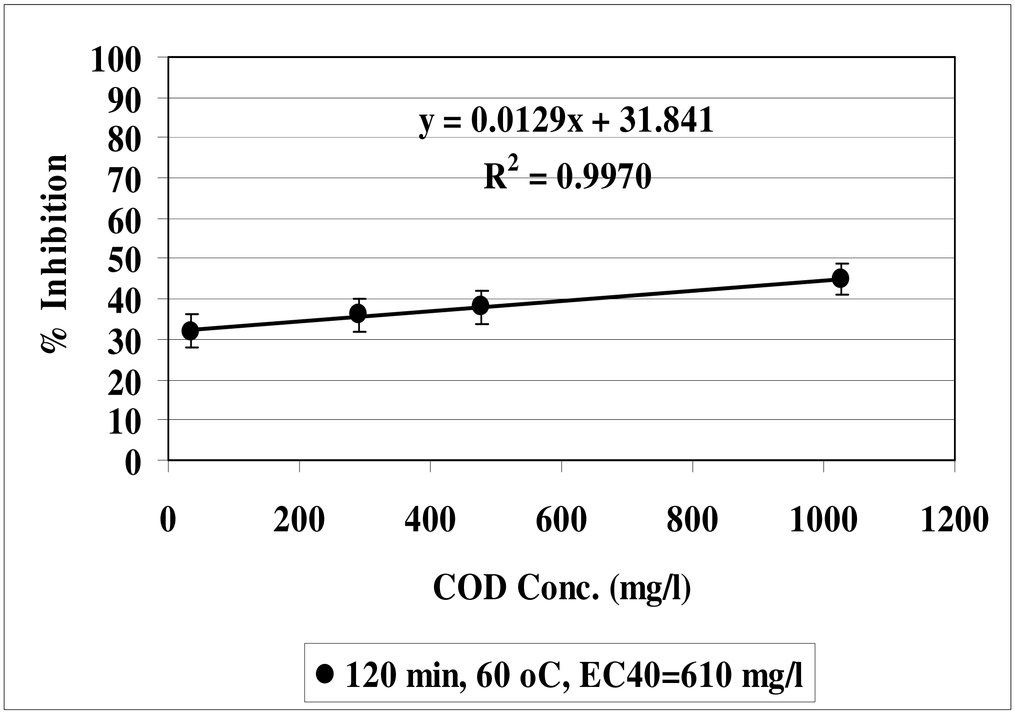


(a)

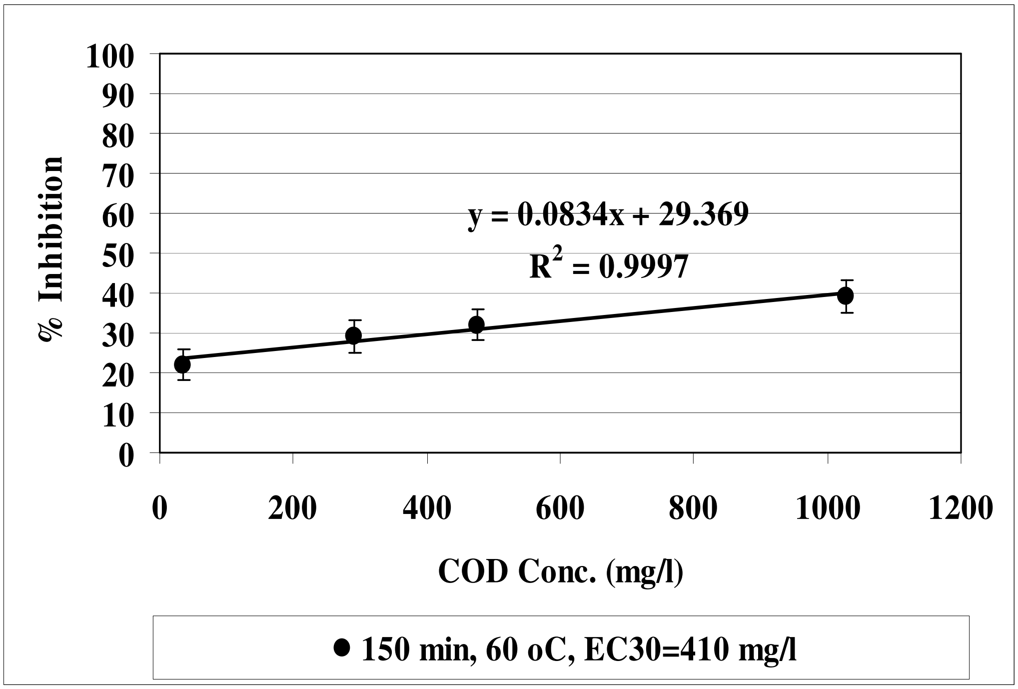


(b)

Figure 5.134 Effect of increasing temperature on Microtox acute toxicity in PCI ww for (a) influent at 25°C and (b) after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.134 Effect of increasing temperature on Microtox acute toxicity in PCI ww for (c) after 120 min sonication time at 60°C and (d) after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.16.2.2 Effect of Increasing Temperature on the Removal of Daphnia magna Acute Toxicity in PCI ww at Increasing Sonication Time

As seen in Table 5.140 (SET 1) and in Figure 5.135a the initial EC_{50} value was obtained as 618 mg/l at 25°C. After 60 min, 120 and 150 min of sonication the EC_{50} value decreased to EC_{40} to EC_{35} and to EC_{30} at 30°C (Table 5.140, SET 2). The EC_{40}, the EC_{35} and the EC_{30} values were measured as 510 mg/l, 340 and 85 mg/l, respectively, at 30°C. This showed that the PAHs were degraded to less toxic by-products via sonication. The toxicity removal efficiencies were 20.00%, 30.00% and 40.00% after 60 min, 120 and 150 min sonication times, respectively, at 30°C (Table 5.140, SET 2).

Table 5.140 Effect of increasing sonication temperature on *Daphnia magna* acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

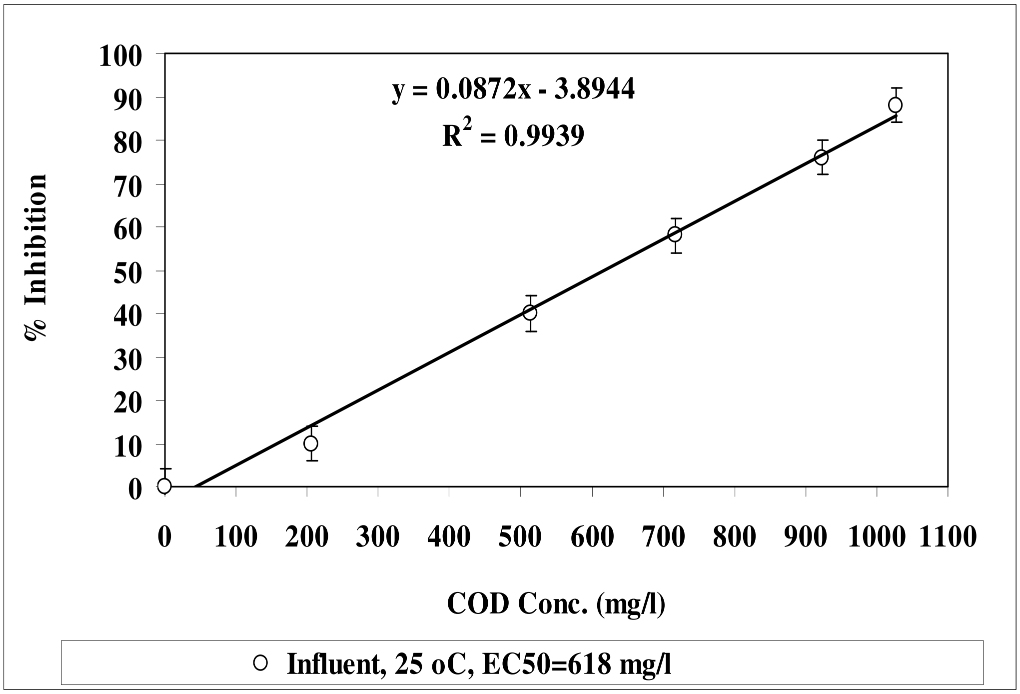
<table>
<tr><th rowspan="4">No</th><th rowspan="4">Parameters</th><th colspan="8"><i>Daphnia magna</i> Acute Toxicity Values, *EC (mg/l)</th></tr>
<tr><th colspan="8">25°C</th></tr>
<tr><th colspan="2">0. min</th><th colspan="2">60. min</th><th colspan="2">120. min</th><th colspan="2">150. min</th></tr>
<tr><th colspan="2">*EC_{50}</th><th colspan="2">*EC</th><th colspan="2">*EC</th><th colspan="2">*EC</th></tr>
<tr><td>1</td><td>Raw ww, control</td><td colspan="2">618</td><td colspan="2">EC_{45}=425</td><td colspan="2">EC_{40}=325</td><td colspan="2">EC_{35}=182</td></tr>
<tr><td rowspan="3"></td><td rowspan="3"></td><th colspan="4">30°C</th><th colspan="4">60°C</th></tr>
<tr><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th></tr>
<tr><th>*EC_{50}</th><th>*EC</th><th>*EC</th><th>*EC</th><th>*EC_{50}</th><th>*EC</th><th>*EC</th><th>*EC</th></tr>
<tr><td>2</td><td>Raw ww, control</td><td>618</td><td>EC_{40}= 510</td><td>EC_{35} =340</td><td>EC_{30} =85</td><td>618</td><td>EC_{40} =425</td><td>EC_{30}= 190</td><td>EC_{25} =32</td></tr>
</table>

* EC values were calculated based on COD (mg/l).

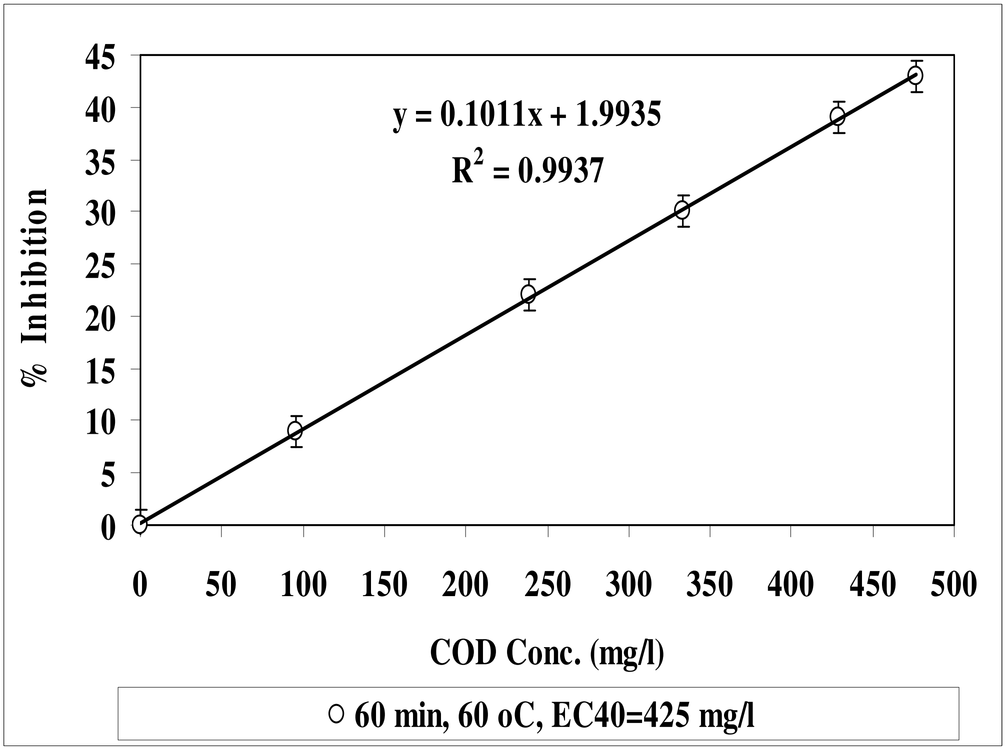
The EC_{50} values decreased to EC_{40} to EC_{30} and to EC_{25} after 60 min, 120 and 150 min of sonication, respectively, at 60°C (Table 5.140, SET 2; Figure 5.135b-c-d). The EC_{40}, the EC_{30} and the EC_{25} values were measured as 425 mg/l, 190 and 32 mg/l, respectively, at 60°C. The toxicity removal efficiencies were 20.00%, 40.00% and 50.00% after 60 min, 120 and 150 min sonication times, respectively, at 60°C (Table

5.140, SET 2; Figure 5.135b-c-d). 50.00% maximum *Daphnia magna* acute toxicity yield was measured at 60°C after 150 min sonication time (Table 5.140, SET 2; Figure 5.135d).

As the temperature increased from 25 to 30 and 60°C the *Daphnia magna* acute toxicity removals increased from 30.00% to 40.00% and to 50.00% after 150 min sonication time.

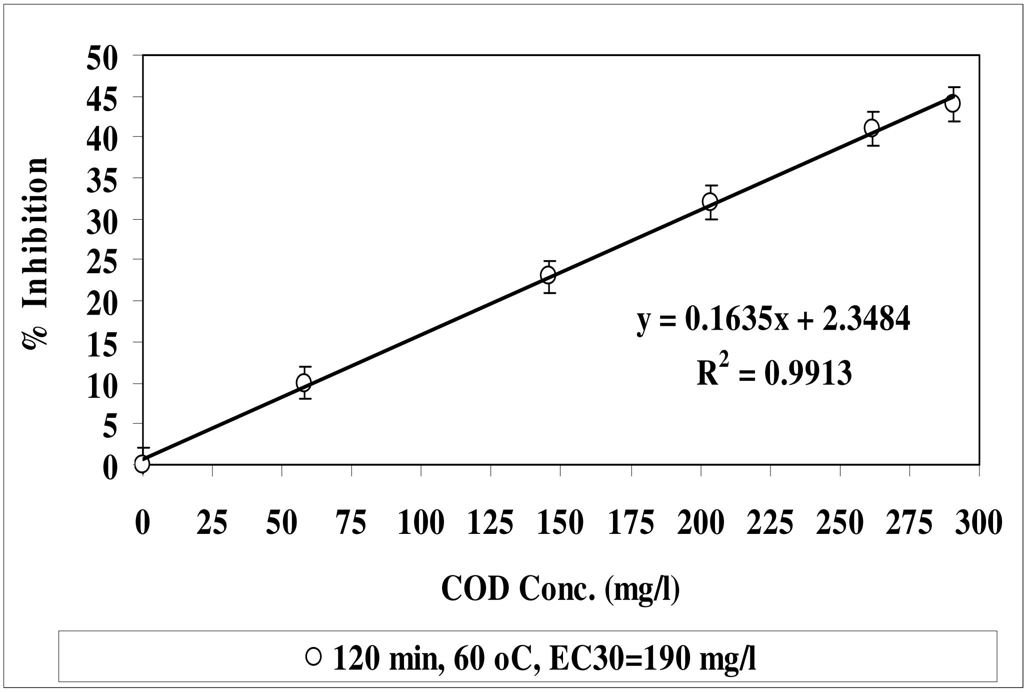


(a)

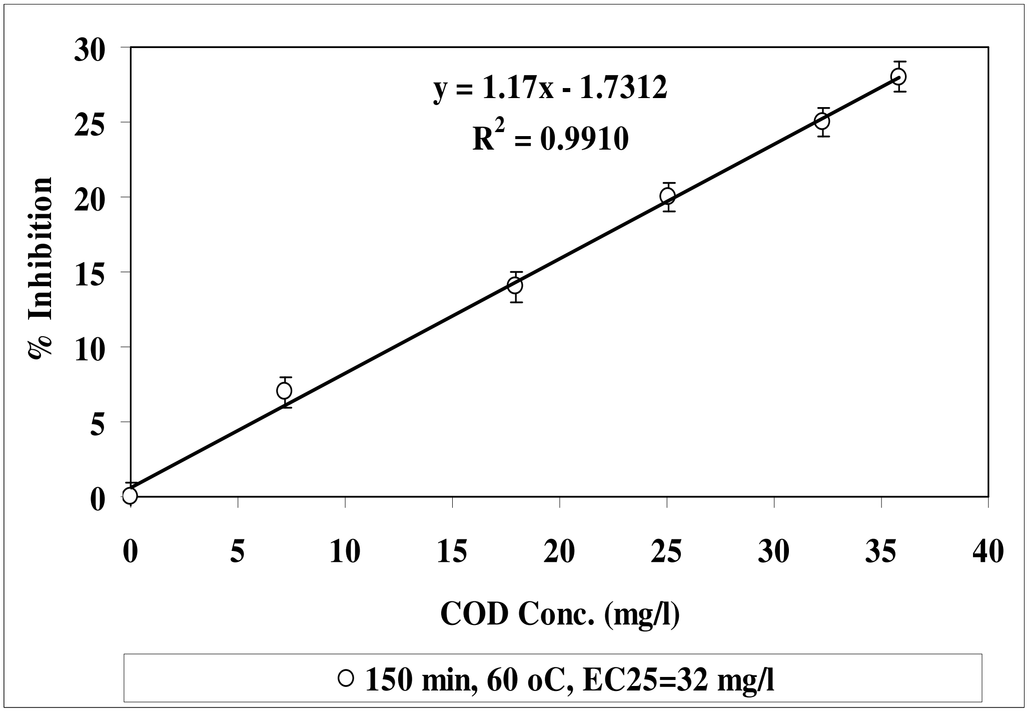


(b)

Figure 5.135 Effect of increasing temperature on *Daphnia magna* acute toxicity in PCI ww for (a) influent at 25°C and (b) after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.141 Effect of increasing temperature on *Daphnia magna* acute toxicity in PCI ww for (c) after 120 min sonication time at 60°C and (d) after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.16.3 Effect of H_2O_2 Concentrations on the Removal of Acute Toxicity in PCI ww at Increasing Sonication Time and Temperature

5.16.3.1 Effect of H_2O_2 Concentrations on the Removal of Microtox Acute Toxicity in PCI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was found as 600 mg/l at 25°C (Table 5.141, SET 1; Figure 5.136a). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{65}=810 mg/l to EC_{30}=651 mg/l and to EC_{10}=629 mg/l in H_2O_2=500 mg/l at 30°C (Table 5.141, SET 3). The toxicity removal efficiencies were 27.78%, 66.67% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 30°C (Table 5.141, SET 3).

The EC_{90} values decreased to EC_{50}, to EC_{20} and to EC_5 after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.141, SET 3; Figure 5.136b-c-d). The $EC_{50,}$ EC_{20} and the EC_5 values were measured as 790, 580 and 680 mg/l, respectively, at H_2O_2=500 mg/l at 60°C. The toxicity removal efficiencies were 44.44%, 77.78% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.141, SET 3; Figure 5.136b-c-d). 94.44% maximum Microtox acute toxicity yield was obtained in H_2O_2=500 mg/l after 150 min sonication time at 60°C (Table 5.141, SET 3; Figure 5.136d).

The EC_{90} values decreased to EC_{70}=815 mg/l to EC_{35}=630 and to EC_{20}=653 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 30°C (Table 5.141, SET 3). The EC_{90} values decreased to EC_{70}=806 mg/l to EC_{35}=627 and to EC_{25}=650 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 30°C. The toxicity removal efficiencies were 77.78% and 72.22% in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of H_2O_2=2000 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.141, SET 3).

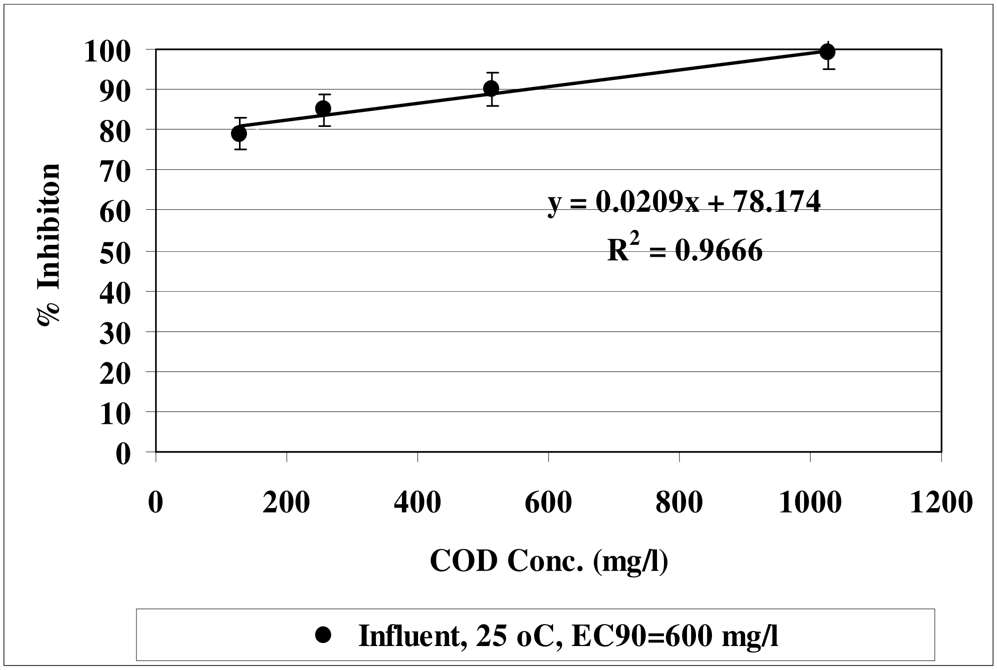
Table 5.141 Effect of increasing H_2O_2 concentrations on Microtox acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, *EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{90}$		***EC**		***EC**		***EC**	
1	Raw ww, control	600		$EC_{80}=610$		$EC_{60}=510$		$EC_{50}=525$	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{90}$	***EC**	***EC**	***EC**	**$*EC_{90}$**	***EC**	***EC**	***EC**
2	Raw ww, control	600	$EC_{70}=610$	$EC_{50}=590$	$EC_{40}=680$	600	$EC_{60}=680$	$EC_{40}=610$	$EC_{30}=410$
3	H_2O_2=100 mg/l	600	$EC_{70}=815$	$EC_{35}=630$	$EC_{20}=653$	600	$EC_{60}=807$	$EC_{30}=596$	$EC_{15}=664$
	H_2O_2=500 mg/l	600	$EC_{65}=810$	$EC_{30}=651$	$EC_{10}=629$	600	$EC_{50}=790$	$EC_{20}=580$	$EC_{5}=680$
	H_2O_2=2000 mg/l	600	$EC_{70}=806$	$EC_{35}=627$	$EC_{25}=650$	600	$EC_{65}=804$	$EC_{30}=587$	$EC_{20}=664$

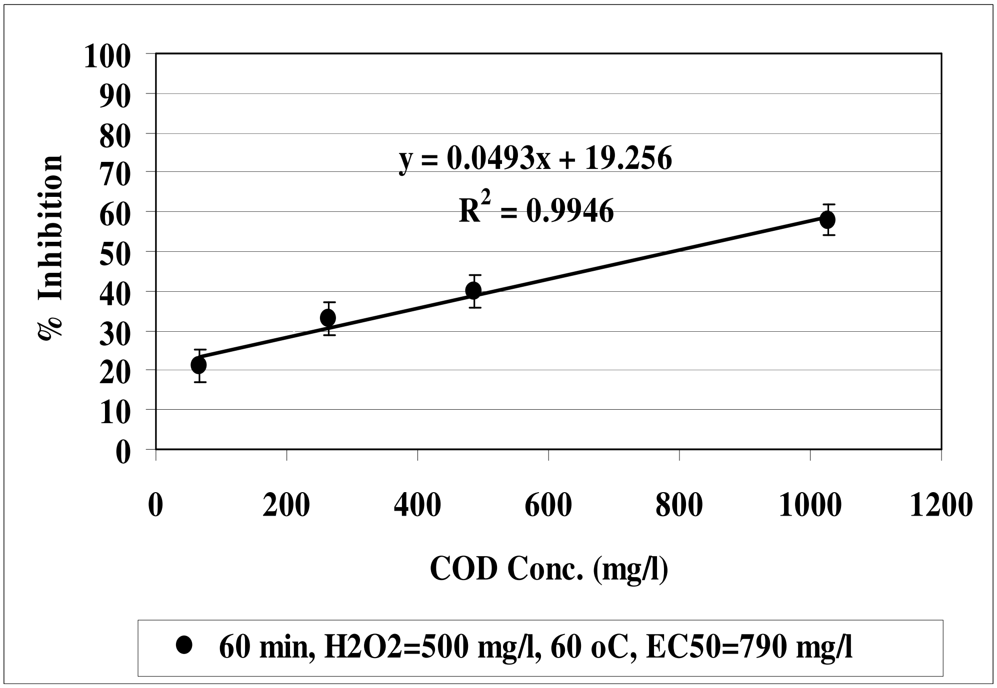
* EC values were calculated based on COD (mg/l).

The EC_{90} values decreased to EC_{60}=807 mg/l to EC_{30}=596 and to EC_{15}=664 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 60°C (Table 5.141, SET 3). The EC_{90} values decreased to EC_{65}=804 mg/l to EC_{30}=587 and to EC_{20}=664 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 60°C. The toxicity removal efficiencies were 83.33% and 77.78% in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at 60°C. It was observed an inhibition effect of H_2O_2=2000 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60°C (Table 5.141, SET 3).

The maximum acute toxicity removal was obtained in the samples containing 500 mg/l H_2O_2 concentration at a temperature of 60°C after 150 min of sonication time (Table 5.141, SET 3; Figure 5.136d). In this study, high H_2O_2 ($>$ 2000 mg/l) concentrations caused inhibitory effect on *Vibrio fischeri.* (Table 5.141, SET 3).

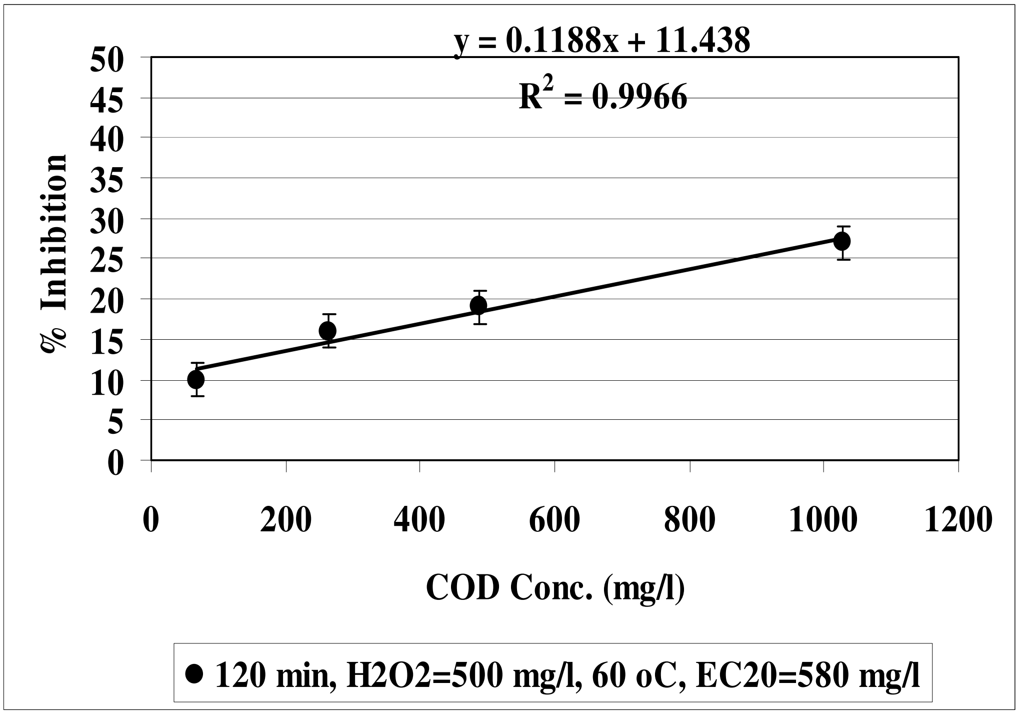


(a)

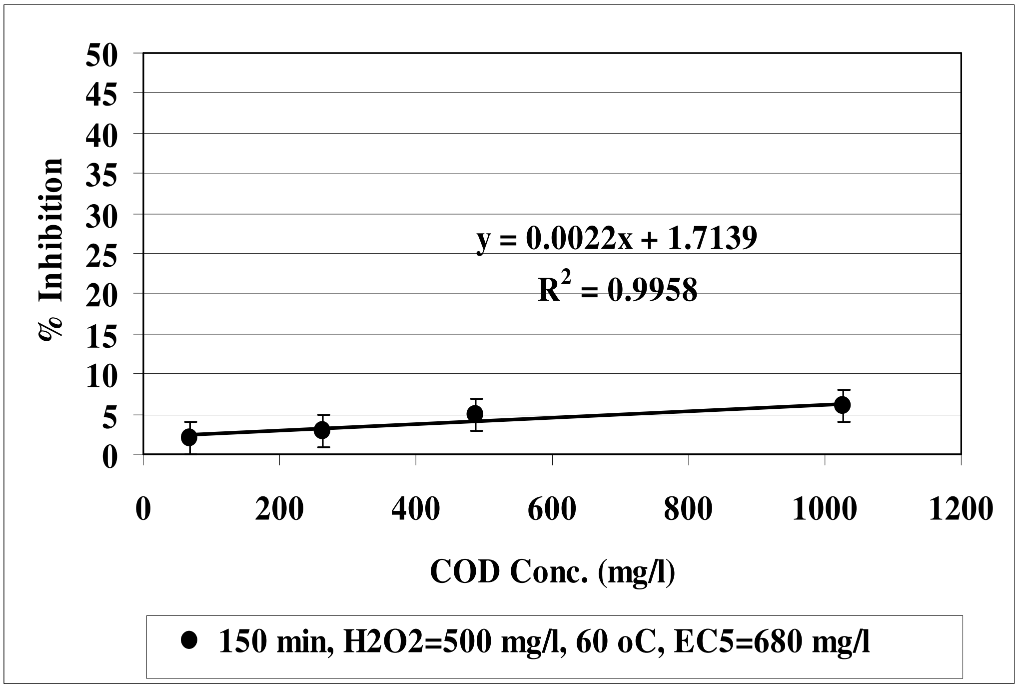


(b)

Figure 5.136 Effect of 500 mg/l H_2O_2 concentration on Microtox acute toxicity in PCI ww for (a) influent at 25°C and (b) H_2O_2=500 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.136 Effect of 500 mg/l H_2O_2 concentration on Microtox acute toxicity in PCI ww for (c) H_2O_2=500 mg/l after 120 min sonication time at 60°C and (d) H_2O_2=500 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.16.3.2 Effect of H_2O_2 Concentrations on the Removal of Daphnia magna Acute Toxicity in PCI ww at Increasing Sonication Time and Temperature

As seen in Table 5.142 (SET 1) and Figure 5.137a, the initial EC_{50} values were obtained as 618 mg/l at 25°C. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{35}=325 mg/l to EC_{20}=57 mg/l and to EC_{10}=180 mg/l in H_2O_2=500 mg/l at 30°C (Table 5.142, SET 3). The toxicity removal efficiencies were 30.00%, 60.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 30°C (Table 5.142, SET 3).

Table 5.142 Effect of increasing H_2O_2 concentrations on *Daphnia magna* acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

<table>
<tr><th rowspan="4">No</th><th rowspan="4">Parameters</th><th colspan="8"><i>Daphnia magna</i> Acute Toxicity Values, *EC (mg/l)</th></tr>
<tr><th colspan="8">25°C</th></tr>
<tr><th colspan="2">0. min</th><th colspan="2">60. min</th><th colspan="2">120. min</th><th colspan="2">150. min</th></tr>
<tr><th colspan="2">*EC_{50}</th><th colspan="2">*EC</th><th colspan="2">*EC</th><th colspan="2">*EC</th></tr>
<tr><td>1</td><td>Raw ww, control</td><td colspan="2">618</td><td colspan="2">EC_{45}=425</td><td colspan="2">EC_{40}=325</td><td colspan="2">EC_{35}=182</td></tr>
<tr><td rowspan="3"></td><td rowspan="3"></td><th colspan="4">30°C</th><th colspan="4">60°C</th></tr>
<tr><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th></tr>
<tr><th>*EC_{50}</th><th>*EC</th><th>*EC</th><th>*EC</th><th>*EC_{50}</th><th>*EC</th><th>*EC</th><th>*EC</th></tr>
<tr><td>2</td><td>Raw ww, control</td><td>618</td><td>EC_{40}= 510</td><td>EC_{35}= 340</td><td>EC_{30}= 85</td><td>618</td><td>EC_{40}= 425</td><td>EC_{30}= 190</td><td>EC_{25}= 32</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>3</td><td>H_2O_2=100 mg/l</td><td>618</td><td>EC_{40}= 87</td><td>EC_{30}= 35</td><td>EC_{15}= 170</td><td>618</td><td>EC_{35}= 38</td><td>EC_{25}= 375</td><td>EC_{10}= 135</td></tr>
<tr><td></td><td>H_2O_2=500 mg/l</td><td>618</td><td>EC_{35}= 325</td><td>EC_{20}= 57</td><td>EC_{10}= 180</td><td>618</td><td>EC_{30}= 425</td><td>EC_{15}= 200</td><td>EC_{5}= 35</td></tr>
<tr><td></td><td>H_2O_2=2000 mg/l</td><td>618</td><td>EC_{40}= 200</td><td>EC_{30}= 100</td><td>EC_{20}= 23</td><td>618</td><td>EC_{35}= 250</td><td>EC_{20}= 110</td><td>EC_{10}= 15</td></tr>
</table>

* EC values were calculated based on COD (mg/l).

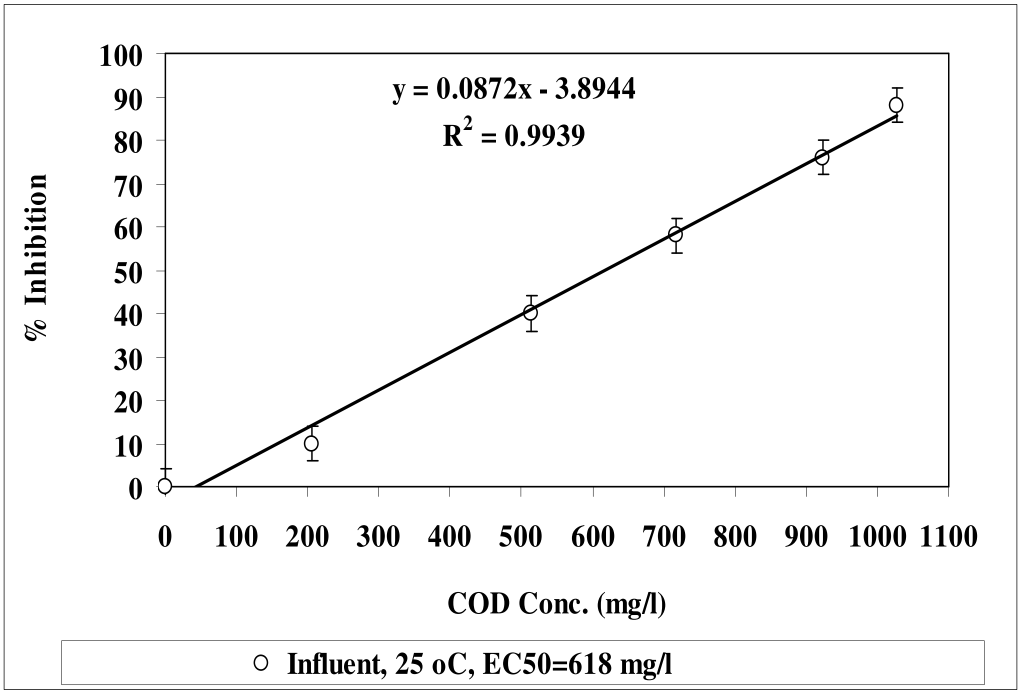
The EC_{50} values decreased to EC_{30} to EC_{15} and to EC_5 after 60 min ,120 and 150 min sonication, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.142, SET 3; Figure 5.137b-c-d). The EC_{30}, the EC_{15} and the EC_5 values were measured as 425 mg/l, 200 and 35 mg/l, respectively, for H_2O_2=500 mg/l at 60°C. The toxicity removal efficiencies were 40.00%, 70.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.142, SET 3; Figure 5.137b-c-d). 90.00% maximum *Daphnia magna* removal was observed for H_2O_2=500 mg/l after 150 min sonication time at 60°C (Table 5.142, SET 3; Figure 5.137d).

The EC_{50} values decreased to EC_{40}=87 mg/l to EC_{30}=35 and to EC_{15}=170 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 30°C (Table 5.142, SET 3). The EC_{50} values decreased to EC_{40}=200 mg/l to EC_{30}=100 and to EC_{20}=23 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 30°C. The toxicity removal efficiencies were 70.00% and 60.00% in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at 30°C. It was obtained an inhibition effect of H_2O_2=2000 mg/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.142, SET 3).

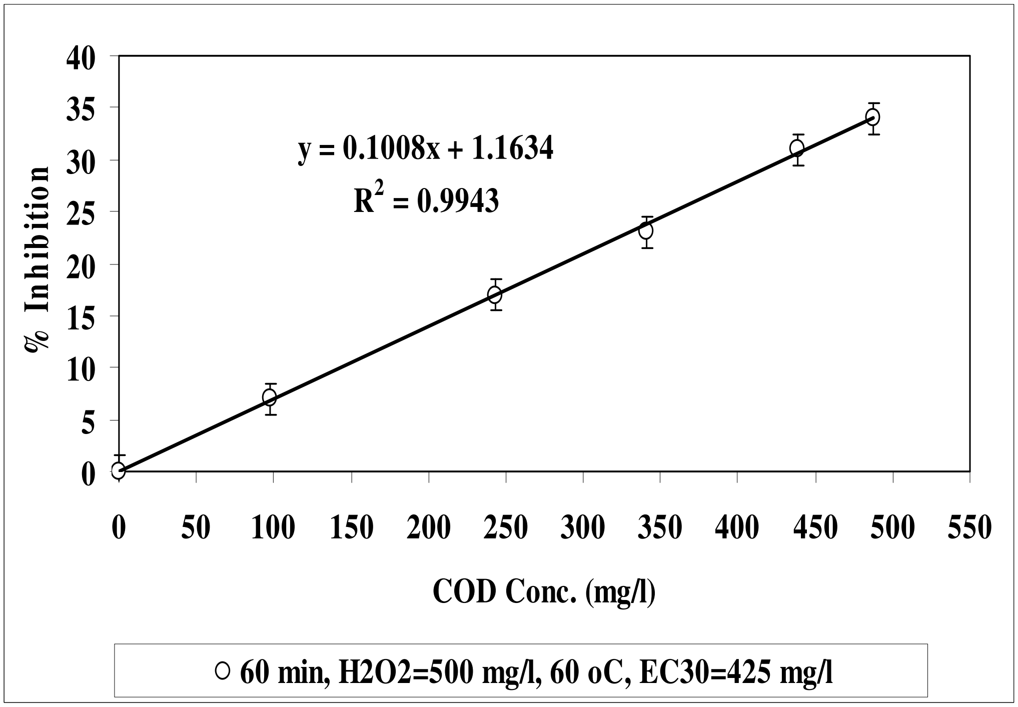
The EC_{50} values decreased to EC_{35}=38 mg/l to EC_{25}=375 and to EC_{10}=135 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 60°C (Table 5.142, SET 3). The EC_{50} values decreased to EC_{35}=250 mg/l to EC_{20}=110 and to EC_{10}=15 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 60°C. The toxicity removal efficiencies were 80.00% and 80.00% in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at 60°C. It was observed an inhibition effect of H_2O_2=2000 mg/l to *Daphnia magna* after 150 min sonication time at 60°C (Table 5.142, SET 3).

H_2O_2 concentrations above 500 mg/l decreased the *Daphnia magna* acute toxicity removals by hindering the sonication process (Table 5.142, SET 3). In other words, the maximum acute toxicity removal was obtained in the samples containing 500 mg/l H_2O_2 concentration at a temperature of 60°C after 150 min of sonication time (Table 5.142, SET 3; Figure 5.137d).

The acute toxicity decreased from an initial value of 618 mg/l to EC_{15}=170 mg/l at a H_2O_2 concentration of 100 mg/l at 30°C after a sonication time of 150 min (Table 5.142, SET 3). Increasing the H_2O_2 concentration to 100 mg/l had no positive effect on the decrease of EC values. Increasing the H_2O_2 concentration did not contribute to acute toxicity removal. H_2O_2 concentrations above 500 mg/l increased the acute toxicities in *D. magna*. In other words, the maximum acute toxicity removal was obtained in the samples containing 500 mg/l H_2O_2 concentration at a temperature of 60°C after 150 min of sonication. The acute toxicity decreased from 618 mg/l initially to EC_5=35 mg/l. This corresponds to an acute toxicity removal efficiency of 90.00% at a temperature of 60°C after 150 min of sonication (Table 5.142, SET 3; Figure 5.137d).

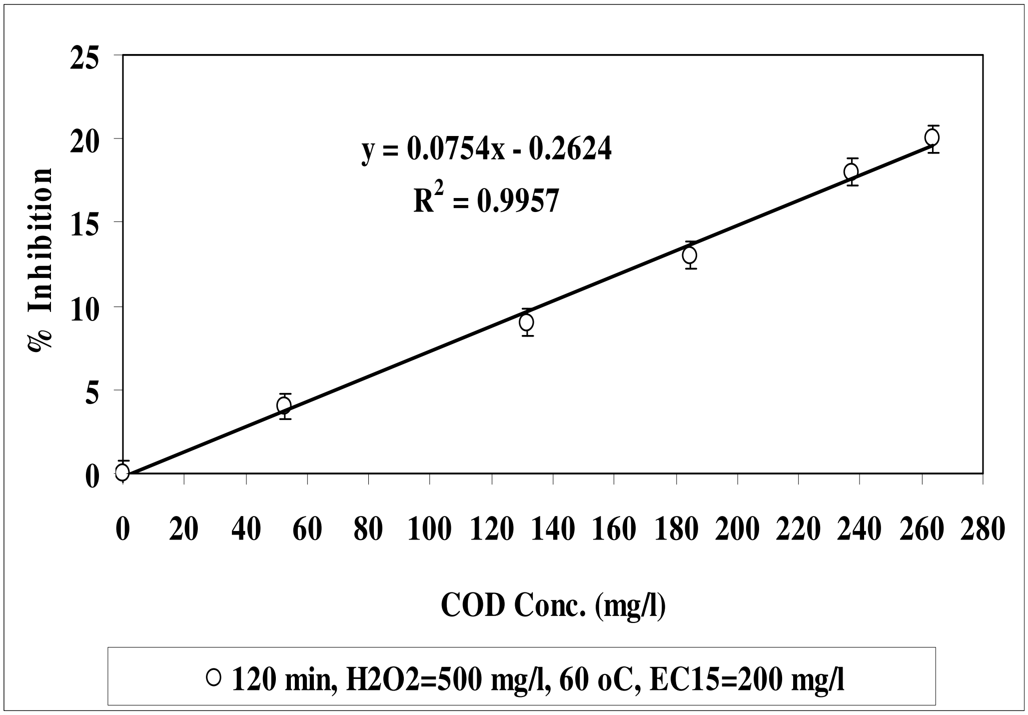


(a)

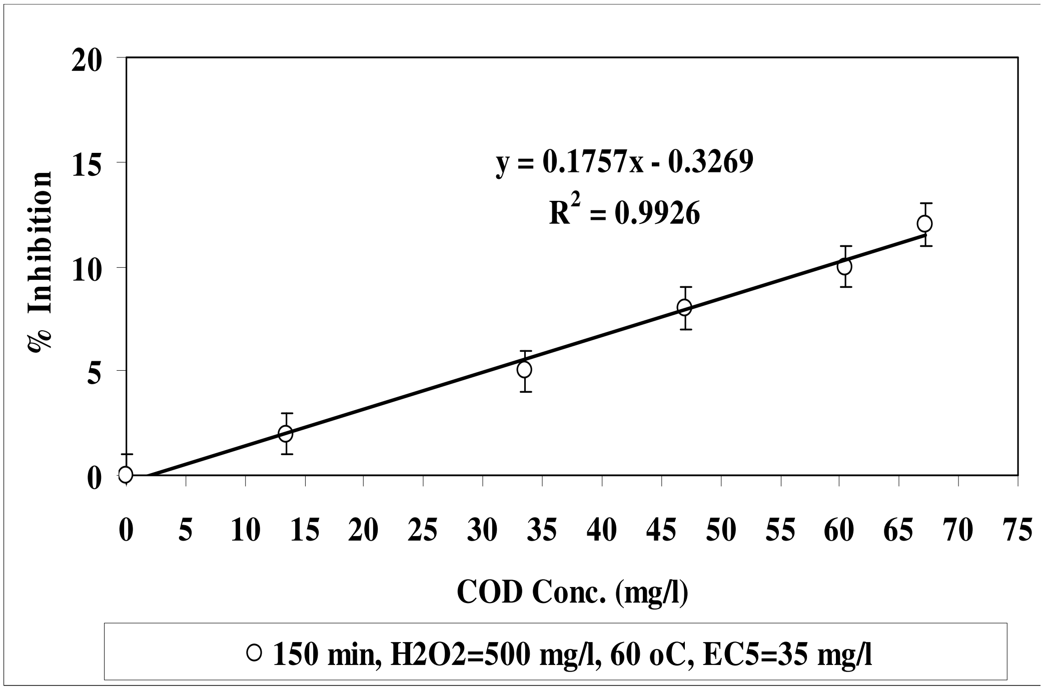


(b)

Figure 5.137 Effect of 500 mg/l H_2O_2 concentration on *Daphnia magna* acute toxicity in PCI ww for (a) influent at 25°C and (b) H_2O_2=500 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.137 Effect of 500 mg/l H_2O_2 concentration on *Daphnia magna* acute toxicity in PCI ww for (c) H_2O_2=500 mg/l after 120 min sonication time at 60°C and (d) H_2O_2=500 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.16.3.3 Direct Effects of H_2O_2 Concentrations on the Acute Toxicity of Microtox and Daphnia magna in PCI ww

The acute toxicity tests were performed in the samples containing some additives such as H_2O_2, TiO_2, NaCl, Fe^{+2} and Fe^{+3}. In order to detect the direct responses of Microtox and *Daphnia magna* to the additives mentioned above the toxicity test were performed without PCI ww. The initial EC values and the the EC_{50} values were measured in the samples containing different additive concentrations after 150 min sonication time Table 5.143 showed the responses of Microtox and *Daphnia magna* to increasing H_2O_2 concentrations.

Table 5.143 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing H_2O_2 concentrations without PCI ww after 150 min sonication time.

	Microtox Test			***Daphnia magna* Test**		
H_2O_2 Conc. (mg/l)	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
100	EC_{10}=20	-	-	EC_{10}=20	-	-
500	EC_{15}=100	4.00	EC_1=2.00	EC_{20}=100	5.00	EC_3=6.00
2000	EC_{20}=200	6.00	EC_3=4.00	EC_{30}=200	8.00	EC_6=11.00

The acute toxicity originating only from 100, 500 and 2000 mg/l H_2O_2 were found to be low (Table 5.143). 100 mg/l H_2O_2 did not exhibited toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 500 and 2000 mg/l H_2O_2 were found to be low in the samples without PCI ww for the test organisms mentioned above. The acute toxicity originated from the H_2O_2 decreased significantly to EC_1 and EC_3 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the H_2O_2 is not significant and the real acute toxicity throughout sonication was

attributed to the PCI ww, to the PAHs in ww, to their metabolites and to the sonodegradation by-products (Table 5.143).

5.16.4 Effect of TiO_2 Concentrations on the Acute Toxicity Removal Efficiencies in PCI ww at Increasing Sonication Time and Temperature

5.16.4.1 Effect of TiO_2 Concentrations on the Microtox Acute Toxicity Removal Efficiencies in PCI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was found as 600 mg/l at 25°C (Table 5.144, SET 1; Figure 5.138a). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{60}=819 mg/l to EC_{25}=771 mg/l and to EC_{10}=652 mg/l in TiO_2=10.00 mg/l at 30°C (Table 5.144, SET 3). The toxicity removal efficiencies were 33.33%, 72.22% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 30°C (Table 5.144, SET 3).

The EC_{90} values decreased to EC_{50}, to EC_{20} and to EC_5 after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.144, SET 3; Figure 5.138b-c-d). The EC_{50}, the EC_{20} and the EC_5 values were measured as 640 mg/l, 600 and 520 mg/l, respectively, in TiO_2=10.00 mg/l at 60°C. The toxicity removal efficiencies were 44.44%, 77.78% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.144, SET 3; Figure 5.138b-c-d). 94.44% maximum Microtox acute toxicity yield was found in TiO_2=10.00 mg/l after 150 min sonication time at 60°C (Table 5.144, SET 3; Figure 5.138d).

The EC_{90} values decreased to EC_{70}=832 mg/l to EC_{35}=796 and to EC_{20}=655 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 30°C (Table 5.144, SET 3). The EC_{90} values decreased to EC_{60}=824 mg/l to EC_{30}=781 and to EC_{15}=652 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 30°C. The EC_{90} values decreased to EC_{65}=813 mg/l to EC_{35}=777 and to EC_{25}=649 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 30°C. The toxicity removal efficiencies were 77.78%, 83.33% and 72.22% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of TiO_2=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.144, SET 3).

Table 5.144 Effect of increasing TiO_2 concentrations on Microtox acute toxicity in PCI ww at 30°C and at 60°C.

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{90}$		**$*EC$**		**$*EC$**		**$*EC$**	
1	Raw ww, control	600		EC_{80}=610		EC_{60}=510		EC_{50}=525	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{90}$	**$*EC$**	**$*EC$**	**$*EC$**	**$*EC_{90}$**	**$*EC$**	**$*EC$**	**$*EC$**
2	Raw ww, control	600	EC_{70}= 610	EC_{50}= 590	EC_{40}= 680	600	EC_{60}= 680	EC_{40}= 610	EC_{30}= 410
3	TiO_2=0.10 mg/l	600	EC_{70}= 832	EC_{35}= 796	EC_{20}= 655	600	EC_{60}= 824	EC_{30}= 765	EC_{20}= 738
	TiO_2=0.50 mg/l	600	EC_{70}= 824	EC_{30}= 781	EC_{15}= 652	600	EC_{60}= 817	EC_{25}= 796	EC_{15}= 665
	TiO_2=10.00 mg/l	600	EC_{60}= 819	EC_{25}= 771	EC_{10}= 652	600	EC_{50}= 640	EC_{20}= 600	EC_{5}= 520
	TiO_2=20.00 mg/l	600	EC_{65}= 813	EC_{35}= 777	EC_{25}= 649	600	EC_{60}= 811	EC_{30}= 796	EC_{20}= 663

* EC values were calculated based on COD_{dis} (mg/l).

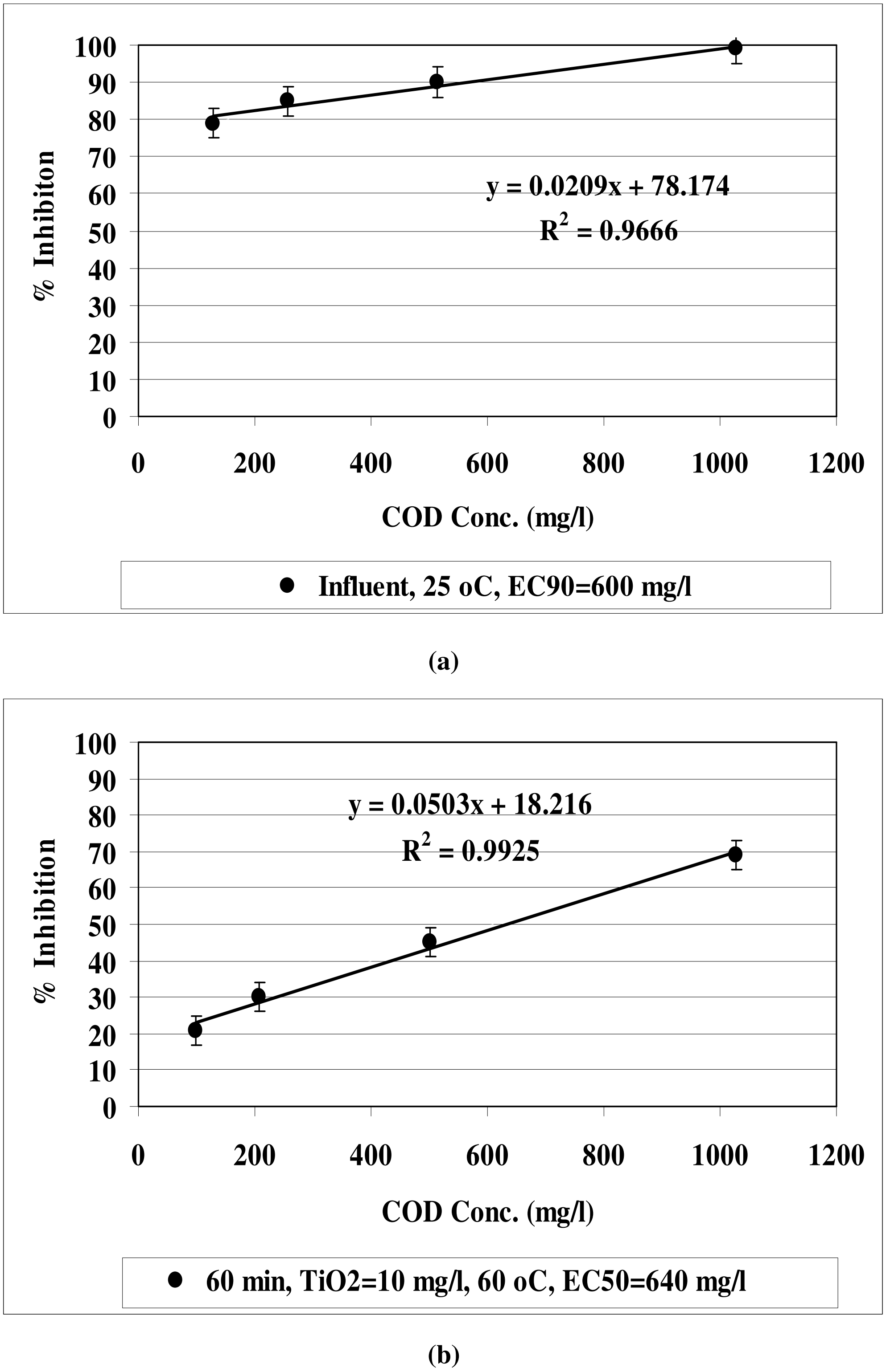
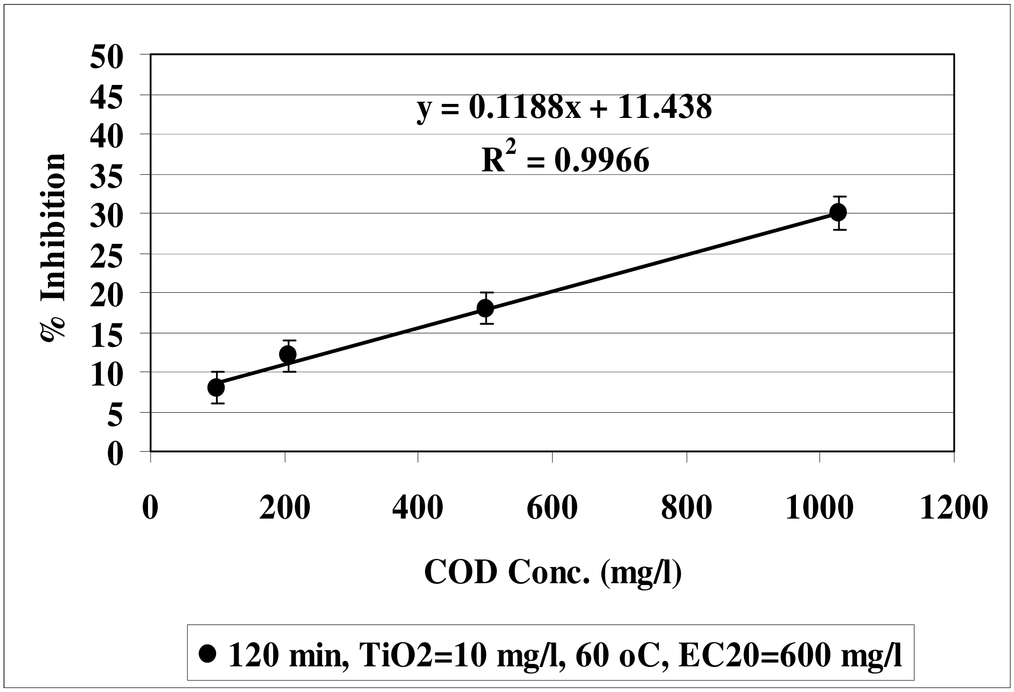
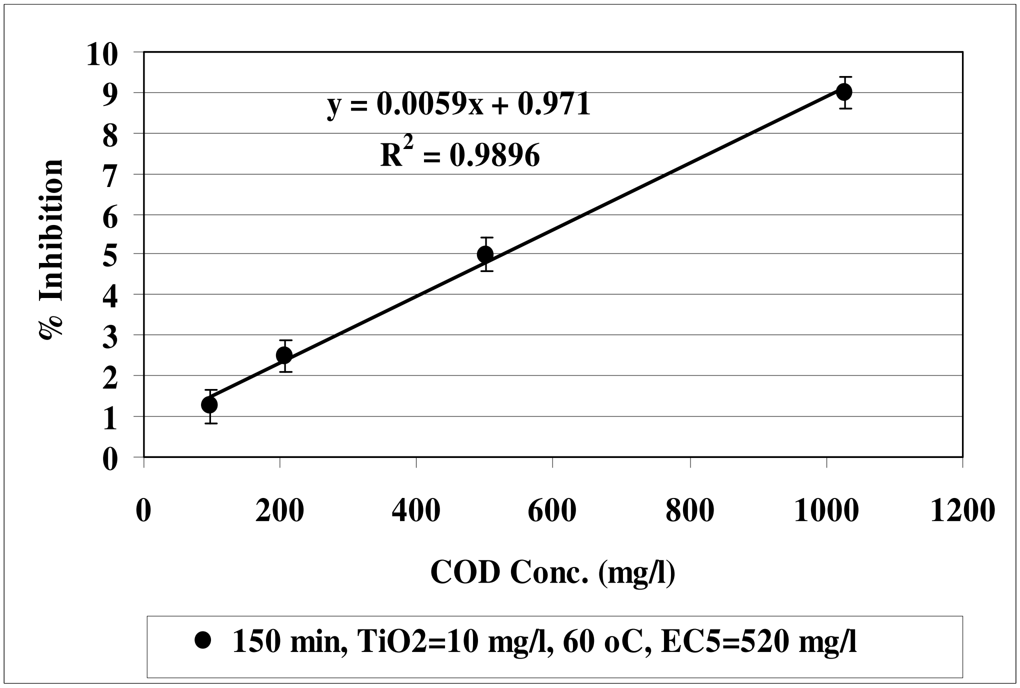


Figure 5.138 Effect of 10.00 mg/l TiO_2 concentration on Microtox acute toxicity in PCI ww for (a) influent at 25°C and (b) TiO_2=10.00 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.138 Effect of 10.00 mg/l TiO_2 concentration on Microtox acute toxicity in PCI ww for (c) TiO_2=10.00 mg/l after 120 min sonication time at 60°C and (d) TiO_2=10.00 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

The EC_{90} values decreased to EC_{60}=824 mg/l to EC_{30}=765 and to EC_{20}=738 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 60°C (Table 5.144, SET 3). The EC_{90} values decreased to EC_{60}=817 mg/l to EC_{25}=796 and to EC_{15}=665 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 60°C. The EC_{90} values decreased to EC_{60}=811 mg/l to EC_{30}=796 and to EC_{20}=663 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 60°C. The toxicity removal efficiencies were 77.78%, 83.33% and 77.78% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication at 60°C. It was observed an inhibition effect of TiO_2=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication at 60°C (Table 5.144, SET 3).

5.16.4.2 Effect of TiO_2 Concentrations on the Daphnia magna Acute Toxicity Removal Efficiencies in PCI ww at Increasing Sonication Time and Temperature

As seen in Table 5.145 (SET 1) and in Figure 5.139a, the initial EC_{50} values were observed as 618 mg/l at 25°C. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{35}=290 mg/l to EC_{20}=200 mg/l and to EC_{10}=122 mg/l in TiO_2=10.00 mg/l at 30°C (Table 5.145, SET 3). The toxicity removal efficiencies were 30.00%, 60.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 30°C (Table 5.145, SET 3).

The EC_{50} values decreased to EC_{30} to EC_{10} and to EC_{5} after 60 min, 120 and 150 min sonication times in TiO_2=10.00 mg/l at 60°C (Table 5.145, SET 3; Figure 5.139b-c-d). The EC_{30}, the EC_{10} and the EC_{5} values were measured as 400 mg/l, 105 and 55 mg/l, respectively, in TiO_2=10.00 mg/l at 60°C. The toxicity removal efficiencies were 40.00%, 80.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.145, SET 3; Figure 5.139b-c-d). 90.00% maximum *Daphnia magna* acute toxicity removal was obtained in TiO_2=10.00 mg/l after 150 min sonication time at 60°C (Table 5.145, SET 3; Figure 5.139d).

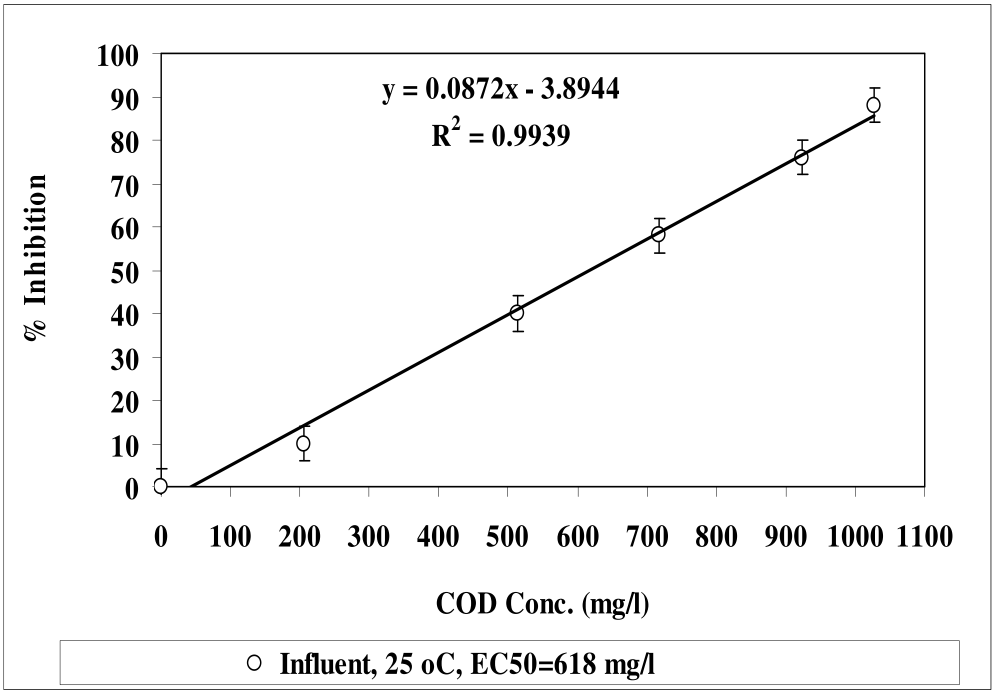
Table 5.145 Effect of increasing TiO_2 concentrations on *Daphnia magna* acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{50}$		***EC**		***EC**		***EC**	
1	Raw ww, control	618		EC_{45}=425		EC_{40}=325		EC_{35}=182	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{50}$	***EC**	***EC**	***EC**	**$*EC_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	618	EC_{40}= 510	EC_{35}= 340	EC_{30}= 85	618	EC_{40}= 425	EC_{30}= 190	EC_{25}= 32
3	TiO_2=0.10 mg/l	618	EC_{40}= 350	EC_{25}= 160	EC_{15}= 200	618	EC_{35}= 165	EC_{15}= 425	EC_{10}= 260
	TiO_2=0.50 mg/l	618	EC_{40}= 340	EC_{20}= 137	EC_{10}= 115	618	EC_{35}= 450	EC_{15}= 120	EC_{5}= 105
	TiO_2=10.00 mg/l	618	EC_{35}= 290	EC_{20}= 200	EC_{10}= 122	618	EC_{30}= 400	EC_{10}= 105	EC_{5}= 55
	TiO_2=20.00 mg/l	618	EC_{45}= 250	EC_{30}= 150	EC_{20}= 87	618	EC_{40}= 325	EC_{20}= 135	EC_{15}= 50

* EC values were calculated based on COD_{dis} (mg/l).

The EC_{50} values decreased to EC_{40}=350 mg/l to EC_{25}=160 and to EC_{15}=200 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 60°C (Table 5.145, SET 3). The EC_{50} values decreased to EC_{40}=340 mg/l to EC_{20}=137 and to EC_{10}=115 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 60°C. The EC_{50} values decreased to EC_{45}=250 mg/l to EC_{30}=150 and to EC_{20}=87 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 60°C. The toxicity removal efficiencies were 70.00%, 80.00% and 60.00% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 60^{o}C. It was obtained an inhibition effect of TiO_2=20.00 mg/l to *Daphnia magna* after 150 min sonication time at 60^{o}C (Table 5.145, SET 3).

The EC_{50} values decreased to EC_{35}=165 mg/l to EC_{15}=425 and to EC_{10}=260 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 60^{o}C (Table 5.145, SET 3). The EC_{50} values decreased to EC_{35}=450 mg/l to EC_{15}=120 and to EC_5=105 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 60^{o}C. The EC_{50} values decreased to EC_{40}=325 mg/l to EC_{20}=135 and to EC_{15}=50 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 60^{o}C. The toxicity removal efficiencies were 80.00%, 90.00% and 70.00% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 60^{o}C. It was observed an inhibition effect of TiO_2=20.00 mg/l to *Daphnia magna* after 150 min sonication time at 60^{o}C (Table 5.145, SET 3).



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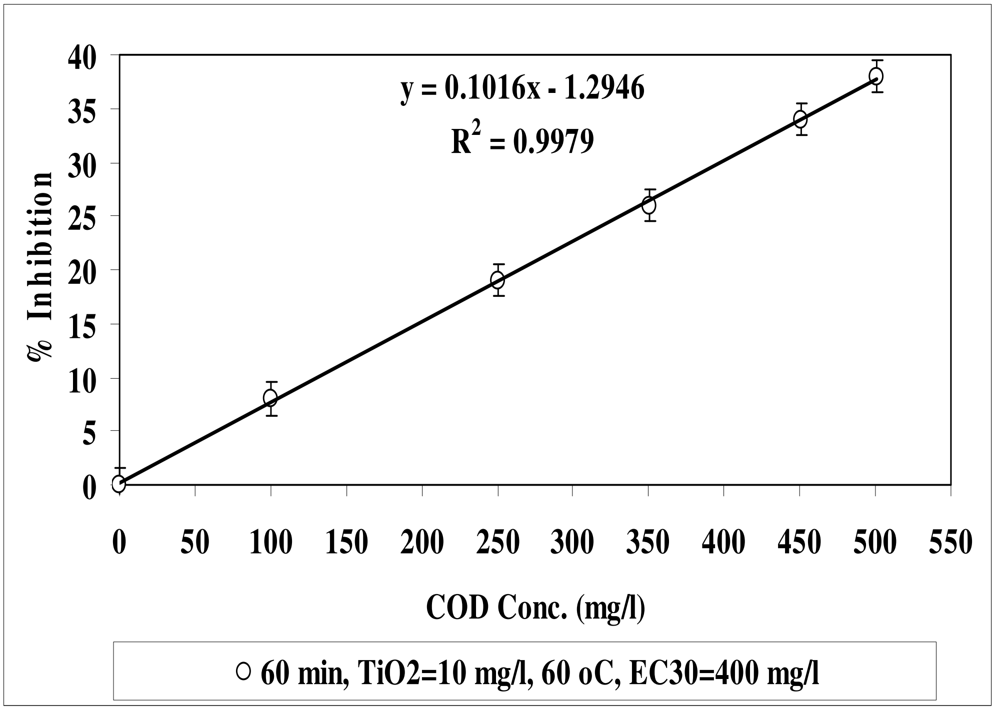
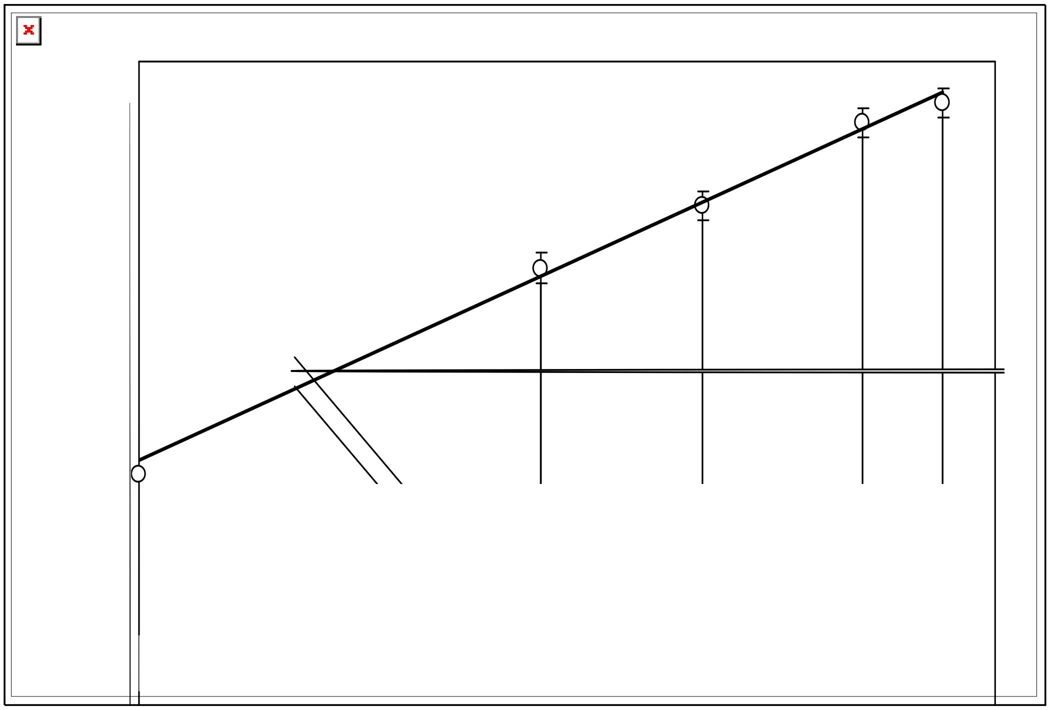


(b)

Figure 5.139 Effect of 10.00 mg/l TiO_2 concentration on *Daphnia magna* acute toxicity in PCI ww for (a) influent at 25°C and (b) TiO_2=10.00 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



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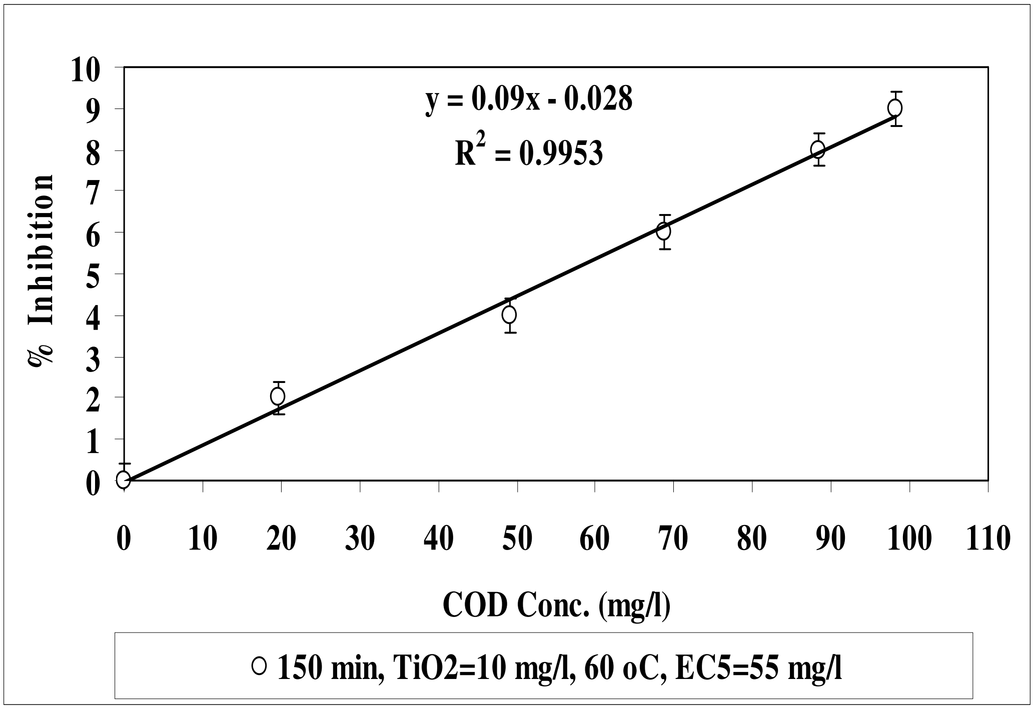


(d)

Figure 5.139 Effect of 10.00 mg/l TiO_2 concentration on *Daphnia magna* acute toxicity in PCI ww for (c) TiO_2=10.00 mg/l after 120 min sonication time at 60°C and (d) TiO_2=10.00 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.16.4.3 Direct Effects of TiO_2 Concentrations on the Acute Toxicity of Microtox and Daphnia magna in PCI ww

The acute toxicity test was performed in the samples containing 0.10, 0.50, 10.00 and 20.00 mg/l TiO_2 concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing TiO_2 the toxicity test were performed without PCI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing TiO_2 concentrations after 150 min sonication time. Table 5.146 showed the responses of Microtox and *Daphnia magna* to increasing TiO_2 concentrations.

Table 5.146 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing TiO_2 concentrations without PCI ww after 150 min sonication time.

TiO_2 Conc. (mg/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
0.10	EC_{10}=20	-	-	EC_{10}=20	-	-
0.50	EC_{15}=100	3.00	EC_1=3.00	EC_{20}=100	4.00	EC_3=6.00
10.00	EC_{20}=200	5.00	EC_3=5.00	EC_{30}=200	6.00	EC_6=11.00
20.00	EC_{25}=250	7.00	EC_6=10.00	EC_{40}=300	9.00	EC_8=22.00

The acute toxicity originating only from 0.10, 0.50, 10.00 and 20.00 mg/l TiO_2 were found to be low (Table 5.146). 0.10 mg/l TiO_2 did not exhibited toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 0.50, 10.00 and 20.00 mg/l TiO_2 were found to be low in the samples without PCI ww for the test organisms mentioned above. The acute toxicity originated from the TiO_2 decreased significantly to EC_1, EC_3 and EC_6 after 150 min sonication. Therefore it can be concluded that the toxicity originating from the TiO_2 is not significant and the real acute toxicity throughout sonication was attributed to the PCI ww, to the PAHs in ww, to their metabolites and to the sonodegradation by-products (Table 5.146).

5.16.5 Effect of NaCl Concentrations on the Acute Toxicity Removal Efficiencies in PCI ww at Increasing Sonication Time and Temperature

5.16.5.1 Effect of NaCl Concentrations on the Microtox Acute Toxicity Removal Efficiencies in PCI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was found as 600 mg/l at 25°C (Table 5.147, SET 1). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{60}=612 mg/l to EC_{30}=429 mg/l and to EC_{10}=350 mg/l in NaCl=2.50 g/l at 30°C (Table 5.147, SET 3). The toxicity removal efficiencies were 33.33%, 66.67% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 30°C (Table 5.147, SET 3).

The EC_{90} values decreased to EC_{50}, to EC_{20} and to EC_{5} after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60°C (Table 5.147, SET 3). The EC_{50}, the EC_{20} and the EC_{5} values were measured as 607 mg/l, 482 and 357 mg/l, respectively, in NaCl=2.50 g/l at 60°C. The toxicity removal efficiencies were 44.44%, 77.78% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60°C. 94.44% maximum Microtox acute toxicity yield was observed in NaCl=2.50 g/l after 150 min sonication time at 60°C (Table 5.147, SET 3).

The EC_{90} values decreased to EC_{60}=614 mg/l to EC_{35}=498 and to EC_{15}=354 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 30°C (Table 5.147, SET 3). The EC_{90} values decreased to EC_{65}=603 mg/l to EC_{40}=448 and to EC_{25}=327 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 30°C. The toxicity removal efficiencies were 83.33% and 72.22% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of NaCl=15.00 g/l to

Photobacterium phosphoreum after 150 min sonication time at 30°C (Table 5.147, SET 3).

Table 5.147 Effect of increasing NaCl concentrations on Microtox acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{90}$		**$*EC$**		**$*EC$**		**$*EC$**	
1	Raw ww, control	600		$EC_{80}=610$		$EC_{60}=510$		$EC_{50}=525$	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{90}$	**$*EC$**	**$*EC$**	**$*EC$**	**$*EC_{90}$**	**$*EC$**	**$*EC$**	**$*EC$**
2	Raw ww, control	600	$EC_{70}=610$	$EC_{50}=590$	$EC_{40}=680$	600	$EC_{60}=680$	$EC_{40}=610$	$EC_{30}=410$
3	NaCl=1.00 g/l	600	$EC_{60}=614$	$EC_{35}=498$	$EC_{15}=354$	600	$EC_{60}=605$	$EC_{30}=494$	$EC_{10}=454$
	NaCl=2.50 g/l	600	$EC_{60}=612$	$EC_{30}=429$	$EC_{10}=350$	600	$EC_{50}=607$	$EC_{20}=482$	$EC_{5}=357$
	NaCl=15.00 g/l	600	$EC_{65}=603$	$EC_{40}=448$	$EC_{25}=327$	600	$EC_{60}=696$	$EC_{35}=579$	$EC_{20}=452$

* EC values were calculated based on COD_{dis} (mg/l).

The EC_{90} values decreased to EC_{60}=605 mg/l to EC_{30}=494 and to EC_{10}=454 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 60°C (Table 5.147, SET 3). The EC_{90} values decreased to EC_{60}=696 mg/l to EC_{35}=579 and to EC_{20}=452 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 60°C. The toxicity removal efficiencies were 88.89% and 77.78% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 60°C. It was observed an inhibition effect of NaCl=15.00 g/l to

Photobacterium phosphoreum after 150 min sonication time at 60^oC (Table 5.147, SET 3).

5.16.5.2 Effect of NaCl Concentrations on the Daphnia magna Acute Toxicity Removal Efficiencies in PCI ww at Increasing Sonication Time and Temperature

As seen in Table 5.148 (SET 1), the initial EC_{50} values were observed as 618 mg/l at 25^oC. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{35}=325 mg/l to EC_{20}=170 mg/l and to EC_{10}=70 mg/l in NaCl=2.50 g/l at 30^oC (Table 5.148, SET 3). The toxicity removal efficiencies were 30.00%, 60.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 30^oC (Table 5.148, SET 3).

The EC_{50} values decreased to EC_{30}=360 mg/l to EC_{15}=140 mg/l and to EC_{5}=39 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60^oC (Table 5.148, SET 3). The toxicity removal efficiencies were 40.00%, 70.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60^oC. 94.44% maximum *Daphnia magna* acute toxicity yield was observed in NaCl=2.50 g/l after 150 min sonication at 60^oC (Table 5.148, SET 3).

The EC_{50} values decreased to EC_{40}=485 mg/l to EC_{25}=370 and to EC_{15}=190 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 30^oC (Table 5.148, SET 3). The EC_{50} values decreased to EC_{45}=330 mg/l to EC_{30}=170 and to EC_{20}=6.50 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 30^oC. The Microtox acute toxicity yields were 70.00% and 60.00% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 30^oC. It was observed an inhibition effect of NaCl=15.00 g/l to *Daphnia magna* after 150 min sonication time at 30^oC (Table 5.148, SET 3).

Table 5.148 Effect of increasing NaCl concentrations on *Daphnia magna* acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{50}$		***EC**		***EC**		***EC**	
1	Raw ww, control	618		EC_{45}=425		EC_{40}=325		EC_{35}=182	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{50}$	***EC**	***EC**	***EC**	**$*EC_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	618	EC_{40}= 510	EC_{35}= 340	EC_{30}= 85	618	EC_{40}= 425	EC_{30}= 190	EC_{25}= 32
3	NaCl=1.00 g/l	618	EC_{40}= 485	EC_{25}= 370	EC_{15}= 190	618	EC_{35}= 375	EC_{20}= 23	EC_{10}= 135
	NaCl=2.50 g/l	618	EC_{35}= 325	EC_{20}= 170	EC_{10}= 70	618	EC_{30}= 360	EC_{15}= 140	EC_{5}= 39
	NaCl=15.00 g/l	618	EC_{45}= 330	EC_{30}= 170	EC_{20}= 6.5	618	EC_{40}= 400	EC_{25}= 125	EC_{15}= 33

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{35}=375 mg/l to EC_{20}=23 and to EC_{10}=135 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 60°C (Table 5.148, SET 3). The EC_{50} values decreased to EC_{40}=400 mg/l to EC_{25}=125 and to EC_{15}=33 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 60°C. The Microtox acute toxicity yields were 80.00% and 70.00% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of NaCl=15.00 g/l to *Daphnia magna* after 150 min sonication time at 60°C (Table 5.148, SET 3).

The maximum acute toxicity removal was 90.00% at the NaCl concentration of 2.50 g/l at 60^{o}C after 150 min sonication time (Table 5.148, SET 3). In this acute toxicity reduction the EC_{50} value of raw PCI ww decreased to EC_5=39 mg/l. Low acute toxicity removals found at high NaCl concentrations could be attributed to their detrimental effect on the *Daphnia magna* cells. High NaCl (> 15.00 g/l) caused lysis in *Daphnia magna* cells. The high salt concentrations caused turgor in *Daphnia magna* cells by increasing the osmotic pressure in the test medium.

A strong significant correlation between EC_{50} values and PAH removals showed that the *Daphnia magna* acute toxicity test alone can be considered a reliable indicator of PCI toxicity (R^2=0.86, F=4.78, p=0.001). Similarly, a strong linear correlation between threshold concentrations of NaCl decrease in inhibitions was observed (R^2=0.87, F=16.72, p=0.001) while the correlation between the inhibition decrease and NaCl concentrations above the threshold values was weak and not significant (R^2=0.31, F=3.42, p=0.001).

The toxicity of wastewater samples to the tested species prior and after sonodegradation varied. The raw wastewater samples induced 95.00% motility inhibition to *D. magna* (Table 5.148, SET 3). This inhibition could be attributed to the mixed recalcitrant carcinogenic hydrophobic PAHs with high benzene rings and to the synergistic effects of the aforementioned more hydrophobic PAHs with less hydrophobic PAHs in PCI ww. When *D. magnas* were exposed to the sonicated effluent samples there was a significant reduction in inhibition (from 98.90% to 99.99%) for the acute toxicity after 150 min sonication time at 60^{o}C (Table 5.148, SET 3).

Low acute toxicity removals found at high NaCl concentrations could be attributed to their detrimental effect on the *D. magna* cells. High NaCl caused lysis in *D. magna* cells. The high salt concentrations caused plasmolysis in *D. magna* cells by increasing the osmotic pressure in the test medium.

5.16.5.3 Direct Effects of NaCl Concentrations on the Acute Toxicity of Microtox and Daphnia magna in PCI ww

The acute toxicity test was performed in the samples containing 1.00, 2.50 and 15.00 g/l NaCl concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing NaCl the toxicity test were performed without PCI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing NaCl concentrations after 150 min sonication time. Table 5.149 showed the responses of Microtox and *Daphnia magna* to increasing NaCl concentrations.

Table 5.149 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing NaCl concentrations without PCI ww after 150 min sonication time.

	Microtox Test			***Daphnia magna* Test**		
NaCl Conc. (g/l)	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
1.00	EC_{10}=25	-	-	EC_{10}=30	-	-
2.50	EC_{15}=130	2.00	EC_{1}=5.00	EC_{20}=150	5.00	EC_{3}=8.00
15.00	EC_{20}=210	5.00	EC_{4}=10.00	EC_{30}=250	7.00	EC_{7}=12.00

The acute toxicity originating only from 1.00, 2.50 and 15.00 g/l NaCl were found to be low (Table 5.149). 1.00 g/l NaCl did not exhibited toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 2.50 and 15.00 g/l NaCl were found to be low in the samples without PCI ww for the test organisms mentioned above. The acute toxicity originated from the NaCl decreased significantly to EC_1 and EC_4 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the NaCl is not significant and the real acute toxicity throughout sonication was

attributed to the PCI ww, to the PAHs in ww, to their metabolites and to the sonodegradation by-products (Table 5.149).

5.16.6 Effect of Fe^{+2} Concentrations on the Removal of Acute Toxicity in PCI ww at Increasing Sonication Time and Temperature

5.16.6.1 Effect of Fe^{+2} Concentrations on the Removal of Microtox Acute Toxicity in PCI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was measured as 600 mg/l at 25°C (Table 5.150, SET 1). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{60}=611 mg/l to EC_{30}=485 mg/l and to EC_{15}=350 mg/l, in Fe^{+2}=8.00 mg/l at 30°C. The toxicity removal efficiencies were 33.33%, 66.67% and 83.33% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 30°C (Table 5.150, SET 3).

The EC_{90} values decreased to EC_{55}, to EC_{20} and to EC_{10} after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C (Table 5.150, SET 3). The EC_{55}, the EC_{20} and the EC_{10} values were measured as 608 mg/l, 463 and 349 mg/l, respectively, at 60°C. The toxicity removal efficiencies were 38.89%, 77.78% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C. 88.89% maximum Microtox acute toxicity yield was found in Fe^{+2}=8.00 mg/l after 150 min sonication time at 60°C (Table 5.150, SET 3).

The EC_{90} values decreased to EC_{65}=622 mg/l to EC_{30}=479 and to EC_{20}=353 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=2.00 mg/l at 30°C (Table 5.150, SET 3). The EC_{90} values decreased to EC_{70}=611 mg/l to EC_{40}=486 and to EC_{25}=348 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 30°C. The toxicity removal efficiencies were 77.78% and 77.78% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of Fe^{+2}=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.150, SET 3).

Table 5.150 Effect of increasing Fe^{+2} concentrations on Microtox acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

<table>
<tr><th rowspan="4">No</th><th rowspan="4">Parameters</th><th colspan="8">Microtox Acute Toxicity Values, *EC (mg/l)</th></tr>
<tr><th colspan="8">25°C</th></tr>
<tr><th colspan="2">0. min</th><th colspan="2">60. min</th><th colspan="2">120. min</th><th colspan="2">150. min</th></tr>
<tr><th colspan="2">*EC_{90}</th><th colspan="2">*EC</th><th colspan="2">*EC</th><th colspan="2">*EC</th></tr>
<tr><td>1</td><td>Raw ww, control</td><td colspan="2">600</td><td colspan="2">EC_{80}=610</td><td colspan="2">EC_{60}=510</td><td colspan="2">EC_{50}=525</td></tr>
<tr><td rowspan="3"></td><td rowspan="3"></td><th colspan="4">30°C</th><th colspan="4">60°C</th></tr>
<tr><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th></tr>
<tr><th>*EC_{90}</th><th>*EC</th><th>*EC</th><th>*EC</th><th>*EC_{90}</th><th>*EC</th><th>*EC</th><th>*EC</th></tr>
<tr><td>2</td><td>Raw ww, control</td><td>600</td><td>EC_{70}= 610</td><td>EC_{50}= 590</td><td>EC_{40}= 680</td><td>600</td><td>EC_{60}= 680</td><td>EC_{40}= 610</td><td>EC_{30}= 410</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>3</td><td>Fe^{+2}=2.00 mg/l</td><td>600</td><td>EC_{65}= 622</td><td>EC_{30}= 479</td><td>EC_{20}= 353</td><td>600</td><td>EC_{60}= 620</td><td>EC_{30}= 477</td><td>EC_{15}= 354</td></tr>
<tr><td></td><td>Fe^{+2}=8.00 mg/l</td><td>600</td><td>EC_{60}= 611</td><td>EC_{30}= 485</td><td>EC_{15}= 350</td><td>600</td><td>EC_{55}= 608</td><td>EC_{20}= 463</td><td>EC_{10}= 349</td></tr>
<tr><td></td><td>Fe^{+2}=20.00 mg/l</td><td>600</td><td>EC_{70}= 609</td><td>EC_{35}= 472</td><td>EC_{20}= 346</td><td>600</td><td>EC_{60}= 604</td><td>EC_{30}= 480</td><td>EC_{20}= 342</td></tr>
</table>

* EC values were calculated based on COD (mg/l).

The EC_{90} values decreased to EC_{60}=620 mg/l to EC_{30}=477 and to EC_{15}=354 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=2.00 mg/l at 60°C (Table 5.150, SET 3). The EC_{90} values decreased to EC_{60}=604 mg/l to EC_{30}=480 and to EC_{20}=342 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 60°C. The toxicity removal efficiencies were 83.33% and 77.78% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 60°C. It was observed an inhibition effect of Fe^{+2}=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60°C (Table 5.150, SET 3).

5.16.6.2 Effect of Fe^{+2} Concentrations on the Removal of Daphnia magna Acute Toxicity in PCI ww at Increasing Sonication Time and Temperature

The initial EC$_{50}$ values were obtained as 618 mg/l at 25°C (Table 5.151, SET 1). After 60 min, 120 and 150 min of sonication the EC$_{50}$ values decreased to EC$_{35}$ to EC$_{25}$ and to EC$_{15}$ in Fe^{+2}=8.00 mg/l at 30°C (Table 5.151, SET 3). The EC$_{35}$, the EC$_{25}$ and the EC$_{15}$ values were measured as 340 mg/l, 160 and 65 mg/l, respectively, in Fe^{+2}=8.00 mg/l at 30°C. The toxicity removal efficiencies were 30.00%, 50.00% and 70.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 30°C (Table 5.151, SET 3).

Table 5.151 Effect of increasing Fe^{+2} concentrations on *Daphnia magna* acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, *EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC$_{50}$**		***EC**		***EC**		***EC**	
1	Raw ww, control	618		EC$_{45}$=425		EC$_{40}$=325		EC$_{35}$=182	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC$_{50}$**	***EC**	***EC**	***EC**	***EC$_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	618	EC$_{40}$= 510	EC$_{35}$= 340	EC$_{30}$= 85	618	EC$_{40}$= 425	EC$_{30}$= 190	EC$_{25}$= 32
3	Fe^{+2}=2.00 mg/l	618	EC$_{40}$= 360	EC$_{30}$= 180	EC$_{20}$= 125	618	EC$_{35}$= 350	EC$_{25}$= 170	EC$_{15}$= 110
	Fe^{+2}=8.00 mg/l	618	EC$_{35}$= 340	EC$_{25}$= 160	EC$_{15}$= 65	618	EC$_{30}$= 310	EC$_{20}$= 150	EC$_{10}$= 47
	Fe^{+2}=20.00 mg/l	618	EC$_{45}$= 300	EC$_{35}$= 150	EC$_{25}$= 50	618	EC$_{35}$= 275	EC$_{30}$= 130	EC$_{20}$= 15

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{30} to EC_{20} and to EC_{10} after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C (Table 5.151, SET 3). The EC_{30}, the EC_{20} and the EC_{10} values were measured as 310 mg/l, 150 and 47 mg/l, respectively, in Fe^{+2}=8.00 mg/l at 60°C. The toxicity removal efficiencies were 40.00%, 60.00% and 80.00% after 60 min, 120 and 150 min sonication time, respectively, in Fe^{+2}=8.00 mg/l at 60°C. 80.00% maximum *Daphnia magna* acute toxicity removal was measured in Fe^{+2}=8.00 mg/l after 150 min sonication time at 60°C (Table 5.151, SET 3).

The EC_{50} values decreased to EC_{40}=360 mg/l to EC_{30}=180 and to EC_{20}=125 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=2.00 mg/l at 30°C (Table 5.151, SET 3). The EC_{50} values decreased to EC_{45}=300 mg/l to EC_{35}=150 and to EC_{25}=50 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 30°C. The toxicity removal efficiencies were 60.00% and 50.00% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 30°C. It was obtained an inhibition effect of Fe^{+2}=20.00 mg/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.151, SET 3).

The EC_{50} values decreased to EC_{35}=350 mg/l to EC_{25}=170 and to EC_{15}=110 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=2.00 mg/l at 60°C (Table 5.151, SET 3). The EC_{50} values decreased to EC_{35}=275 mg/l to EC_{30}=130 and to EC_{20}=15 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 60°C. The toxicity removal efficiencies were 70.00% and 60.00% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 60°C. It was observed an inhibition effect of Fe^{+2}=20.00 mg/l to *Daphnia magna* after 150 min sonication time at 60°C (Table 5.151, SET 3).

The acute toxicity decreased from an initial 618 mg/l to EC_{10}=47 mg/l at a Fe^{+2} concentration of 8.00 mg/l at 60°C after a sonication time of 150 min (Table 5.151, SET 3). The maximum acute toxicity removal was approximately 80.00% in the samples containing 8.00 mg/l Fe^{+2} concentrations at a temperature of 60°C after 150 min of sonication time. The acute toxicity removal decreased at Fe^{+2} concentrations above 8.00 mg/l (Table 5.151, SET 3).

5.16.6.3 Direct Effects of Fe^{+2} Concentrations on the Acute Toxicity of Microtox and Daphnia magna in PCI ww

The acute toxicity test was performed in the samples containing 2.00, 8.00 and 20.00 mg/l Fe^{+2} concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing Fe^{+2} the toxicity test were performed without PCI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing Fe^{+2} concentrations after 150 min sonication time. Table 5.152 showed the responses of Microtox and *Daphnia magna* to increasing Fe^{+2} concentrations.

Table 5.152 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing Fe^{+2} concentrations without PCI ww after 150 min sonication time.

Fe^{+2} Conc. (mg/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
2.00	EC_{10}=28	-	-	EC_{10}=35	-	-
8.00	EC_{15}=150	1.00	EC_1=6.00	EC_{20}=200	3.00	EC_3=9.00
20.00	EC_{20}=240	4.00	EC_3=11.00	EC_{30}=270	6.00	EC_5=15.00

The acute toxicity originating only from 2.00, 8.00 and 20.00 mg/l Fe^{+2} were found to be low (Table 5.152). 2.00 mg/l Fe^{+2} did not exhibit toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 8.00 and 20.00 mg/l Fe^{+2} were found to be low in the samples without PCI ww for the test organisms mentioned above. The acute toxicity originated from the Fe^{+2} decreased significantly to EC_1 and EC_3 after

150 min sonication time. Therefore it can be concluded that the toxicity originating from the Fe^{+2} is not significant and the real acute toxicity throughout sonication was attributed to the PCI ww, to the PAHs in ww, to their metabolites and to the sonodegradation by-products (Table 5.152).

5.16.7 Effect of Fe^{+3} Concentrations on the Removal of Acute Toxicity in PCI ww at Increasing Sonication Time and Temperature

5.16.7.1 Effect of Fe^{+3} Concentrations on the Removal of Microtox Acute Toxicity in PCI ww at Increasing Sonication Time and Temperature

As seen in Table 5.153 (SET 1), the initial EC_{90} values at pH=7.0 was found as 600 mg/l at 25°C. The EC_{90} values decreased to EC_{60}=613 mg/l to EC_{30}=477 mg/l and to EC_{15}=351 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 30°C (Table 5.153, SET 3). The toxicity removal efficiencies were 33.33%, 66.67% and 83.33% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 30°C (Table 5.153, SET 3).

The EC_{90} values decreased to EC_{55}, to EC_{20} and to EC_{10} after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C (Table 5.153, SET 3). The EC_{55}, the EC_{20} and the EC_{10} values were measured as 611 mg/l, 475 and 353 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 60°C. The toxicity removal efficiencies were 38.89%, 77.78% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C. 88.89% maximum Microtox acute toxicity yield was observed in Fe^{+3}=20.00 mg/l after 150 min sonication time at 60°C (Table 5.153, SET 3).

The EC_{90} values decreased to EC_{65}=624 mg/l to EC_{35}=469 and to EC_{20}=353 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 30°C (Table 5.153, SET 3). The EC_{90} values decreased to EC_{70}=611 mg/l to EC_{40}=486 and to EC_{25}=348 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 30°C. The toxicity removal efficiencies were 77.78% and 72.22% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of Fe^{+3}=50.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.153, SET 3).

Table 5.153 Effect of increasing Fe^{+3} concentrations on Microtox acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{90}$		**$*EC$**		**$*EC$**		**$*EC$**	
1	Raw ww, control	600		EC_{80}=610		EC_{60}=510		EC_{50}=525	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{90}$	**$*EC$**	**$*EC$**	**$*EC$**	**$*EC_{90}$**	**$*EC$**	**$*EC$**	**$*EC$**
2	Raw ww, control	600	EC_{70}= 610	EC_{50}= 590	EC_{40}= 680	600	EC_{60}= 680	EC_{40}= 610	EC_{30}= 410
3	Fe^{+3}=10 mg/l	600	EC_{65}= 624	EC_{35}= 469	EC_{20}= 353	600	EC_{55}= 623	EC_{30}= 478	EC_{15}= 354
	Fe^{+3}=20 mg/l	600	EC_{60}= 613	EC_{30}= 477	EC_{15}= 351	600	EC_{55}= 611	EC_{20}= 475	EC_{10}= 353
	Fe^{+3}=50 mg/l	600	EC_{70}= 611	EC_{40}= 486	EC_{25}= 348	600	EC_{60}= 606	EC_{35}= 464	EC_{20}= 346

* EC values were calculated based on COD (mg/l).

The EC_{90} values decreased to EC_{55}=623 mg/l to EC_{30}=478 and to EC_{15}=354 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 60°C (Table 5.153, SET 3). The EC_{90} values decreased to EC_{60}=606 mg/l to EC_{35}=464 and to EC_{20}=346 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 60°C. The toxicity removal efficiencies were 83.33% and 77.78% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 60^{o}C. It was obtained an inhibition effect of Fe^{+3}=50.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60^{o}C (Table 5.153, SET 3).

5.16.7.2 Effect of Fe^{+3} Concentrations on the Removal of Daphnia magna Acute Toxicity in PCI ww at Increasing Sonication Time and Temperature

The initial EC$_{50}$ values were observed as 618 mg/l at 25^{o}C (Table 5.154, SET 1). After 60 min, 120 and 150 min of sonication the EC$_{50}$ values decreased to EC$_{35}$=360 mg/l to EC$_{25}$=175 mg/l and to EC$_{15}$=70 mg/l in Fe^{+3}=20.00 mg/l at 30^{o}C (Table 5.154, SET 3). The toxicity removal efficiencies were 30.00%, 50.00% and 70.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 30^{o}C (Table 5.154, SET 3).

The EC$_{50}$ values decreased to EC$_{30}$ to EC$_{20}$ and to EC$_{10}$ after 60 min, 120 and 150 min sonication, respectively, in Fe^{+3}=20.00 mg/l at 60^{o}C (Table 5.154, SET 3). The EC$_{30}$, the EC$_{20}$ and the EC$_{10}$ values were measured as 355 mg/l, 180 and 60 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 60^{o}C. The toxicity removal efficiencies were 40.00%, 60.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60^{o}C. 80.00% maximum *Daphnia magna* acute toxicity removal was obtained in Fe^{+3}=20.00 mg/l after 150 min sonication time at 60^{o}C (Table 5.154, SET 3).

The EC$_{50}$ values decreased to EC$_{40}$=350 mg/l to EC$_{30}$=210 and to EC$_{20}$=160 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 30^{o}C (Table 5.154, SET 3). The EC$_{50}$ values decreased to EC$_{45}$=460 mg/l to EC$_{40}$=180 and to EC$_{25}$=65 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 30^{o}C. The toxicity removal efficiencies were 60.00% and 50.00% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 30^{o}C. It was obtained an inhibition effect of Fe^{+3}=50.00 mg/l to *Daphnia magna* after 150 min sonication time at 30^{o}C (Table 5.154, SET 3).

Table 5.154 Effect of increasing Fe^{+3} concentrations on *Daphnia magna* acute toxicity in PCI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{50}$		***EC**		***EC**		***EC**	
1	Raw ww, control	618		EC_{45}=425		EC_{40}=325		EC_{35}=182	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{50}$	***EC**	***EC**	***EC**	**$*EC_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	618	EC_{40}= 510	EC_{35}= 340	EC_{30}= 85	618	EC_{40}= 425	EC_{30}= 190	EC_{25}= 32
3	Fe^{+3}=10.00 mg/l	618	EC_{40}= 350	EC_{30}= 210	EC_{20}= 160	618	EC_{35}= 390	EC_{25}= 170	EC_{15}= 130
	Fe^{+3}=20.00mg/l	618	EC_{35}= 360	EC_{25}= 175	EC_{15}= 70	618	EC_{30}= 355	EC_{20}= 180	EC_{10}= 60
	Fe^{+3}=50.00 mg/l	618	EC_{45}= 460	EC_{40}= 180	EC_{25}= 65	618	EC_{40}= 300	EC_{30}= 160	EC_{20}= 32

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{35}=390 mg/l to EC_{25}=170 and to EC_{15}=130 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 60°C (Table 5.154, SET 3). The EC_{50} values decreased to EC_{40}=300 mg/l to EC_{30}=160 and to EC_{20}=32 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 60°C. The toxicity removal efficiencies were 70.00% and 60.00% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 60°C. It was observed an inhibition effect of Fe^{+3}=50.00 mg/l to *Daphnia magna* after 150 min sonication time at 60°C (Table 5.154, SET 3).

5.16.7.3 Direct Effects of Fe^{+3} Concentrations on the Acute Toxicity of Microtox and Daphnia magna in PCI ww

The acute toxicity test was performed in the samples containing 10.00, 20.00 and 50.00 mg/l Fe^{+3} concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing Fe^{+3} the toxicity test were performed without PCI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing Fe^{+3} concentrations after 150 min sonication time. Table 5.155 showed the responses of Microtox and *Daphnia magna* to increasing Fe^{+3} concentrations.

Table 5.155 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing Fe^{+3} concentrations without PCI ww after 150 min sonication time.

Fe^{+3} Conc. (mg/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
10.00	EC_{10}=34	-	-	EC_{10}=40	-	-
20.00	EC_{15}=160	3.00	EC_2=8.00	EC_{20}=200	4.00	EC_3=10.00
50.00	EC_{20}=250	5.00	EC_4=14.00	EC_{30}=280	8.00	EC_6=20.00

The acute toxicity originating only from 10.00, 20.00 and 50.00 mg/l Fe^{+3} were found to be low (Table 5.155). 10.00 mg/l Fe^{+3} did not exhibit toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication. The toxicity atributed to the 20.00 and 50.00 mg/l Fe^{+3} were found to be low in the samples without PCI ww for the test organisms mentioned above. The acute toxicity originated from the Fe^{+3} decreased significantly to EC_2 and EC_4 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the Fe^{+3} is not significant and the real acute toxicity throughout sonication was

attributed to the PCI ww, to the PAHs in ww, to their metabolites and to the sonodegradation by-products (Table 5.155).

5.16.8 PAH Toxicities, Interspecies Correlation and Sensitivities

In order to determine the sensitivity of *Daphnia magna* (water flea) for the acute toxicity tests described above and to show the responses of two different organisms, to sonicated and non-sonicated wastewater samples the acute toxicity test was also performed with *Vibrio fischeri* bacteria. Sensitivity ranking indicates the sum of toxicity responses of every organism used in acute toxicity tests (Sponza, 2001a; 2001b; 2002a; 2002b; 2003; 2006; Sponza & Selcuk-Kuscu, 2010). To explain the sensitivity of acute toxicity test results based on *Daphnia magna* and *Photobacterium phosphoreum* a table was constructed ranking the samples in order of acute toxicity (Sponza, 2001a; 2001b; 2002a; 2002b; 2003; 2006; Sponza & Selcuk-Kuscu, 2010) A score of “1” was assigned to the most sensitive test for each sample down to 2 for the least sensitive organism representing two trophic levels which were classified according to the test results (Sponza, 2001a; 2001b; 2002a; 2002b; 2003; 2006; Sponza & Selcuk-Kuscu, 2010). The comparison of toxicity response and sensitivity ranking was assessed in PCI ww before sonication process.

The acute toxicity classification of an effluent should always be based on the results of testing all trophic levels at least once. The EC_{50} value of PCI ww increased from EC_{50}=333.33 mg/l (converted from EC_{90}=600.00 mg/l in PCI ww for Microtox acute toxicity assay before sonication) to EC_{50}=618.00 mg/l as the trophic level increased from bacteria in Microtox test to water flea in *Daphnia magna* test in the influent samples. The EC_{50} values measured for *Daphnia magna* differed significantly from *Photobacterium phosphoreum* in the decline of sensitivity scores and exhibited lower mortalities in the influents (t test statistic 3.72, $p \leq 0.05$). The t statistics showed that *Daphnia magna* had higher EC_{50} values and lower sensitivity scores than *Photobacterium phosphoreum.* The *Photobacterium phosphoreum* and *Daphnia magna* had different responses to toxicity and mortalities (t-test statistic=3.88, p=0.10) and this difference was significant (t test statistic=11.99, p=0.05). The *Photobacterium phosphoreum* bacteria had lower EC_{50} values than

Daphnia magna and these differences were significant (t-test statistics=14.42, $p < 0.10$). The sensitivity score of *Daphnia magna* was higher than *Photobacterium phosphoreum* and the difference was significant (t-test statistic=11.50, $p \leq 0.05$). In other words, the *Daphnia magna* was found to be resistant compared to *Photobacterium phosphoreum*. This indicated that the water fleas exhibited less acute toxicity to PCI ww. The differences in test sensitivities can be attributed to the differences in the responses of the two different trophic organisms in PCI ww. From the acute toxicity tests it can be seen that different organisms were affected differently by the influent PCI ww samples (before sonication process). It should be pointed out, however, that the *Photobacterium phosphoreum* bacteria and water flea tests are reference standards used world-wide for toxicity testing and represent one of the trophic level tests required in toxicity evaluation. In this study showed that the Microtox acute toxicity test is more sensitive than that *Daphnia magna* in the PCI ww samples before sonication process.

Table 5.156 shows the sensitivity ranking and the EC_{50} values of PCI ww in *Photobacterium phosphoreum* and *Daphnia magna* in sonicated samples containing some additives after 150 min sonication time at 60^oC. The EC_{50} value of PCI ww increased from 2.78 mg/l (converted from 5.00 mg/l at original EC values in PCI ww for Microtox acute toxicity assay after 150 min sonication time) to 25.00 mg/l as the trophic level increased from bacteria in Microtox test to water flea in *Daphnia magna* test in the sonicated PCI ww samples containing some additives after 150 min sonication at 60^oC (Table 5.156). To verify the relationships between the acute toxicity data of two organisms the EC_{50} values of *Photobacterium phosphoreum* were correlated to those of *Daphnia magna* by statistical analysis using their EC_{50} values in the effluent of PCI ww. It was found that the EC_{50} values differed in both test organisms for the sonicated samples containing some additives after 150 min sonication time at 60^oC. The coefficient of correlation and t-test statistics ($R^2=0.88$, $p=0.01$, t-test statistics=9.15) show a significant linear relationship between the acute toxicities of PCI ww to *Photobacterium phosphoreum* and to *Daphnia magna* in the after 150 min sonication samples (Table 5.156). This indicated that the water fleas exhibited less acute toxicity to PCI ww. The differences in test sensitivities can be attributed to the differences in the responses of the two different trophic organisms in PCI ww. As a conclusion, this study showed that the Microtox acute toxicity test is more sensitive than that *Daphnia magna* in the sonicated PCI ww samples containing some additives after 150 min sonication time at 60^oC (Table 5.156).

Table 5.156 Sensitivity ranking and EC_{50} values of PCI ww in *Photobacterium phosphoreum* and *Daphnia magna* in sonicated samples containing some additives after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

Parameters	***Photobacterium phosphoreum***		***Daphnia magna***	
	EC_{50} value and 95.00% Confidence Limits (mg/l) 48 h	**Sensitivity Ranking**	**EC_{50} value and 95.00% Confidence Limits (mg/l) 48 h**	**Sensitivity Ranking**
Raw ww, control	16.67 (16.43 – 16.91)	1	25.00 (24.71 – 25.29)	2
1 h aeration	4.33 (4.21 – 4.45)	1	5.00 (4.87 – 5.13)	2
30 min N_2(g) (6.00 mg/l N_2)	4.33 (4.21 – 4.45)	1	5.00 (4.87 – 5.13)	2
pH=7.0	16.67 (16.43 – 16.91)	1	25.00 (24.71 – 25.29)	2
DO=10.00 mg/l	4.11 (3.99 – 4.23)	1	5.00 (4.87 – 5.13)	2
H_2O_2=500 mg/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
TiO_2=10.00 mg/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
NaCl=2.50 g/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
Fe^{+2}=8.00 mg/l	5.56 (5.42 – 5.70)	1	10.00 (9.82 – 10.18)	2
Fe^{+3}=20.00 mg/l	5.56 (5.42 – 5.70)	1	10.00 (9.82 – 10.18)	2
HCO_3^{-1}=1.00 g/l	8.33 (8.16 – 8.50)	1	10.00 (9.82 – 10.18)	2
C_4H_9OH=0.50 g/l	5.56 (5.42 – 5.70)	1	10.00 (9.82 – 10.18)	2

5.16.9 Correlation of Acute Toxicities with Physicochemical Properties of PAHs after 150 min Sonication at 30^{o}C

In this study, the acute toxicities of less and more hydrophobic PAHs and their physicochemical characteristics were correlated with linear regression for both *Vibrio fischeri* and *Daphnia magna* (Tables 5.157a and b). Although, the octanol/water partition coefficient (log K_{ow}) has been proposed as a method for evaluating the toxicity of refractory organics in aquatic systems (Sponza, 2000; 2003) log K_{ow} is often insufficient to account for the varying toxicity of the chemicals. In this study, it is clear that with *Vibrio fischeri* and *Daphnia magna* high correlations would be found between log K_{ow} and acute toxicity for the substituted less and more hydrophobic PAHs (DahA and BkF) (Tables 5.157a and b). The DahA and BkF pass through the bio-membrane of the organisms and accumulate before being up taken by the test organisms due to their hydrophobicities. On the other hand, Henry's law constant characterizes the relative amount of a substrate that will enter the organisms; hence this parameter has been investigated to identify the uptake of a organic substance by an organism. In this study, the Henry's law constant was strongly associated with the PAH transfer rates to the *Vibrio fischeri* and *Daphnia magna.* Significant correlations between Henry's law constants (R^2=0.88 and R^2=0.80 for *Vibrio fischeri* and *Daphnia magna*), densities (1.12 and 1.5 g/cm^3 for DahA and BkF), solubilities (2.49x10^{-4} and 1.24 g/100 ml for DahA and BkF), vapor pressure (1.00x10^{-10} and 0.32 mm Hg for DahA and BkF) octanol/water partition coefficients (6.75 and 1.91 for DahA and BkF) and molecular mass (278 and 139.10 g/mol for DahA and BkF) of PAHs and acute toxicities in *Vibrio fischeri* and *Daphnia magna* was observed (Tables 5.157a and b). Decreasing the vapor pressure results in more PAH diffusing into the bacteria from the wastewater samples. It has been suggested that the Henry's law constant and vapor pressure influences the rate of degradation of some poly-aromatic compounds. This result suggests that the acute toxicities of studied compounds to *D. magna* and *Vibrio fischeri* were relative to hydrophobicity and to other properties given in Table 5.157. The acute toxicity yields in sonicated samples containing less hydrophobic PAHs were higher in *Vibrio fischeri* than the *Daphnia magna.* The 48 h EC_{50} values suggested the decreasing rank order of acute toxicity of PAHs to *Daphnia magna* and *Vibrio fischeri* was as follows: BghiP > DahA > IcdP > BaP > BkF > BbF.

The coefficient of correlation (R^2=0.372, $p \leq 0.01$, n=3) and t test correlation (t statistic=0.893) suggested that the interrelationship with the acute toxicities (in *D. magna* and *V. fischeri*) of both more and less hydrophobic PAHs showed a low degree of linear correlation (data not shown). The relationship between the toxicity data for the PAHs tested in this study on *Daphnia magna* was also compared with corresponding data for *Vibrio fischeri* (R^2=0.395; $p \leq 0.01$). A weak correlation was found between the EC_{50} values of these organisms; however this correlation was not significant. The water flea (*D. Magna)* was generally more resistant to the acute toxicity than *Vibrio fischeri*.

Table 5.157a. Correlations between EC_{50} values and physicochemical properties of DahA and BkF in *Daphnia magna* acute toxicity test after 30 min N_2(g) (6.00 mg/l N_2) sparging and 150 min sonicated samples at 30°C at a frequency of 35 kHz and a power of 640 W (n=3, mean values *) .

Parameters	**More Hydrophobic PAH**			***Less Hydrophobic PAH***		
	DahA	***R^2**	**p**	**BkF**	***R^2**	***p***
Boiling point (°C)	524	0.22	NS	279	0.05	*NS*
Melting point (°C)	270	0.11	NS	111-116	0.09	*NS*
Relative density (g/cm^3)	1.12	0.69	p=0.01	1.50	0.59	*NS*
Henry’slaw constant (atm m^3 /mol)	1.23×10^{-7}	0.77	p=0.01	1.99×10^{-4}	0.88	*p= 0.01*
Solubility in water (g /100 ml)	2.49×10^{-4}	0.87	p=0.01	1.24	0.89	*p=0.01*
Vapor pressure (mm Hg)	1.00×10^{-10}	0.80	p=0.01	0.32	0.77	*p=0.01*
Relative vapor density (kg/m^3)	3.2	0.83	p=0.01	3.5	0.84	*p=0.01*
Relative density of the vap./air-mix. at 20°C	12.59	0.83	p=0.01	1.21	0.79	*p=0.01*
Flash point	105	0.01	NS	103	0.02	*NS*
Explosive limits vol % in air	0.18	0.02	NS	2.00-4.00	0.20	*NS*
Oct./wat. partition coefficient (log P_{ow})	6.75	0.88	p=0.01	1.91	0.89	*p=0.01*
Molecular mass (g)	*278* ($C_{22}H_{14}$)	*0.84*	*p=0.01*	*139.10* ($C_6H_5NO_3$)	*0.79*	*p=0.01*

NS: Not significant; R^2 : Correlation coefficient; p: Statistical significance

Table 5.157b Correlations between EC_{50} values and physicochemical properties of DahA and BkF to *Vibrio fischeri* acute toxicity test after 30 min $N_2(g)$ (6.00 mg/l N_2) sparging and 150 min sonicated samples at 30°C at a frequency of 35 kHz and a power of 640 W (n=3, mean values *).

Parameters	**More Hydrophobic PAH**			***Less Hydrophobic PAH***		
	DahA	***R^2**	**p**	**BkF**	***R^2**	***p***
Boiling point (°C)	524	0.18	NS	279	0.09	*p= 0.1*
Melting point (°C)	270	0.20	NS	111-116	0.01	*p= 0.1*
Relative density (g/cm^3)	1.12	0.59	p=0.01	1.50	0.57	*p= 0.1*
Henry'slaw constant (atm m^3 /mol)	1.23×10^{-7}	0.88	p=0.01	1.99×10^{-4}	0.80	*P=0.01*
Solubility in water (g /100 ml)	2.49×10^{-4}	0.85	p=0.01	1.24	0.79	*p=0.01*
Vapor pressure (mm Hg)	1.00×10^{-10}	0.74	p=0.01	0.32	0.78	*p=0.01*
Relative vapor density (kg/m^3)	3.20	0.73	p=0.01	3.50	0.69	*p=0.01*
Relative density of the vap./air-mix. at 20°C	12.59	0.84	p=0.01	1.21	0.83	*p=0.01*
Flash point	105	0.03	NS	103	0.05	*NS*
Explosive limits vol % in air	0.18	0.04	NS	2.00-4.00	0.34	*NS*
Oct./wat. partition coefficient (log P_{ow})	6.75	0.86	p=0.01	1.91	0.83	*p=0.01*
Molecular mass (g)	*278* ($C_{22}H_{14}$)	*0.78*	*p=0.01*	*139.10* ($C_6H_5NO_3$)	*0.72*	*p=0.01*

NS: Not significant; R^2: Correlation coefficient; p: Statistical significance

5.17 Acute Toxicity Evaluations in OMI ww

5.17.1 Effect of Increasing Sonication Time on the Acute Toxicity Removal Efficiencies in OMI ww at Ambient Conditions

5.17.1.1 Effect of Increasing Sonication Time on the Microtox Acute Toxicity Removal Efficiencies in OMI ww at Ambient Conditions

Microtox test is an acute toxicity test. Toxicity was estimated in terms of EC_{50}, defined as the concentration of the toxicant causing 50.00% reduction in activity of the *Photobacterium phosphoreum*. Figure 5.140 was shown the acute toxicity test results obtained from the Microtox acute toxicity test through sonication with increasing sonication time (60 min, 120 and 150 min) at pH=7.0 and at 25^{o}C ambient condition.

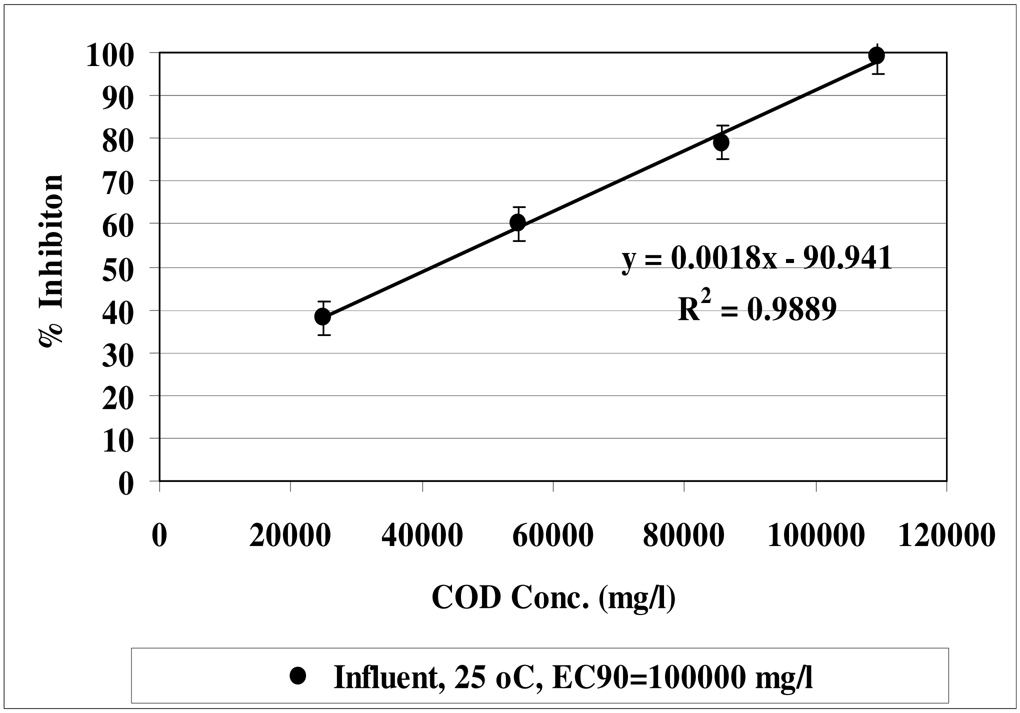
All OMI ww samples were serially diluted in 2.00% NaCI (w/v) and each assay was performed at pH=7.0 and a temperature of 15°C. NaCl (2.00%) was used as the control. The initial EC_{90} values at pH=7.0 was found as 100000 mg/l at 25^{o}C ambient conditions (Table 5.158; Figure 5.140a). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{80}=90000 mg/l to EC_{75}=98000 mg/l and to EC_{70}=95000 mg/l at 25^{o}C (Table 5.158; Figure 5.140b-c-d). The toxicity removal efficiencies were 11.11%, 16.67% and 22.22% after 60 min, 120 and 150 min sonication times, respectively, at 25^{o}C. (Table 5.158; Figure 5.140b-c-d). 22.22% maximum Microtox acute toxicity removal was found after 150 min sonication time at 25^{o}C (Table 5.158; Figure 5.140d).

Table 5.158 Effect of increasing sonication time on Microtox acute toxicity in OMI ww at 25^{o}C ambient conditions (640 W power, 35 kHz frequency).

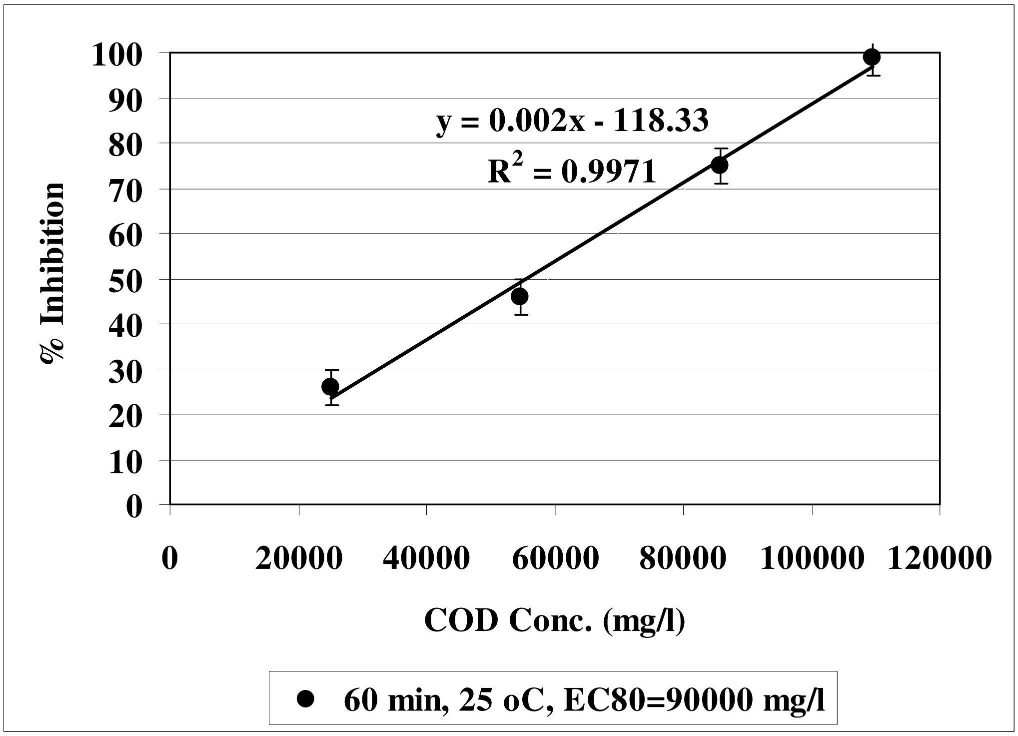
No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**			
		25^{o}C			
		0. min	**60. min**	**120. min**	**150. min**
		***EC$_{90}$**	***EC**	***EC**	***EC**
1	Raw ww, control	100000	EC$_{80}$=90000	EC$_{75}$=98000	EC$_{70}$=95000

*EC values were calculated based on COD$_{dis}$ (mg/l).

Increasing sonication times (from 60 to 150 min) positively affected at acute toxicity test. The maximum acute toxicity removal efficiency was found at long sonication time (150 min).

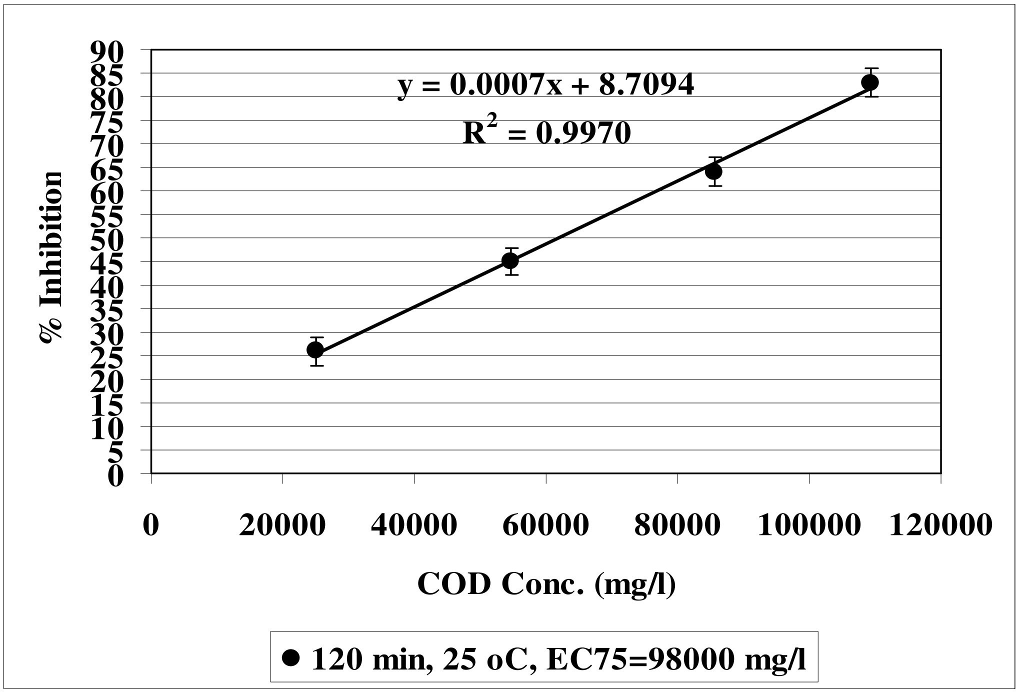


(a)

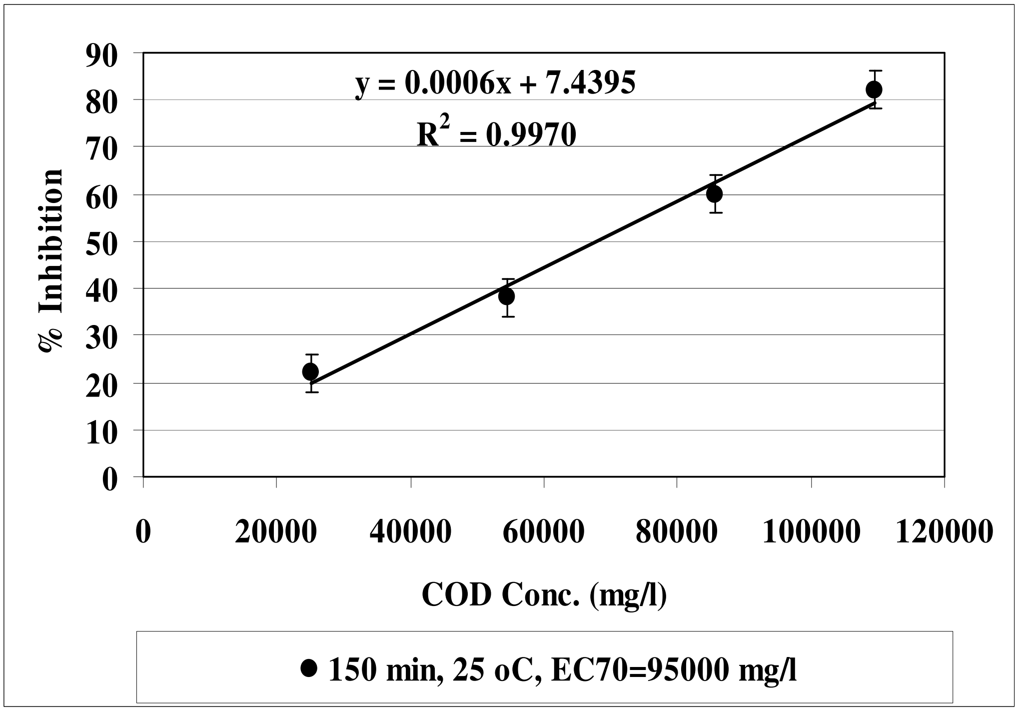


(b)

Figure 5.140 Effect of increasing sonication time on Microtox acute toxicity in OMI ww for (a) influent at 25°C and (b) after 60 min sonication time at 25°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.140 Effect of increasing sonication time on Microtox acute toxicity in OMI ww for (c) after 120 min sonication time at 25°C and (d) after 150 min sonication time at 25°C (640 W power, 35 kHz frequency).

5.17.1.2 Effect of Increasing Sonication Time on the Daphnia magna Acute Toxicity Removal Efficiencies in OMI ww at Ambient Conditions

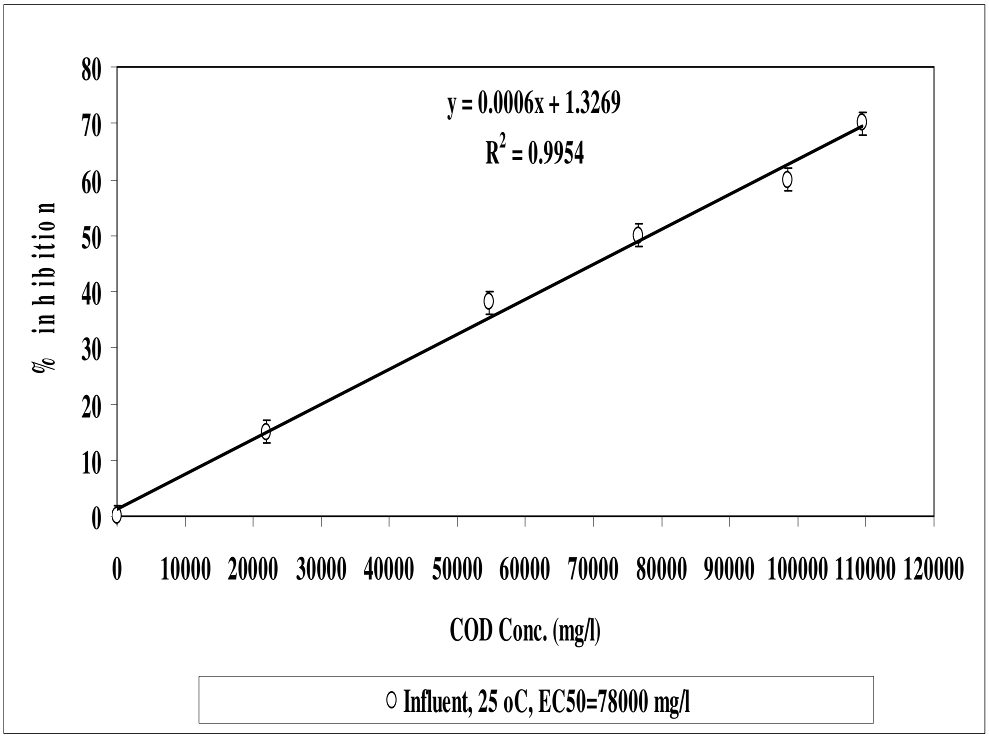
The *Daphnia magna* test is accepted as an acute toxicity test. Toxicity was estimated in terms of EC_{50}, defined as the concentration of the toxicant causing 50% reduction in activity of the water flea. The effective COD_{dis} concentrations caused 50.00% mortality in *Daphnia magna* cells EC_{50} (mg/l) in raw and sonicated wastewater samples which were monitored based on COD_{dis} (mg/l) concentrations. The EC_{50} values and the other EC values were calculated by taking into consideration the dilution ratios and the inhibitory concentrations. Figure 5.141 was shown the acute toxicity test results obtained from the *Daphnia magna* test through sonication with increasing sonication time (60 min, 120 and 150 min) at pH=7.0 and at 25^{o}C.

The test samples containing an initial COD_{dis} concentration of 109444 mg/l were diluted at 1/1, 1/2, 1/8, 1/16 and 1/24 ratios after sonication experiments. The young 10 *Daphnids* (< 24h old) were added to each test vessel at the initiation time (t=0). After 24 h of exposure, the EC values of COD_{dis} concentrations were calculated. The initial EC_{50} values were obtained as 78000 mg/l at 25^{o}C (Table 5.159; Figure 5.141a). After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{40}=85000 mg/l to EC_{30}=55000 mg/l and to EC_{25}=39000 mg/l at 25^{o}C (Figure 5.141b-c-d). The toxicity removal efficiencies were 20.00%, 40.00% and 50.00% after 60 min, 120 and 150 min sonication times, respectively, at 25^{o}C. (Table 5.159; Figure 5.141b-c-d). 50.00% maximum *Daphnia magna* acute toxicity removal was found after 150 min sonication time at 25^{o}C (Table 5.159; Figure 5.141d).

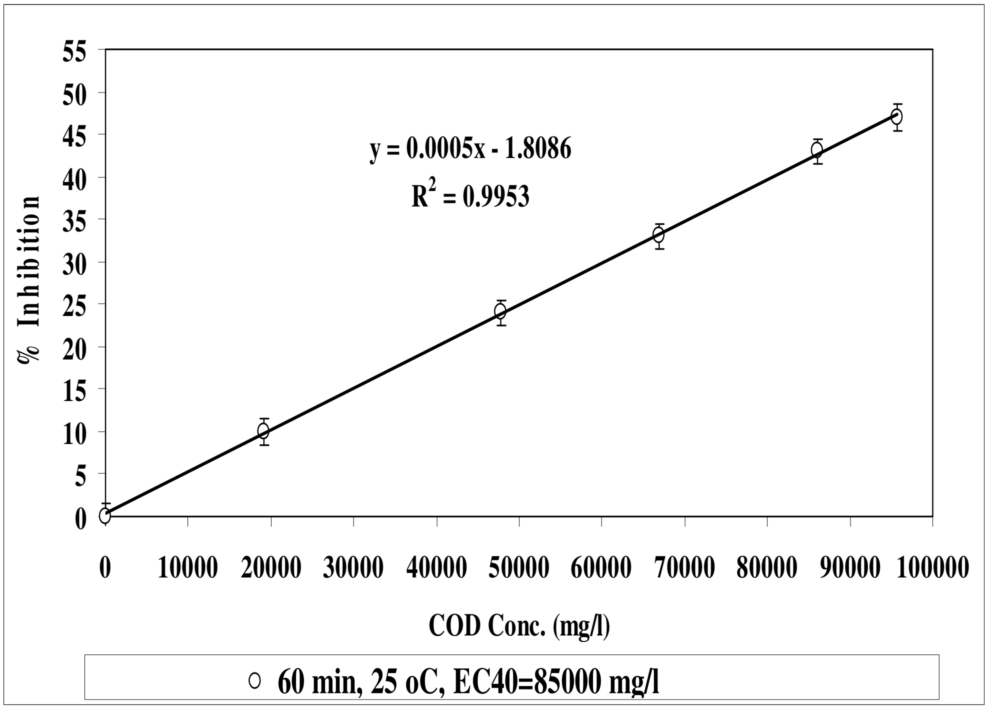
Table 5.159 Effect of increasing sonication time on *Daphnia magna* acute toxicity in OMI ww at 25^{o}C ambient conditions (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**			
		25^{o}C			
		0. min	**60. min**	**120. min**	**150. min**
		***EC$_{50}$**	***EC**	***EC**	***EC**
1	Raw ww, control	78000	EC$_{40}$=85000	EC$_{30}$=55000	EC$_{25}$=39000

* EC$_{50}$ values were calculated based on COD (mg/l).

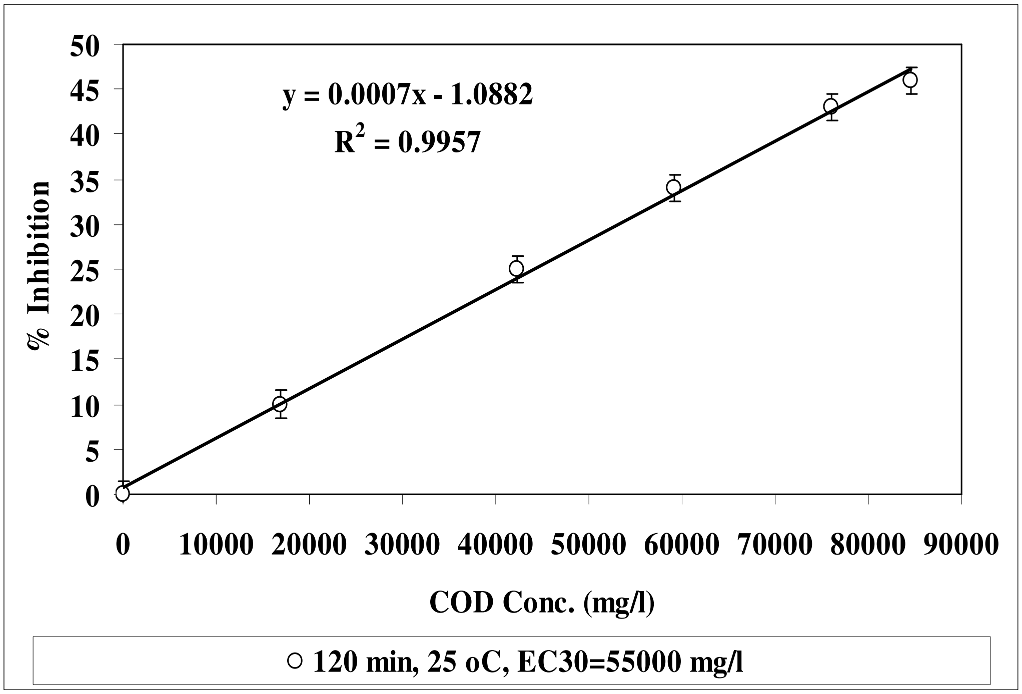


(a)

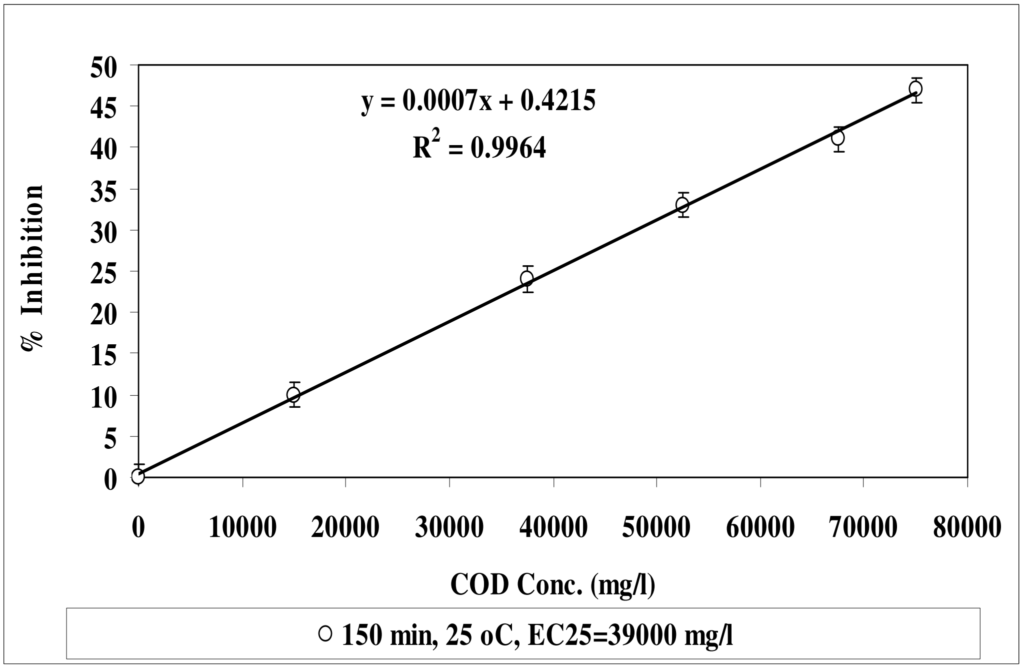


(b)

Figure 5.141 Effect of increasing sonication time on *Daphnia magna* acute toxicity in OMI ww for (a) influent at 25°C and (b) after 60 min sonication time at 25°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.141 Effect of increasing sonication time on *Daphnia magna* acute toxicity in OMI ww for (c) after 120 min sonication time at 25^{o}C and (d) after 150 min sonication time at 25^{o}C (640 W power, 35 kHz frequency).

5.17.2 Effect of Increasing Temperature on the Removal of Acute Toxicity in OMI ww at Increasing Sonication Time

5.17.2.1 Effect of Increasing Temperature on the Removal of Microtox Acute Toxicity in OMI ww at Increasing Sonication Time

The initial EC$_{90}$ values at pH=7.0 was found as 100000 mg/l at 25°C (Table 5.160, SET 1; Figure 5.142a). After 60 min, 120 and 150 min of sonication the EC$_{90}$ values decreased to EC$_{75}$=90000 mg/l to EC$_{70}$=94000 and to EC$_{60}$=95000 mg/l at 30°C (Table 5.160, SET 2). The toxicity removal efficiencies were 16.67%, 22.22% and 33.33% after 60 min, 120 and 150 min sonication times, respectively, at 30°C (Table 5.160, SET 2).

Table 5.160 Effect of increasing sonication temperature on Microtox acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

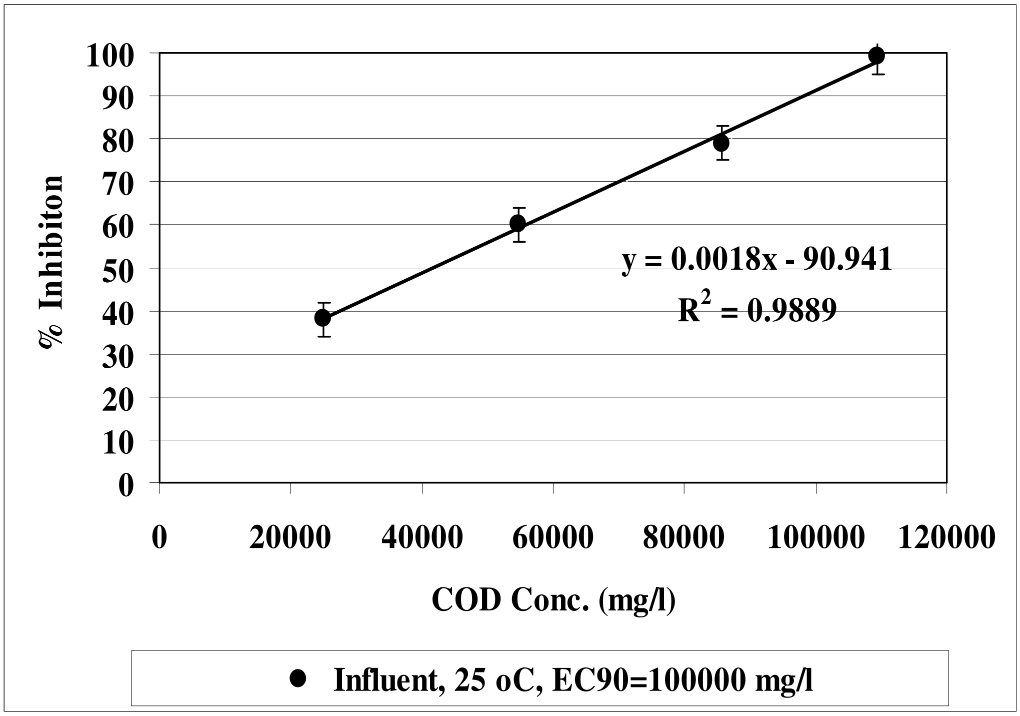
No	Parameters	Microtox Acute Toxicity Values, * EC (mg/l)							
		25°C							
		0. min		60. min		120. min		150. min	
		*EC$_{90}$		*EC		*EC		*EC	
1	Raw ww, control	100000		EC$_{80}$=90000		EC$_{75}$=98000		EC$_{70}$=95000	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
		*EC$_{90}$	*EC	*EC	*EC	*EC$_{90}$	*EC	*EC	*EC
2	Raw ww, control	100000	EC$_{75}$=90000	EC$_{70}$=94000	EC$_{60}$=95000	100000	EC$_{70}$=65000	EC$_{70}$=65000	EC$_{50}$=60000

* EC values were calculated based on COD$_{dis}$ (mg/l).

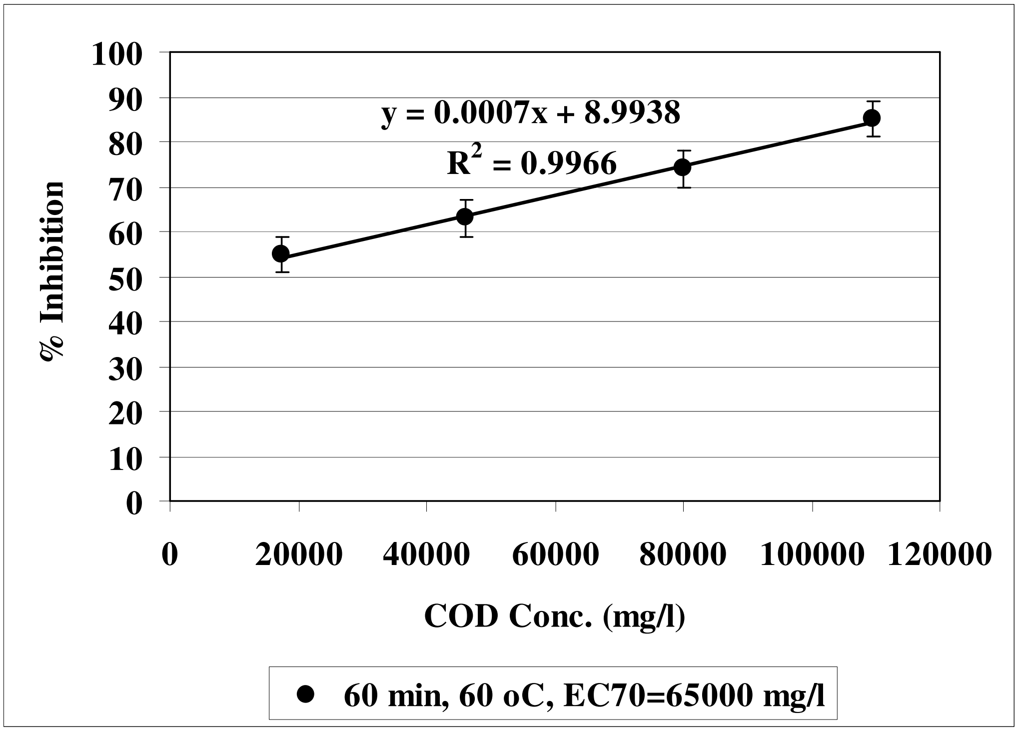
The EC$_{90}$ values decreased to EC$_{70}$=65000 mg/l, to EC$_{70}$=65000 mg/l and to EC$_{50}$=60000 mg/l after 60 min, 120 and 150 min of sonication, respectively, at 60°C (Table 5.160, SET 2; Figure 5.142b-c-d). The toxicity removal efficiencies were 22.22%, 22.22% and 44.44% after 60 min, 120 and 150 min sonication times, respectively, at 60°C (Table 5.160, SET 2; Figure 5.142b-c-d). 44.44% maximum

Microtox acute toxicity removal was observed at 60^oC after 150 min sonication time (Table 5.160, SET 2; Figure 5.142d).

Increasing sonication temperature (from 30^oC to 60^oC) positively affected at the Microtox acute toxicity removal. Also, high acute toxicity removals obtained high temperature conditions (at 60^oC). Lower acute toxicity removal was found at the lower temperature conditions (at 30^oC) and short sonication time (60 min).

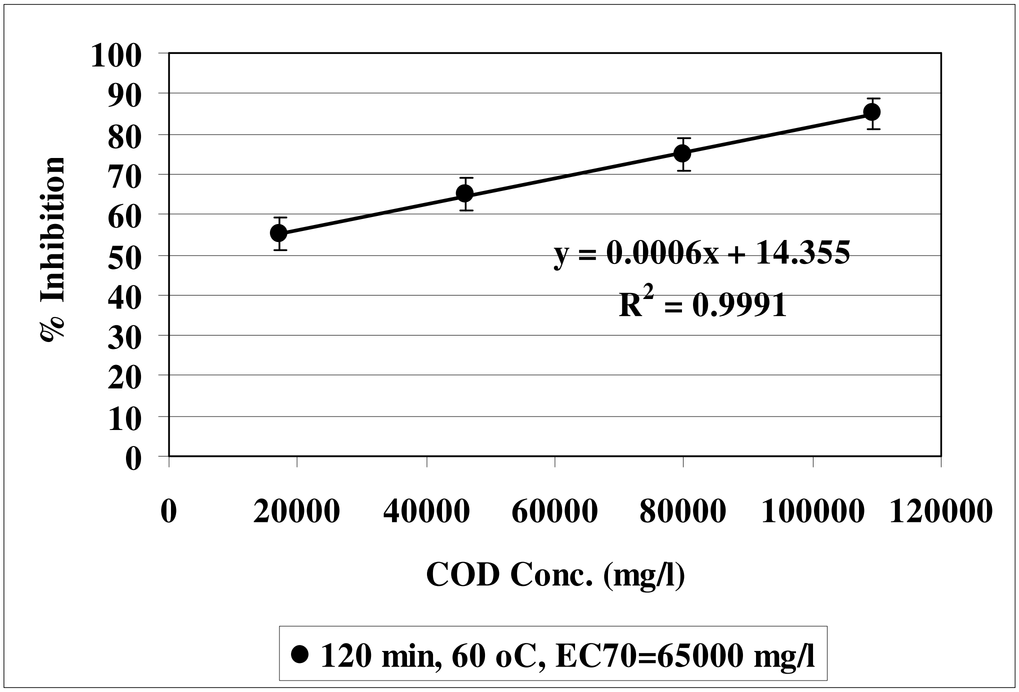


(a)

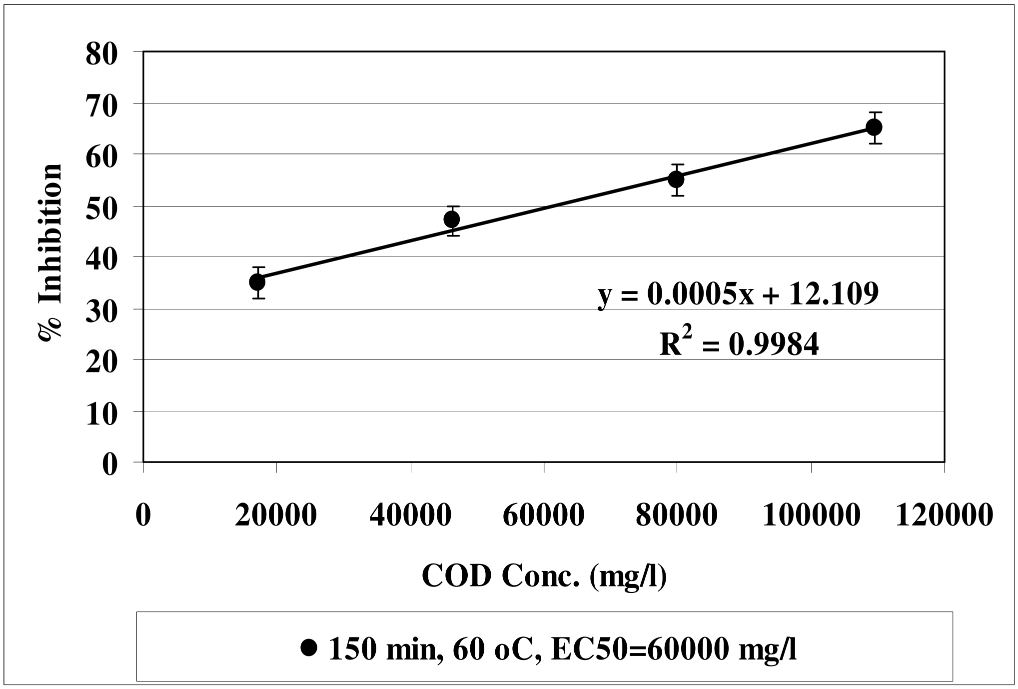


(b)

Figure 5.142 Effect of increasing temperature on Microtox acute toxicity in OMI ww for (a) influent at 25°C and (b) after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.142 Effect of increasing temperature on Microtox acute toxicity in OMI ww for (c) after 120 min sonication time at 60°C and (d) after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.17.2.2 Effect of Increasing Temperature on the Removal of Daphnia magna Acute Toxicity in OMI ww at Increasing Sonication Time

As seen in Table 5.161 (SET 1) and Figure 5.143a, the initial EC_{50} values were obtained as 78000 mg/l at 25°C. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{35} to EC_{30} and to EC_{25} at 30°C (Table 5.161, SET 2). The EC_{35}, the EC_{30} and the EC_{25} values were measured as 70000 mg/l, 65000 and 40000 mg/l, respectively, at 30°C. This showed that the PAHs were degraded to less toxic by-products via sonication. The toxicity removal efficiencies were 30.00%, 40.00% and 50.00% after 60 min, 120 and 150 min sonication times, respectively, at 30°C (Table 5.161, SET 2).

Table 5.161 Effect of increasing sonication temperature on *Daphnia magna* acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

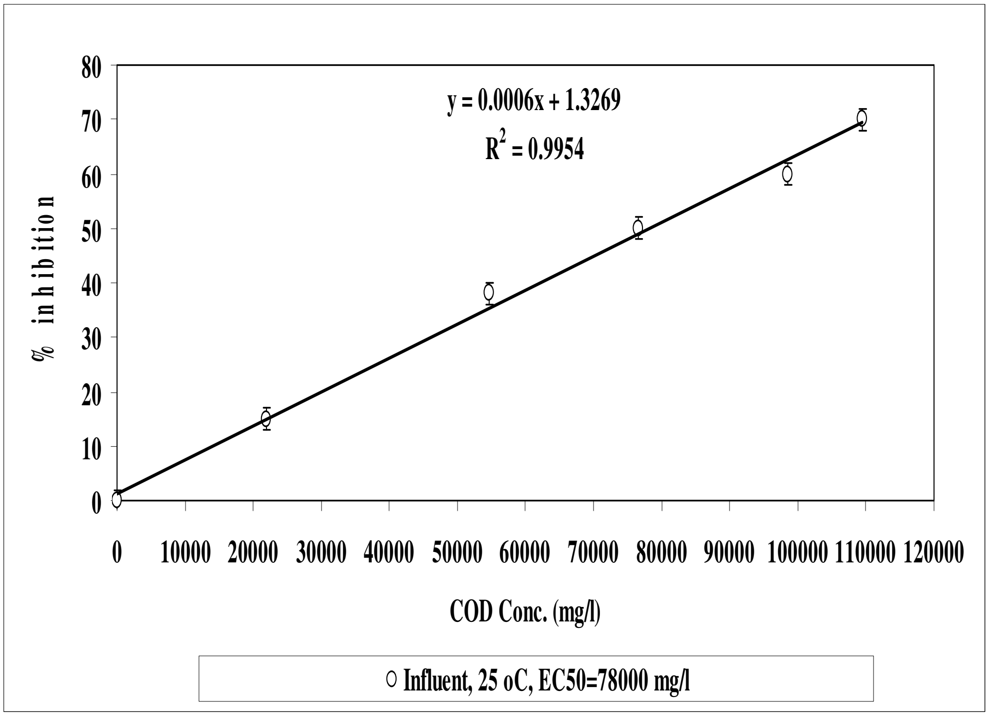
No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC_{50}**		***EC**		***EC**		***EC**	
1	Raw ww, control	78000		EC_{40}=85000		EC_{30}=55000		EC_{25}=39000	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC_{50}**	***EC**	***EC**	***EC**	***EC_{50}**	***EC**	***EC**	***EC**
2	Raw ww, control	78000	EC_{35}= 70000	EC_{30}= 65000	EC_{25}= 40000	78000	EC_{30}= 60000	EC_{25}= 37000	EC_{20}= 29000

* EC values were calculated based on COD (mg/l).

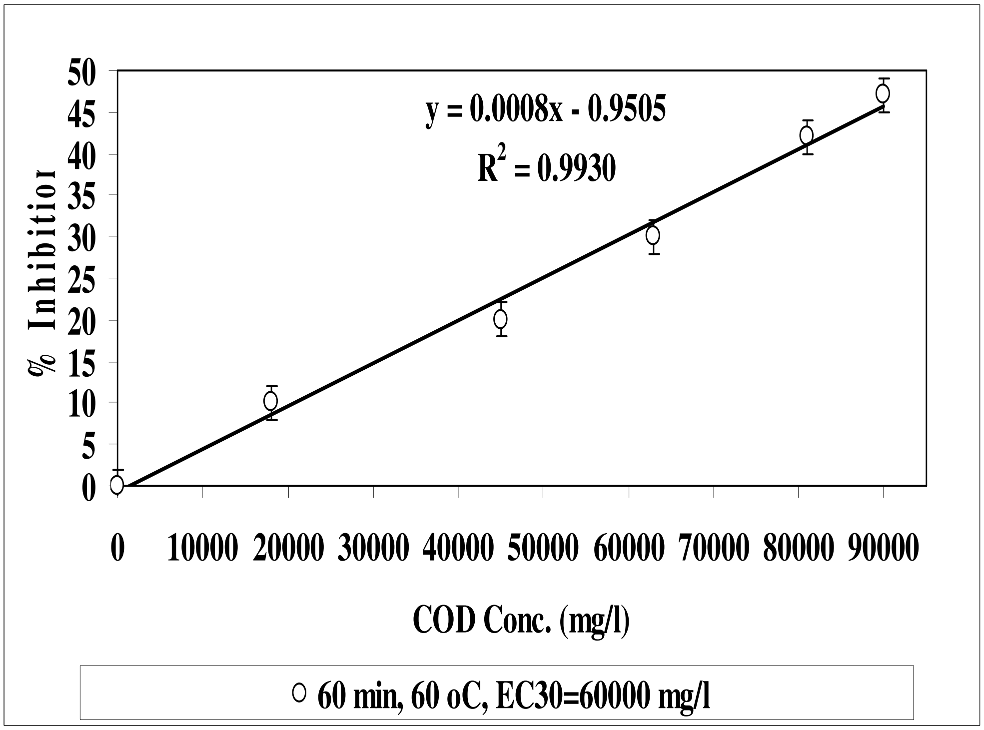
The EC_{50} values decreased to EC_{30} to EC_{25} and to EC_{20} after 60 min, 120 and 150 min of sonication, respectively, at 60°C (Table 5.161, SET 2; Figure 5.143b-c-d). The EC_{30}, the EC_{25} and the EC_{20} values were observed as 60000 mg/l, 37000 and 29000 mg/l, respectively, at 60°C. The toxicity removal efficiencies were 40.00%, 50.00% and 60.00% after 60 min, 120 and 150 min sonication times, respectively, at

60^{o}C (Table 5.161, SET 2; Figure 5.143b-c-d). 60.00% maximum *Daphnia magna* acute toxicity yield was measured at 60^{o}C after 150 min sonication time (Table 5.161, SET 2; Figure 5.143d).

Daphnia magna acute toxicity was operated at increasing sonication temperature (from 30^{o}C to 60^{o}C) and long sonication time (150 min). Also, the high *Daphnia magna* acute toxicity removals obtained high temperature conditions (at 60^{o}C), long sonication time (150 min).

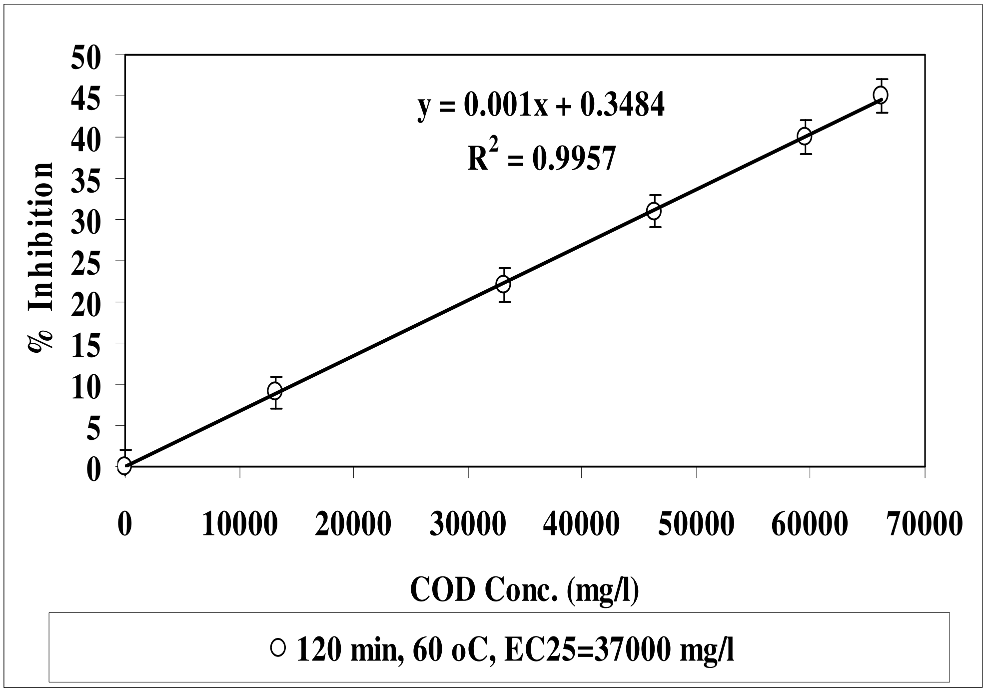


(a)

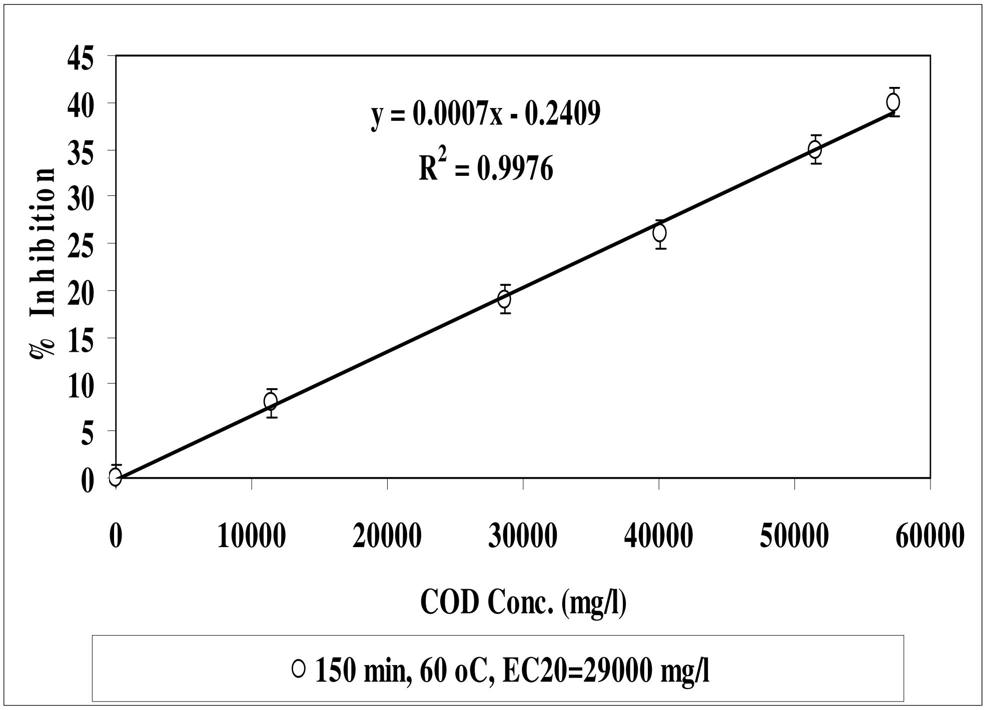


(b)

Figure 5.143 Effect of increasing temperature on *Daphnia magna* acute toxicity in OMI ww for (a) influent at 25°C and (b) after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.143 Effect of increasing temperature on *Daphnia magna* acute toxicity in OMI ww for (c) after 120 min sonication time at 60°C and (d) after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.17.3 Effect of H_2O_2 Concentrations on the Removal of Acute Toxicity in OMI ww at Increasing Sonication Time and Temperature

5.17.3.1 Effect of H_2O_2 Concentrations on the Removal of Microtox Acute Toxicity in OMI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was found as 100000 mg/l at 25°C (Table 5.162, SET 1; Figure 5.144a). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{40}, to EC_{20} and to EC_{10} in H_2O_2=500 mg/l at 30°C (Table 5.162, SET 3). The EC_{40}, the EC_{20} and the EC_{10} values were measured as 63374 mg/l, 45660 and 26124 mg/l, respectively, in H_2O_2=500 mg/l at 30°C. The toxicity removal efficiencies were 55.56%, 77.78% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 30°C (Table 5.162, SET 3).

Table 5.162 Effect of increasing H_2O_2 concentrations on Microtox acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

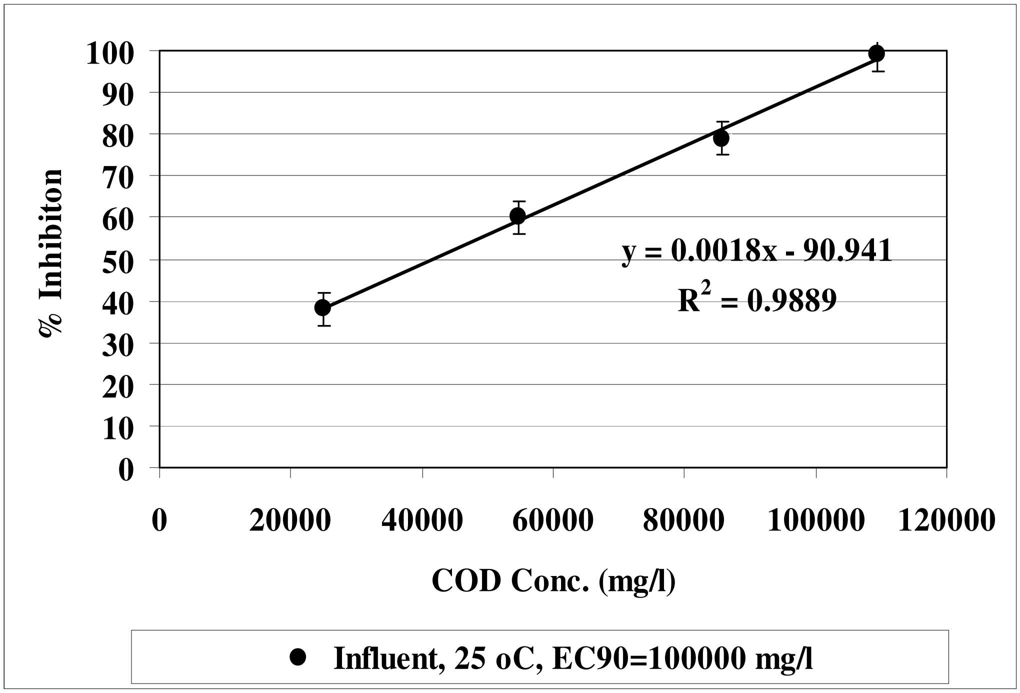
No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{90}$		**$*EC$**		**$*EC$**		**$*EC$**	
1	Raw ww, control	100000		EC_{80}=90000		EC_{75}=98000		EC_{70}=95000	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{90}$	**$*EC$**	**$*EC$**	**$*EC$**	**$*EC_{90}$**	**$*EC$**	**$*EC$**	**$*EC$**
2	Raw ww, control	100000	EC_{75}= 90000	EC_{70}= 94000	EC_{60}= 95000	100000	EC_{70}= 65000	EC_{70}= 65000	EC_{50}= 60000
3	H_2O_2=100 mg/l	100000	EC_{45}= 72500	EC_{25}= 56175	EC_{15}= 30282	100000	EC_{40}= 66782	EC_{20}= 34183	EC_{10}= 23271
	H_2O_2=500 mg/l	100000	EC_{40}= 63374	EC_{20}= 45660	EC_{10}= 26124	100000	EC_{35}= 60000	EC_{15}= 60000	EC_{5}= 60000
	H_2O_2=2000 mg/l	100000	EC_{50}= 61884	EC_{30}= 34131	EC_{20}= 19822	100000	EC_{45}= 59024	EC_{25}= 33418	EC_{15}= 11289

* EC values were calculated based on COD (mg/l).

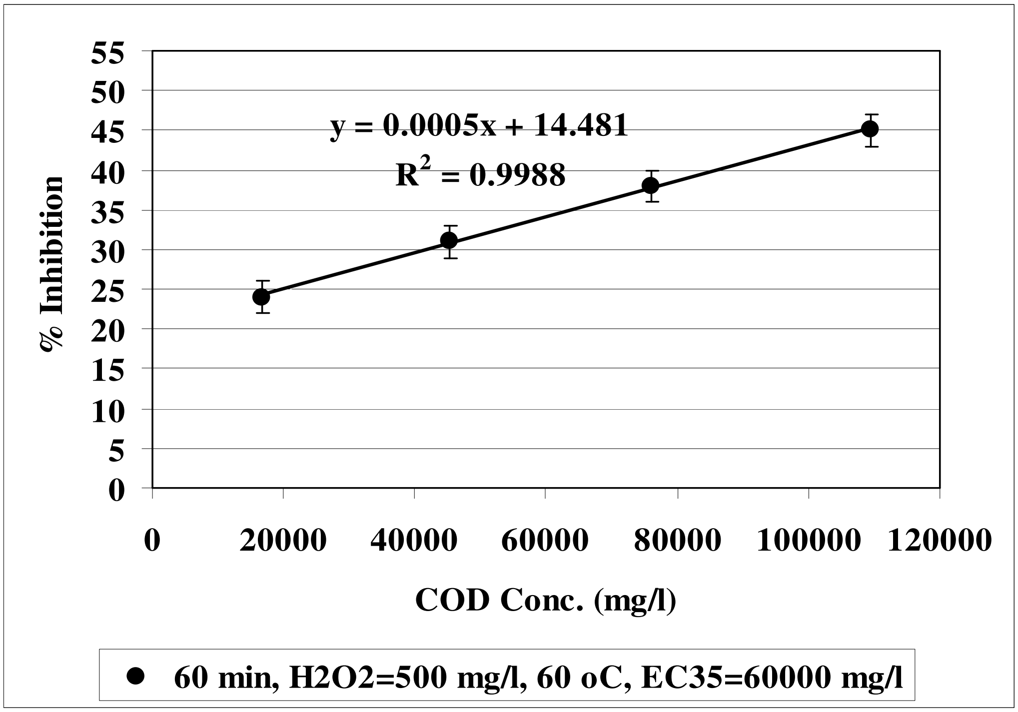
The EC_{90} values decreased to EC_{35}, to EC_{15} and to EC_5 after 60 min, 120 and 150 min sonication, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.162, SET 3; Figure 5.144b-c-d). The EC_{35}, the EC_{15} and the EC_5 values were measured as 60000 mg/l, 60000 and 60000 mg/l, respectively, in H_2O_2=500 mg/l at 60°C. The toxicity removal efficiencies were 61.11%, 83.33% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.162, SET 3; Figure 5.144b-c-d). 94.44% maximum Microtox acute toxicity yield was obtained in H_2O_2=500 mg/l after 150 min sonication time at 60°C (Table 5.162, SET 3; Figure 5.144d).

The EC_{90} values decreased to EC_{45}=72500 mg/l to EC_{25}=56175 and to EC_{15}=30282 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 30°C (Table 5.162, SET 3). The EC_{90} values decreased to EC_{50}=61884 mg/l to EC_{30}=34131 and to EC_{20}=19822 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 30°C. The toxicity removal efficiencies were 83.33% and 77.78% in 500 and 2000 mg/l H_2O_2 concentrations, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of H_2O_2=2000 mg/l to *Photobacterium phosphoreum* after 150 min sonication at 30°C (Table 5.162, SET 3).

The EC_{90} values decreased to EC_{40}=66782 mg/l to EC_{20}=34183 and to EC_{10}=23271 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 60°C (Table 5.162, SET 3). The EC_{90} values decreased to EC_{45}=59024 mg/l to EC_{25}=33418 and to EC_{15}=11289 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 60°C. The toxicity removal efficiencies were 88.89% and 83.33% in 500 and 2000 mg/l H_2O_2 concentrations, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of H_2O_2=2000 mg/l to *Photobacterium phosphoreum* after 150 min sonication at 60°C (Table 5.162, SET 3).

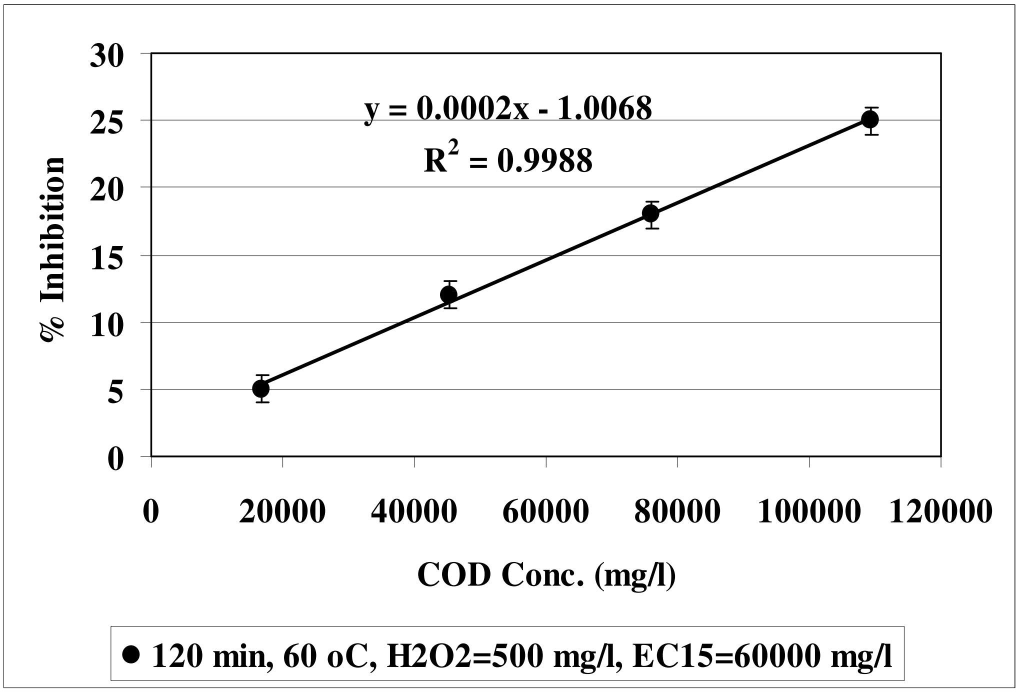


(a)

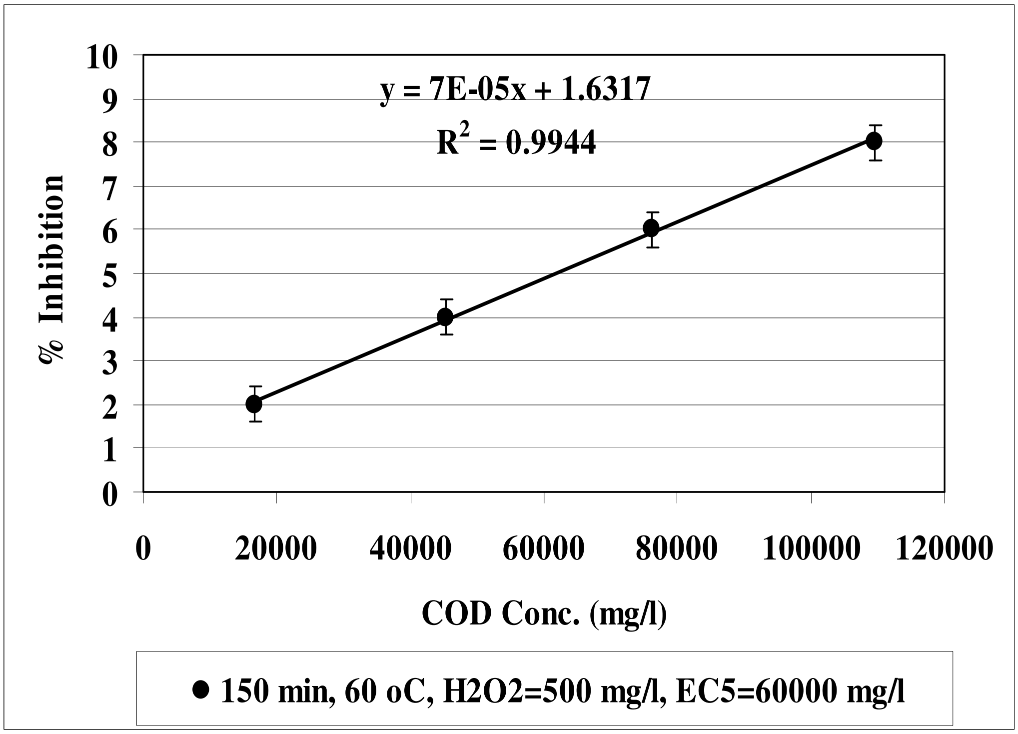


(b)

Figure 5.144 Effect of 500 mg/l H_2O_2 concentration on Microtox acute toxicity in OMI ww for (a) influent at 25°C and (b) H_2O_2=500 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.144 Effect of 500 mg/l H_2O_2 concentration on Microtox acute toxicity in OMI ww for (c) H_2O_2=500 mg/l after 120 min sonication time at 60°C and (d) H_2O_2=500 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.17.3.2 Effect of H_2O_2 Concentrations on the Removal of Daphnia magna Acute Toxicity in OMI ww at Increasing Sonication Time and Temperature

As seen in Table 5.163 (SET 1) and Figure 5.145a, the initial EC_{50} values were obtained as 78000 mg/l at 25°C. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{30}=54000 mg/l to EC_{20}=25000 mg/l and to EC_{10}=40000 mg/l in H_2O_2=500 mg/l at 30°C (Table 5.163, SET 3). The toxicity removal efficiencies were 40.00%, 60.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 30°C (Table 5.163, SET 3).

Table 5.163 Effect of increasing H_2O_2 concentrations on *Daphnia magna* acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

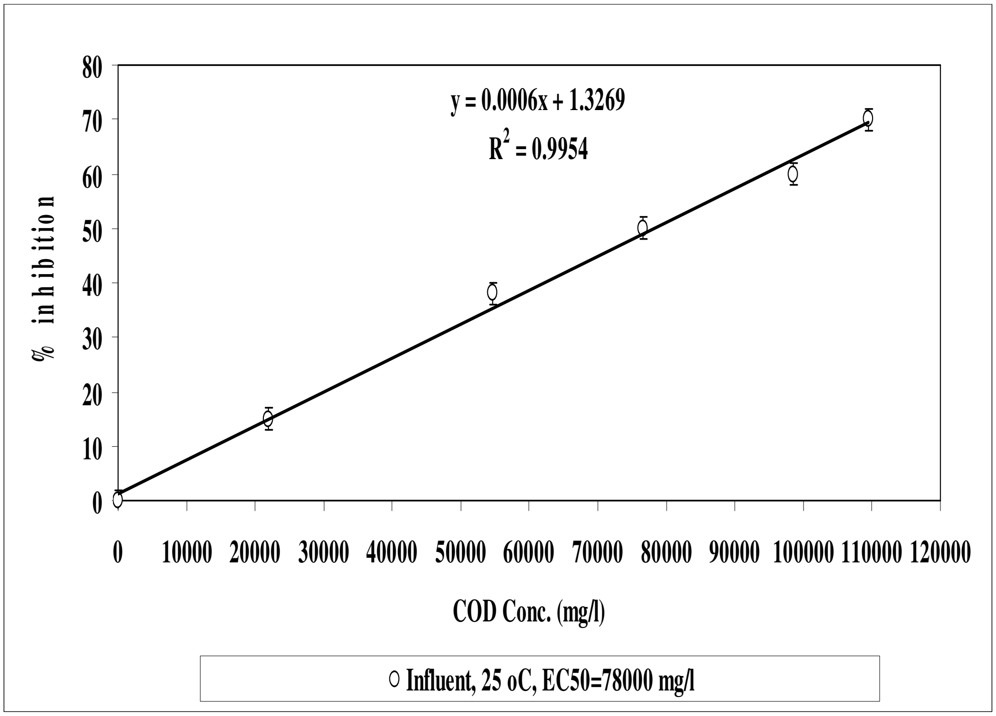
No	**Parameters**	***Daphnia magna* Acute Toxicity Values, *EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC_{50}**		***EC**		***EC**		***EC**	
1	Raw ww, control	78000		EC_{40}=85000		EC_{30}=55000		EC_{25}=39000	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC_{50}**	***EC**	***EC**	***EC**	***EC_{50}**	***EC**	***EC**	***EC**
2	Raw ww, control	78000	EC_{35}= 70000	EC_{30}= 65000	EC_{25}= 40000	78000	EC_{30}= 60000	EC_{25}= 37000	EC_{20}= 29000
3	H_2O_2=100 mg/l	78000	EC_{35}= 29000	EC_{25}= 60000	EC_{15}= 50000	78000	EC_{30}= 27500	EC_{20}= 60000	EC_{10}= 40000
	H_2O_2=500 mg/l	78000	EC_{30}= 54000	EC_{20}= 25000	EC_{10}= 40000	78000	EC_{30}= 42000	EC_{15}= 27000	EC_{5}= 15000
	H_2O_2=2000 mg/l	78000	EC_{35}= 35000	EC_{30}= 22500	EC_{20}= 12500	78000	EC_{35}= 30000	EC_{25}= 22500	EC_{15}= 8500

* EC values were calculated based on COD (mg/l).

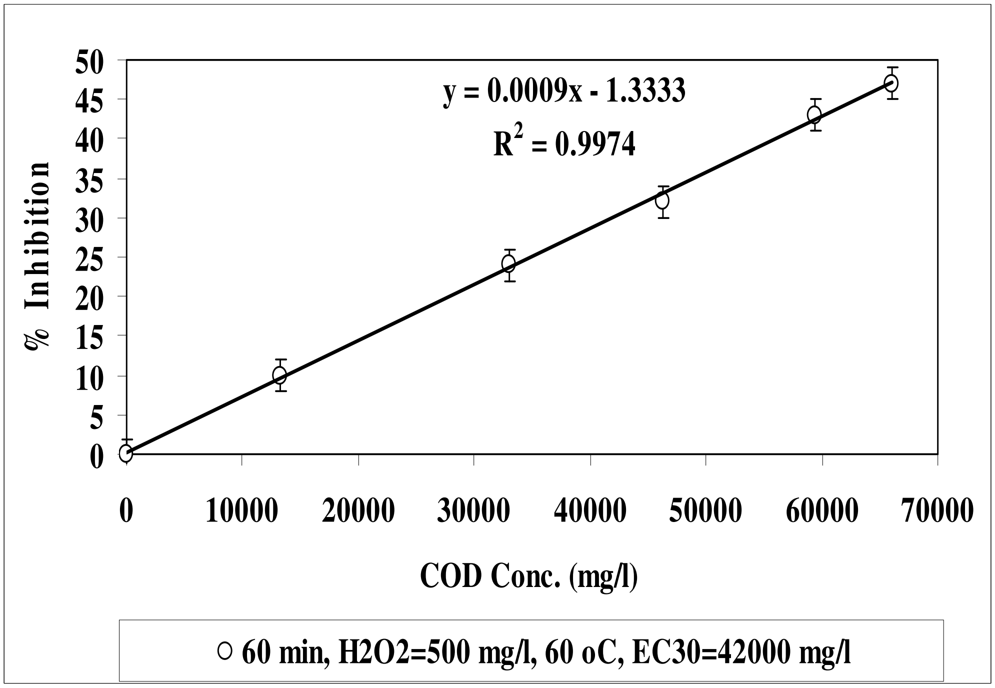
The EC_{50} values decreased to EC_{30} to EC_{15} and to EC_5 after 60 min ,120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.163, SET 3; Figure 5.145b-c-d). The EC_{30}, the EC_{15} and the EC_5 values were measured as 42000 mg/l, 27000 and 15000 mg/l, respectively, in H_2O_2=500 mg/l at 60°C. The toxicity removal efficiencies were 40.00%, 70.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.163, SET 3; Figure 5.145b-c-d). 90.00% maximum *Daphnia magna* removal was observed in H_2O_2=500 mg/l after 150 min sonication time at 60°C (Table 5.163, SET 3; Figure 5.145d).

The EC_{50} values decreased to EC_{35}=29000 mg/l to EC_{25}=60000 and to EC_{15}=50000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 30°C (Table 5.163, SET 3). The EC_{90} values decreased to EC_{35}=35000 mg/l to EC_{30}=22500 and to EC_{20}=12500 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 30°C. The toxicity removal efficiencies were 70.00% and 60.00% in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at 30°C. It was obtained an inhibition effect of H_2O_2=2000 mg/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.163, SET 3).

The EC_{50} values decreased to EC_{30}=27500 mg/l to EC_{20}=60000 and to EC_{10}=40000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 60°C (Table 5.163, SET 3). The EC_{90} values decreased to EC_{35}=30000 mg/l to EC_{25}=22500 and to EC_{15}=8500 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 60°C. The toxicity removal efficiencies were 80.00% and 70.00% in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication at 60°C. It was observed an inhibition effect of H_2O_2=2000 mg/l to *Daphnia magna* after 150 min sonication time at 60°C (Table 5.163, SET 3).

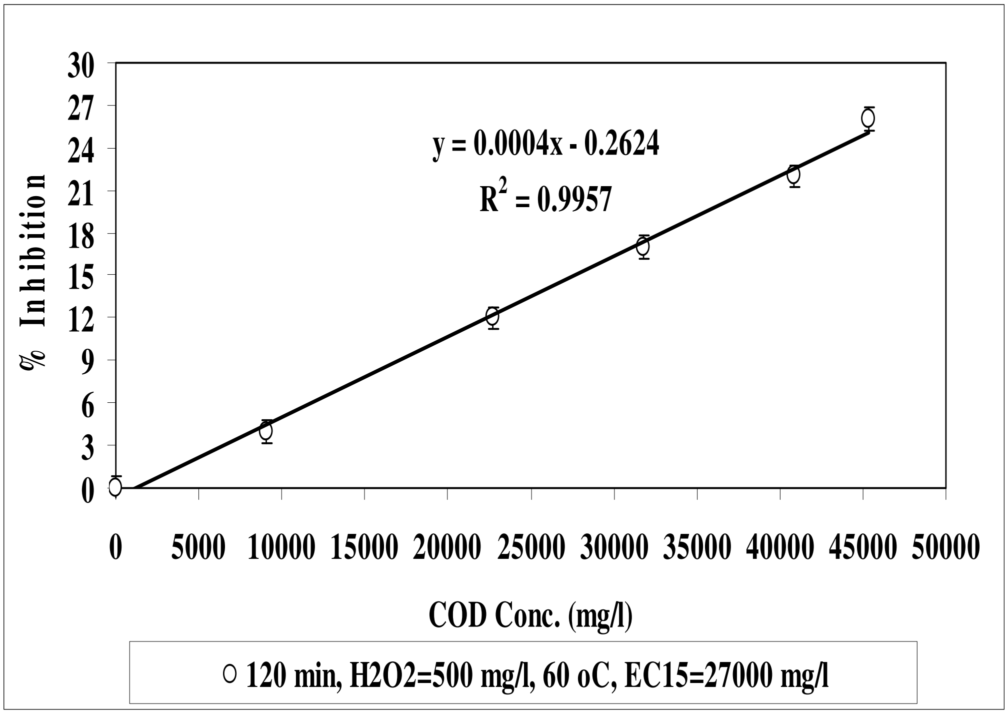


(a)

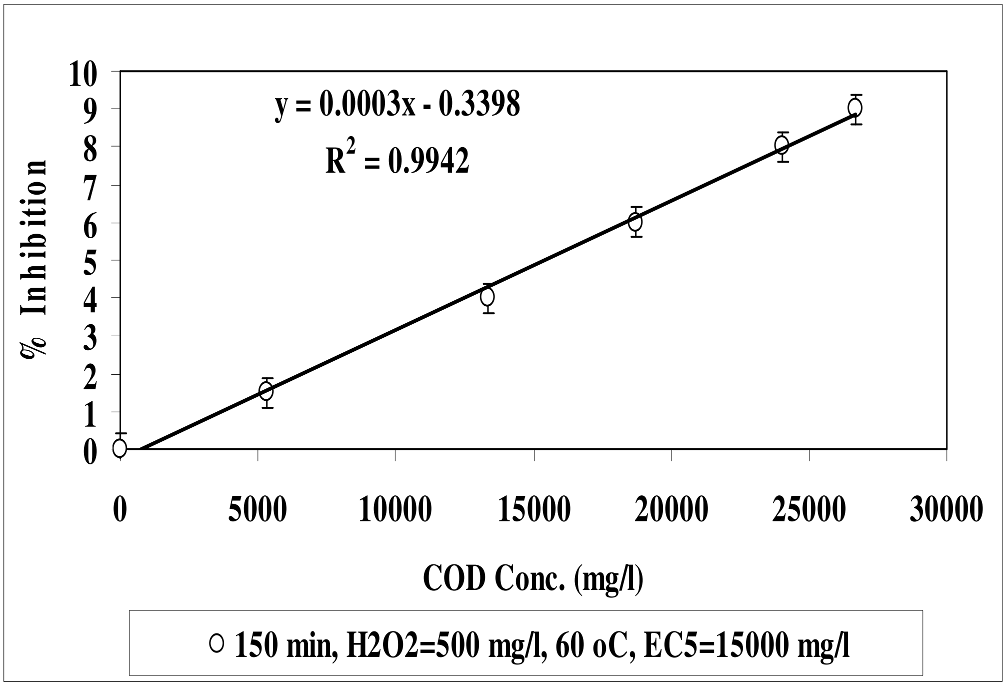


(b)

Figure 5.145 Effect of 500 mg/l H_2O_2 concentration on *Daphnia magna* acute toxicity in OMI ww for (a) influent at 25°C and (b) H_2O_2=500 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.145 Effect of 500 mg/l H_2O_2 concentration on *Daphnia magna* acute toxicity in OMI ww for (c) H_2O_2=500 mg/l after 120 min sonication time at 60°C and (d) H_2O_2=500 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

High H_2O_2 concentrations (> 2000 mg/l) caused to the hindering effect of *Daphnia magna* (Table 5.163, SET 3). Although, high H_2O_2 concentrations led to low acute toxicity removal efficiency. The maximum *Daphnia magna* acute toxicity yield was observed low H_2O_2 concentrations (< 1000 mg/l), long sonication time (150 min) and high sonication temperature (60^{o}C) (Table 5.163, SET 3).

5.17.3.3 Direct Effects of H_2O_2 *Concentrations on the Acute Toxicity of Microtox and Daphnia magna in OMI ww*

The acute toxicity tests were performed in the samples containing some additives such as H_2O_2, TiO_2, NaCl, Fe^{+2} and Fe^{+3}. In order to detect the direct responses of Microtox and *Daphnia magna* to the additives mentioned above the toxicity test were performed without OMI ww. The initial EC values and the EC_{50} values were measured in the samples containing different additive concentrations after 150 min sonication time Table 5.164 showed the responses of Microtox and *Daphnia magna* to increasing H_2O_2 concentrations.

Table 5.164 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing H_2O_2 concentrations without OMI ww after 150 min sonication time.

	Microtox Test			***Daphnia magna* Test**		
H_2O_2 Conc. (mg/l)	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
100	EC_{10}=24	-	-	EC_{10}=20	-	-
500	EC_{15}=140	2.00	EC_1=5.00	EC_{20}=100	4.00	EC_3=8.00
2000	EC_{20}=220	5.00	EC_3=8.00	EC_{30}=200	7.00	EC_5=10.00

The acute toxicity originating only from 100, 500 and 2000 mg/l H_2O_2 were found to be low (Table 5.164). 100 mg/l H_2O_2 did not exhibited toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time The toxicity atributed to the 500 and 2000 mg/l H_2O_2 were found to be low in the samples without OMI ww for the test organisms mentioned above. The acute toxicity originated from the H_2O_2 decreased significantly to EC_1 and EC_3 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the H_2O_2 is not significant and the real acute toxicity throughout sonication was attributed to the OMI ww, to their metabolites and to the sonodegradation by-products (Table 5.164).

5.17.4 Effect of TiO_2 Concentrations on the Acute Toxicity Removal Efficiencies in OMI ww at Increasing Sonication Time and Temperature

5.17.4.1 Effect of TiO_2 Concentrations on the Microtox Acute Toxicity Removal Efficiencies in OMI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was found as 100000 mg/l at 25°C (Table 5.165, SET 1; Figure 5.146a). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{40}=60316 mg/l to EC_{15}=37802 mg/l and to EC_{10}=23804 mg/l in TiO_2=10.00 mg/l at 30°C (Table 5.165, SET 3). The toxicity removal efficiencies were 55.56%, 83.33% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 30°C (Table 5.165, SET 3).

The EC_{90} values decreased to EC_{35}, to EC_{10} and to EC_5 after 60 min, 120 and 150 min sonication, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.165, SET 3; Figure 5.146b-c-d). The EC_{35}, the EC_{10} and the EC_5 values were measured as 75000 mg/l, 62000 and 58000 mg/l, respectively, in TiO_2=10.00 mg/l at 60°C. The toxicity removal efficiencies were 61.11%, 88.89% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.165, SET 3; Figure 5.146b-c-d). 94.44% maximum Microtox acute toxicity yield was found in TiO_2=10.00 mg/l after 150 min sonication time at 60°C (Table 5.165, SET 3; Figure 5.146d).

The EC_{90} values decreased to EC_{50}=60955 mg/l to EC_{25}=43126 and to EC_{20}=31168 mg/l after 60 min, 120 and 150 min sonication times, respectively, in

TiO_2=0.10 mg/l at 30°C (Table 5.165, SET 3). The EC_{90} values decreased to EC_{45}=63188 mg/l to EC_{20}=37713 and to EC_{15}=23515 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 30°C. The EC_{90} values decreased to EC_{55}=54774 mg/l to EC_{30}=34630 and to EC_{20}=15280 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 30°C. The Microtox acute toxicity removals were 77.78%, 83.33% and 77.78% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 30°C. It was obtained an inhibition effect of TiO_2=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.165, SET 3).

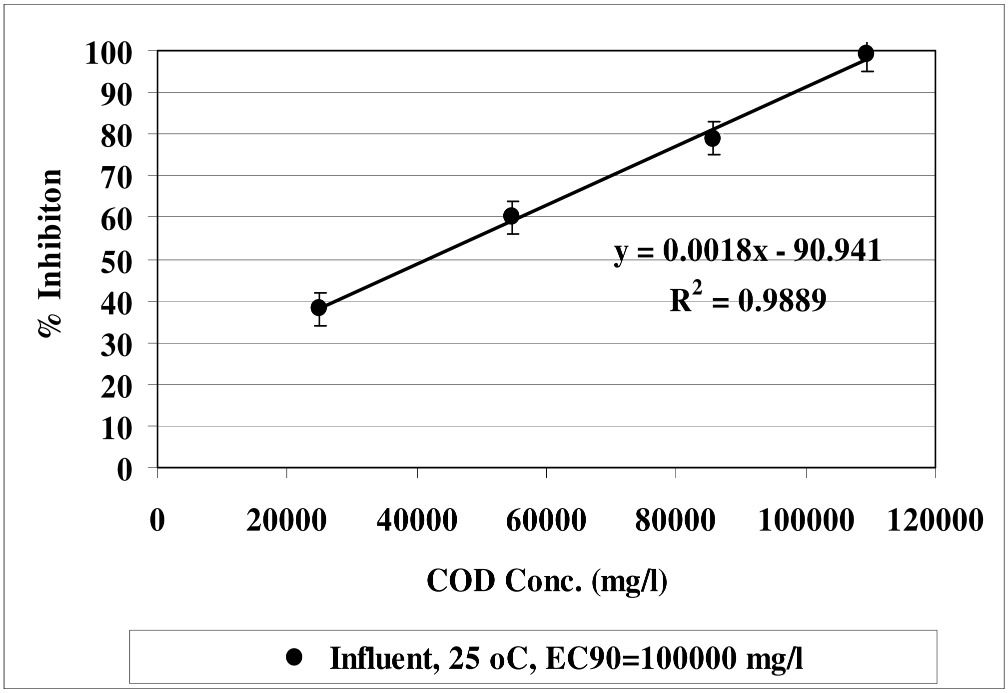
Table 5.165 Effect of increasing TiO_2 concentrations on Microtox acute toxicity in OMI ww at 30°C and at 60°C.

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{90}$		**$*EC$**		**$*EC$**		**$*EC$**	
1	Raw ww, control	100000		EC_{80}=90000		EC_{75}=98000		EC_{70}=95000	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{90}$	**$*EC$**	**$*EC$**	**$*EC$**	**$*EC_{90}$**	**$*EC$**	**$*EC$**	**$*EC$**
2	Raw ww, control	100000	EC_{75}= 90000	EC_{70}= 94000	EC_{60}= 95000	100000	EC_{70}= 65000	EC_{70}= 65000	EC_{50}= 60000
3	TiO_2=0.10 mg/l	100000	EC_{50}= 60955	EC_{25}= 43126	EC_{20}= 31168	100000	EC_{45}= 67776	EC_{20}= 43439	EC_{15}= 29255
	TiO_2=0.50 mg/l	100000	EC_{45}= 63188	EC_{20}= 37713	EC_{15}= 23515	100000	EC_{40}= 55019	EC_{15}= 32326	EC_{10}= 49620
	TiO_2=10.00 mg/l	100000	EC_{40}= 60316	EC_{15}= 37802	EC_{10}= 23804	100000	EC_{35}= 75000	EC_{10}= 62000	EC_{5}= 58000
	TiO_2=20.00 mg/l	100000	EC_{55}= 54774	EC_{30}= 34630	EC_{20}= 15280	100000	EC_{50}= 45350	EC_{25}= 30267	EC_{15}= 14580

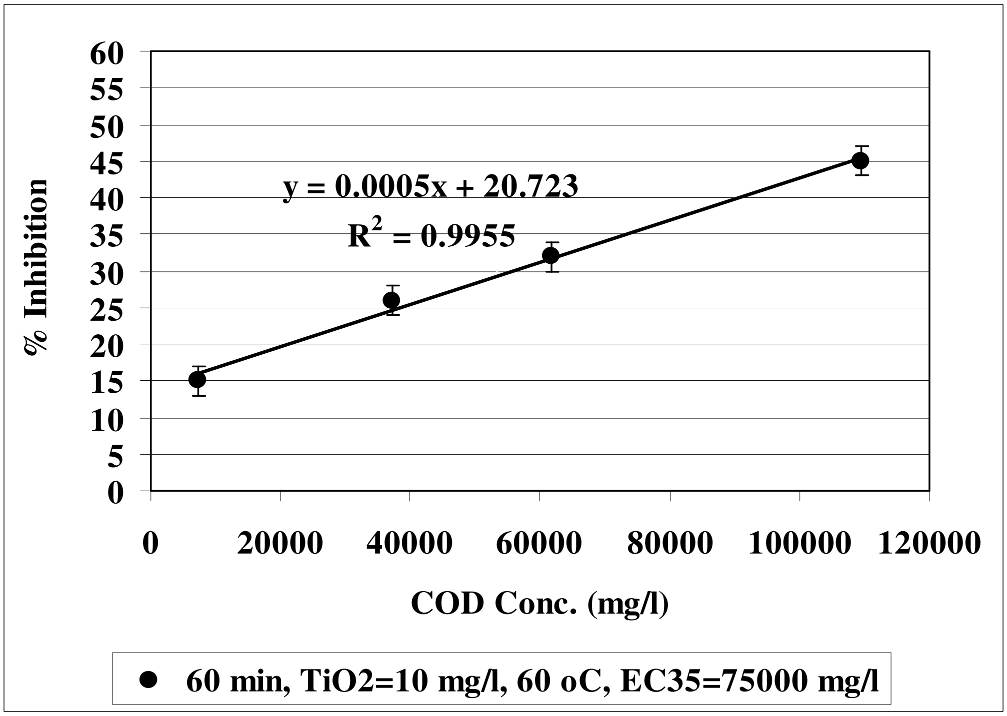
* EC values were calculated based on COD_{dis} (mg/l).

The EC_{90} values decreased to EC_{45}=67776 mg/l to EC_{20}=43439 and to EC_{15}=29255 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 60°C (Table 5.165, SET 3). The EC_{90} values decreased to EC_{40}=55019 mg/l to EC_{15}=32326 and to EC_{10}=49620 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 60°C. The EC_{90} values decreased to EC_{50}=45320 mg/l to EC_{25}=30267 and to EC_{15}=14580 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 60°C. The Microtox acute toxicity removals were 83.33%, 88.89% and 83.33% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 60°C. It was observed an inhibition effect of TiO_2=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60°C (Table 5.165, SET 3).

Increasing TiO_2 concentrations (from 0.10 to 20.00 mg/l) were applied to the Microtox acute toxicity test (Table 5.165, SET 3). The maximum acute toxicity removal was found at 10.00 mg/l TiO_2 concentrations after 150 min sonication time at 60°C. High TiO_2 ($>$ 10.00 mg/l) concentrations caused to the inhibition effect of *Photobacterium phosphoreum* during Microtox acute toxicity assay. Low acute toxicity yield was measured above 10.00 mg/l TiO_2 concentrations and low sonication temperature (30°C) (Table 5.165, SET 3).

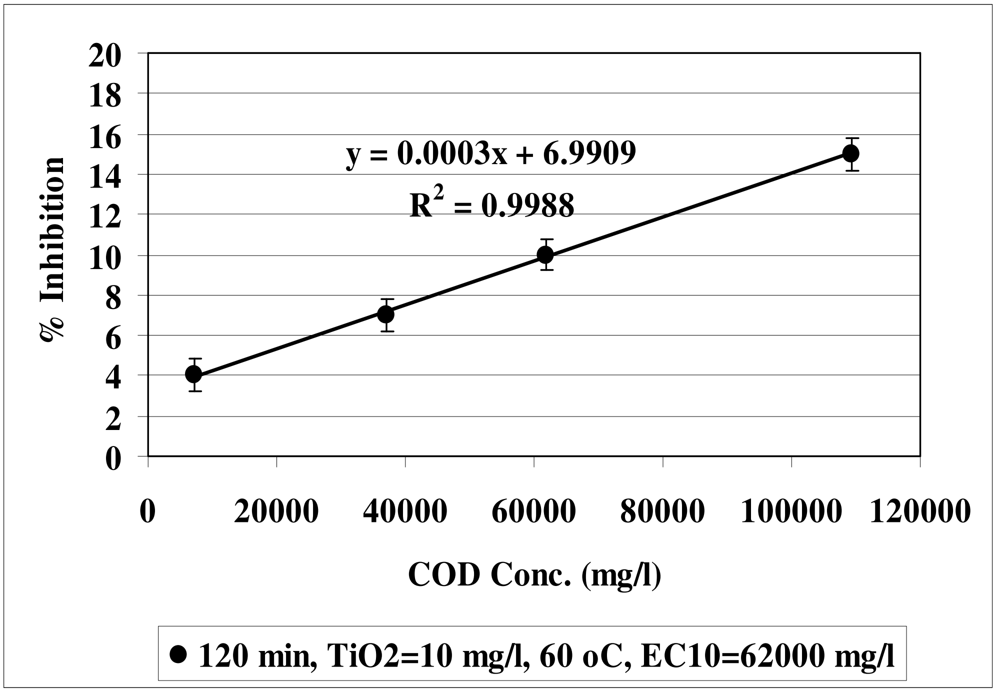


(a)

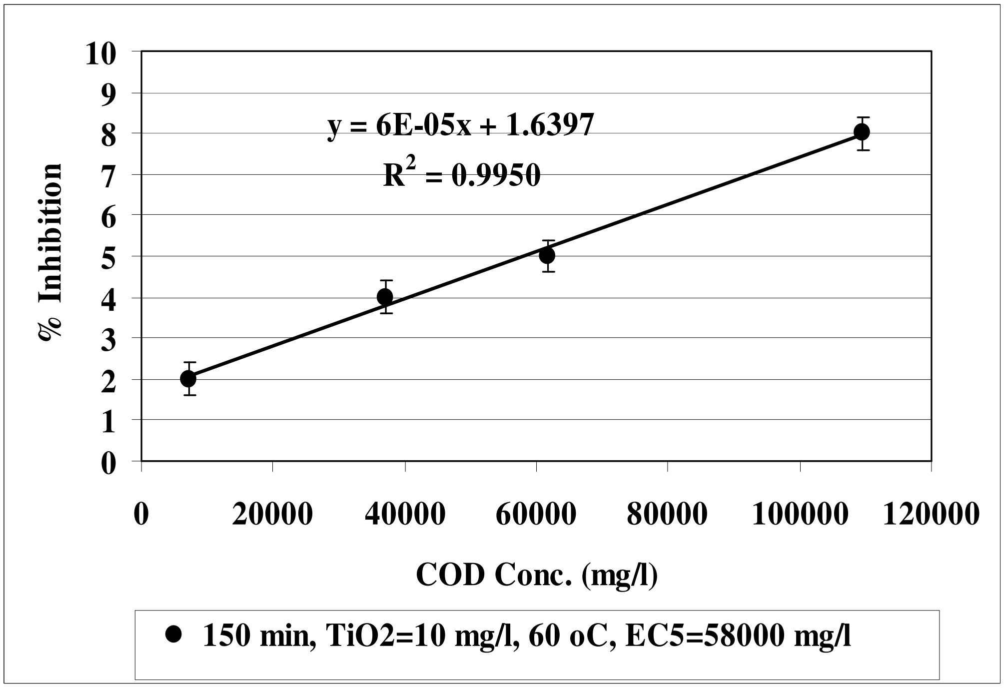


(b)

Figure 5.146 Effect of 10.00 mg/l TiO_2 concentration on Microtox acute toxicity in OMI ww for (a) influent at 25°C and (b) TiO_2=10.00 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.146 Effect of 10.00 mg/l TiO_2 concentration on Microtox acute toxicity in OMI ww for (c) TiO_2=10.00 mg/l after 120 min sonication time at 60°C and (d) TiO_2=10.00 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.17.4.2 Effect of TiO_2 Concentrations on the Daphnia magna Acute Toxicity Removal Efficiencies in OMI ww at Increasing Sonication Time and Temperature

The initial EC_{50} values were observed as 78000 mg/l at 25°C (Table 5.166, SET 1; Figure 5.147a). After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{30}=50000 mg/l to EC_{20}=40000 mg/l and to EC_{10}=24000 mg/l in TiO_2=10.00 mg/l at 30°C (Table 5.166, SET 3). The toxicity removal efficiencies were 40.00%, 60.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 30°C (Table 5.166, SET 3).

Table 5.166 Effect of increasing TiO_2 concentrations on *Daphnia magna* acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

<table>
<tr><th rowspan="4">No</th><th rowspan="4">Parameters</th><th colspan="8">*Daphnia magna* Acute Toxicity Values, *EC (mg/l)</th></tr>
<tr><th colspan="8">25°C</th></tr>
<tr><th colspan="2">0. min</th><th colspan="2">60. min</th><th colspan="2">120. min</th><th colspan="2">150. min</th></tr>
<tr><th colspan="2">*EC_{50}</th><th colspan="2">*EC</th><th colspan="2">*EC</th><th colspan="2">*EC</th></tr>
<tr><td>1</td><td>Raw ww, control</td><td colspan="2">78000</td><td colspan="2">EC_{40}=85000</td><td colspan="2">EC_{30}=55000</td><td colspan="2">EC_{25}=39000</td></tr>
<tr><td rowspan="3"></td><td rowspan="3"></td><th colspan="4">30°C</th><th colspan="4">60°C</th></tr>
<tr><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th></tr>
<tr><th>*EC_{50}</th><th>*EC</th><th>*EC</th><th>*EC</th><th>*EC_{50}</th><th>*EC</th><th>*EC</th><th>*EC</th></tr>
<tr><td>2</td><td>Raw ww, control</td><td>78000</td><td>EC_{35}= 70000</td><td>EC_{30}= 65000</td><td>EC_{25}= 40000</td><td>78000</td><td>EC_{30}= 60000</td><td>EC_{25}= 37000</td><td>EC_{20}= 29000</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>3</td><td>TiO_2=0.10 mg/l</td><td>78000</td><td>EC_{35}= 60000</td><td>EC_{25}= 32500</td><td>EC_{15}= 37500</td><td>78000</td><td>EC_{30}= 29000</td><td>EC_{20}= 60000</td><td>EC_{10}= 44000</td></tr>
<tr><td></td><td>TiO_2=0.50 mg/l</td><td>78000</td><td>EC_{35}= 60000</td><td>EC_{25}= 27500</td><td>EC_{15}= 20000</td><td>78000</td><td>EC_{30}= 57500</td><td>EC_{20}= 27500</td><td>EC_{5}= 20000</td></tr>
<tr><td></td><td>TiO_2=10.00 mg/l</td><td>78000</td><td>EC_{30}= 50000</td><td>EC_{20}= 40000</td><td>EC_{10}= 24000</td><td>78000</td><td>EC_{30}= 37000</td><td>EC_{15}= 21500</td><td>EC_{5}= 9750</td></tr>
<tr><td></td><td>TiO_2=20.00 mg/l</td><td>78000</td><td>EC_{35}= 45000</td><td>EC_{25}= 32500</td><td>EC_{20}= 22000</td><td>78000</td><td>EC_{30}= 34000</td><td>EC_{20}= 24000</td><td>EC_{15}= 6000</td></tr>
</table>

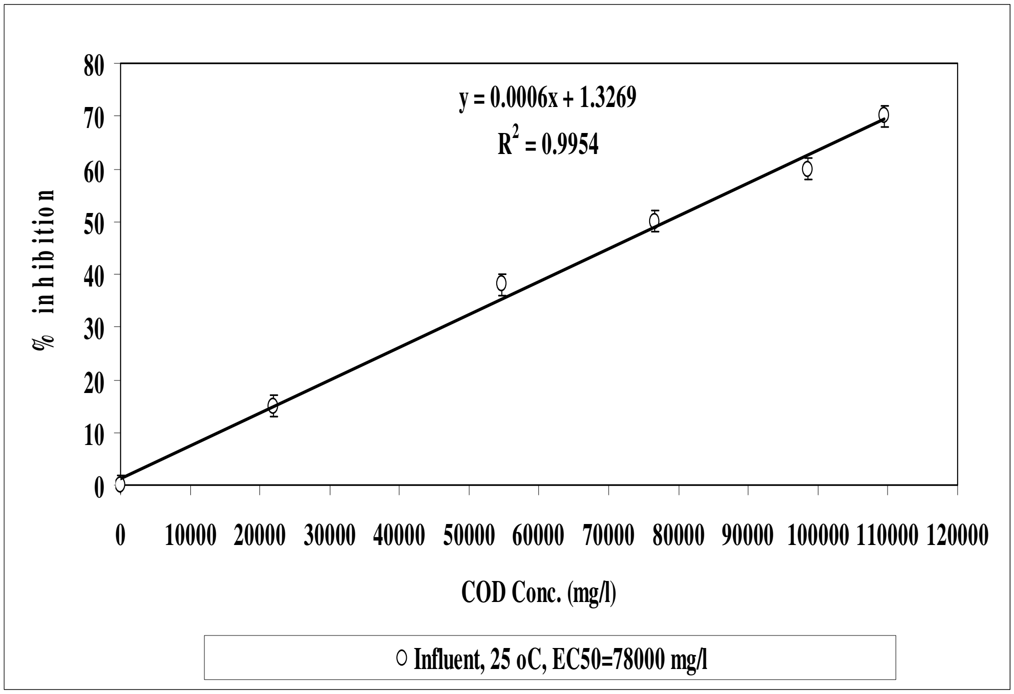
* EC values were calculated based on COD_{dis} (mg/l)

The EC_{50} values decreased to EC_{30} to EC_{15} and to EC_5 after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.166, SET 3; Figure 5.147b-c-d). The EC_{30}, the EC_{15} and the EC_5 values were measured as 37000 mg/l, 21500 and 9750 mg/l, respectively, in TiO_2=10.00 mg/l at 60°C. The toxicity removal efficiencies were 40.00%, 70.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.166, SET 3; Figure 5.147b-c-d). 90.00% maximum *Daphnia magna* acute toxicity removal was obtained in TiO_2=10.00 mg/l after 150 min sonication time at 60°C (Table 5.166, SET 3; Figure 5.147d).

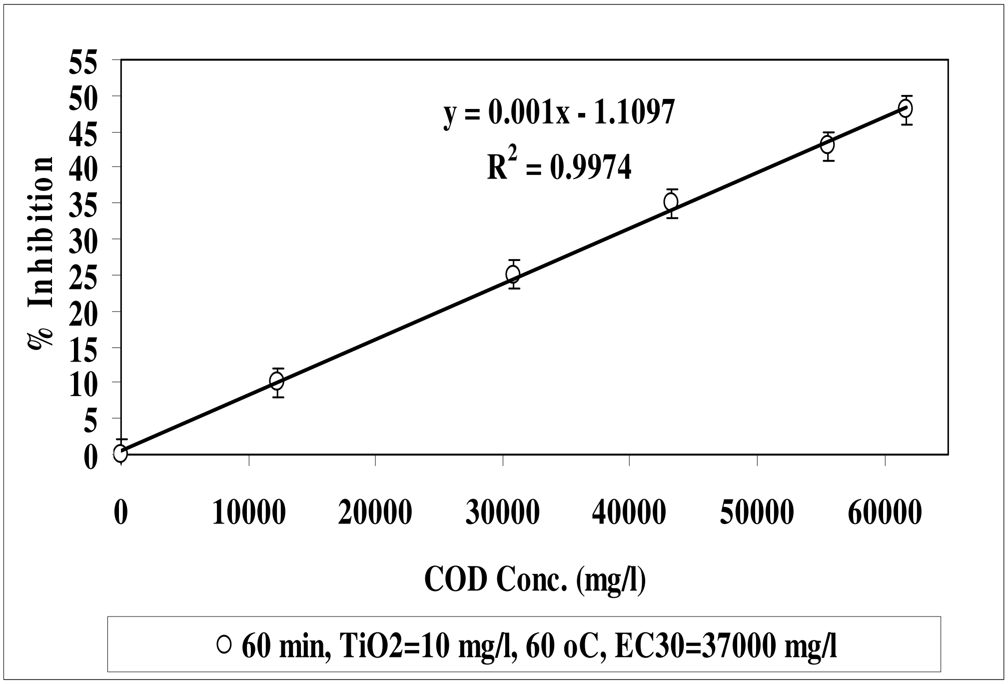
The EC_{50} values decreased to EC_{35}=60000 mg/l to EC_{25}=32500 and to EC_{15}=37500 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 30°C (Table 5.166, SET 3). The EC_{50} values decreased to EC_{35}=60000 mg/l to EC_{25}=27500 and to EC_{15}=20000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 30°C. The EC_{50} values decreased to EC_{35}=45000 mg/l to EC_{25}=32500 and to EC_{20}=22000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 30°C. The *Daphnia magna* acute toxicity removals were 70.00%, 70.00% and 60.00% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of TiO_2=20.00 mg/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.166, SET 3).

The EC_{50} values decreased to EC_{30}=29000 mg/l to EC_{20}=60000 and to EC_{10}=44000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 60°C (Table 5.166, SET 3). The EC_{50} values decreased to EC_{30}=57500 mg/l to EC_{20}=27500 and to EC_5=20000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 60°C. The EC_{50} values decreased to EC_{30}=34000 mg/l to EC_{20}=24000 and to EC_{15}=6000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 60°C. The *Daphnia magna* acute toxicity removals were 80.00%, 90.00% and 70.00% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of TiO_2=20.00 mg/l to *Daphnia magna* after 150 min sonication at 60°C (Table 5.166, SET 3).

The maximum acute toxicity removals were approximately 90.00% at the TiO_2 concentration of 10.00 mg/l at 60°C after 150 min of sonication (Table 5.166, SET 3; Figure 5.147d). TiO_2 concentrations > 10.00 mg/l decreased the acute toxicity removals by hindering the sonication process. Similarly, a significant contribution of increasing TiO_2 concentration to acute toxicity removal at 60°C after 150 min of sonication time was not observed. Low toxicity removals found at high TiO_2 concentrations could be attributed to their detrimental effect on the *Daphnia magna* (Table 5.166, SET 3).

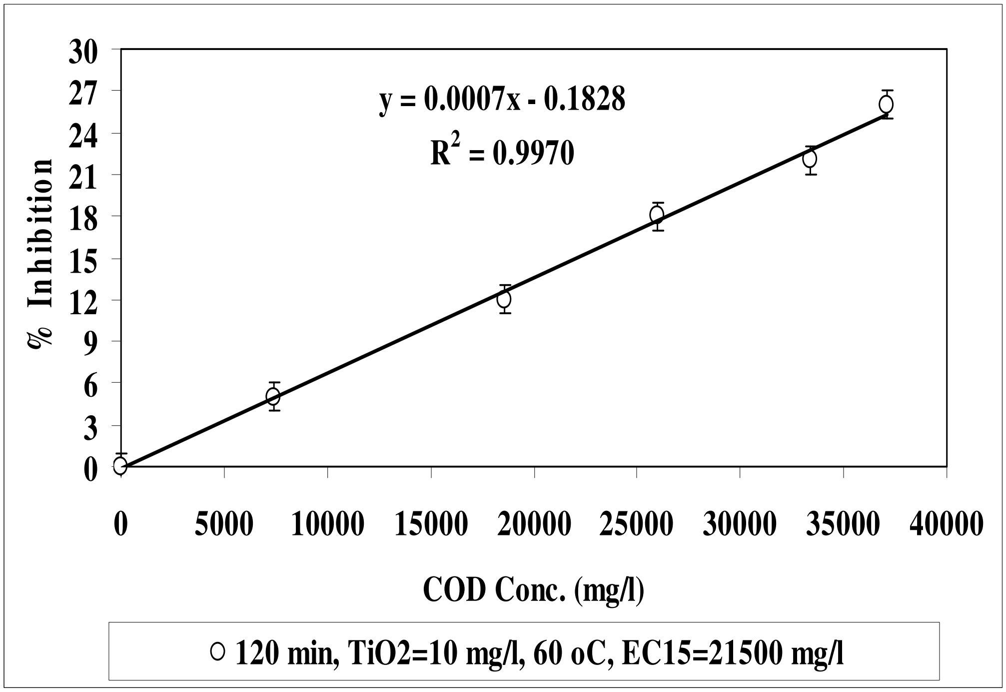


(a)

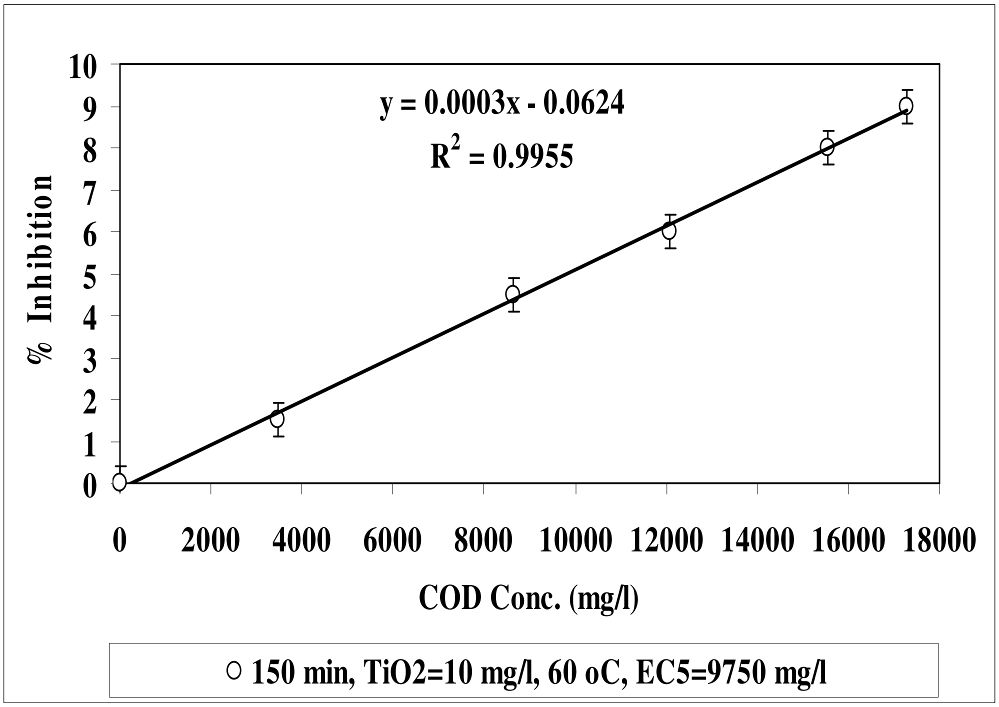


(b)

Figure 5.147 Effect of 10.00 mg/l TiO_2 concentration on *Daphnia magna* acute toxicity in OMI ww for (a) influent at 25°C and (b) TiO_2=10.00 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.147 Effect of 10.00 mg/l TiO_2 concentration on *Daphnia magna* acute toxicity in OMI ww for (c) TiO_2=10.00 mg/l after 120 min sonication time at 60°C and (d) TiO_2=10.00 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.17.4.3 Direct Effects of TiO_2 Concentrations on the Acute Toxicity of Microtox and Daphnia magna in OMI ww

The acute toxicity test was performed in the samples containing 0.10, 0.50, 10.00 and 20.00 mg/l TiO_2 concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing TiO_2 concentrations the toxicity test were performed without OMI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing TiO_2 concentrations after 150 min sonication time. Table 5.167 showed the responses of Microtox and *Daphnia magna* to increasing TiO_2 concentrations.

Table 5.167 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing TiO_2 concentrations without OMI ww after 150 min sonication time.

	Microtox Test			***Daphnia magna* Test**		
TiO_2 Conc. (mg/l)	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
0.10	EC_{10}=25	-	-	EC_{10}=30	-	-
0.50	EC_{15}=150	3.00	EC_1=5.00	EC_{20}=200	4.00	EC_3=8.00
10.00	EC_{20}=200	6.00	EC_3=7.00	EC_{30}=250	8.00	EC_5=10.00
20.00	EC_{25}=250	8.00	EC_7=11.00	EC_{40}=300	10.00	EC_9=20.00

The acute toxicity originating only from 0.10, 0.50, 10.00 and 20.00 mg/l TiO_2 were found to be low (Table 5.167). 0.10 mg/l TiO_2 did not exhibited toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication. The toxicity atributed to the 0.50, 10.00 and 20.00 mg/l TiO_2 were found to be low in the samples without OMI ww for the test organisms mentioned above. The acute toxicity originated from the TiO_2 decreased significantly to EC_1, EC_3 and EC_7 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the TiO_2 is not significant and the real acute toxicity throughout sonication was attributed to the OMI ww, to their metabolites and to the sonodegradation by-products (Table 5.167).

5.17.5 Effect of NaCl Concentrations on the Acute Toxicity Removal Efficiencies in OMI ww at Increasing Sonication Time and Temperature

5.17.5.1 Effect of NaCl Concentrations on the Microtox Acute Toxicity Removal Efficiencies in the Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was found as 100000 mg/l at 25°C (Table 5.168, SET 1). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{50}=63400 mg/l to EC_{20}=37164 mg/l and to EC_{10}=26393 mg/l in NaCl=2.50 g/l at 30°C (Table 5.168, SET 3). The toxicity removal efficiencies were 44.44%, 77.78% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 30°C (Table 5.168, SET 3).

The EC_{90} values decreased to EC_{45}, to EC_{15} and to EC_5 after 60 min, 120 and 150 min sonication, respectively, in NaCl=2.50 g/l at 60°C (Table 5.168, SET 3). The EC_{45}, the EC_{15} and the EC_5 values were measured as 58836 mg/l, 31172 and 11817 mg/l, respectively, in NaCl=2.50 g/l at 60°C. The toxicity removal efficiencies were 50.00%, 83.33% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60°C. 94.44% maximum Microtox acute toxicity yield was observed in NaCl=2.50 g/l after 150 min sonication time at 60°C (Table 5.168, SET 3).

The EC_{50} values decreased to EC_{55}=66693 mg/l to EC_{25}=42196 and to EC_{15}=27633 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 30°C (Table 5.168, SET 3). The EC_{50} values decreased to EC_{60}=57650 mg/l to EC_{30}=29623 and to EC_{20}=21807 mg/l after 60 min, 120 and 150 min sonication, respectively, in NaCl=15.00 g/l at 30°C. The Microtox acute toxicity yields were 83.33% and 72.22% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of NaCl=15.00 g/l to *Photobacterium phosphoreum* in after 150 min sonication time at 30^{o}C (Table 5.168, SET 3).

Table 5.168 Effect of increasing NaCl concentrations on Microtox acute toxicity in OMI ww at 30^{o}C and at 60^{o}C (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25^{o}C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC_{90}**		***EC**		***EC**		***EC**	
1	Raw ww, control	100000		EC_{80}=90000		EC_{75}=98000		EC_{70}=95000	
		30^{o}C				**60^{o}C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC_{90}**	***EC**	***EC**	***EC**	***EC_{90}**	***EC**	***EC**	***EC**
2	Raw ww, control	100000	EC_{75}= 90000	EC_{70}= 94000	EC_{60}= 95000	100000	EC_{70}= 65000	EC_{70}= 65000	EC_{50}= 60000
3	NaCl=1.00 g/l	100000	EC_{55}= 66693	EC_{25}= 42196	EC_{15}= 27633	100000	EC_{50}= 65100	EC_{20}= 39671	EC_{10}= 27330
	NaCl=2.50 g/l	100000	EC_{50}= 63400	EC_{20}= 37164	EC_{10}= 26393	100000	EC_{45}= 58836	EC_{15}= 31172	EC_{5}= 11817
	NaCl=15.00 g/l	100000	EC_{60}= 57560	EC_{30}= 29623	EC_{25}= 21807	100000	EC_{55}= 46795	EC_{25}= 20554	EC_{20}= 6744

* EC values were calculated based on COD_{dis} (mg/l).

The EC_{50} values decreased to EC_{50}=65100 mg/l to EC_{20}=39671 and to EC_{10}=27330 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 60^{o}C (Table 5.168, SET 3). The EC_{50} values decreased to EC_{55}=46795 mg/l to EC_{25}=20554 and to EC_{20}=6744 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 60^{o}C. The Microtox acute toxicity yields were 88.89% and 77.78% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 60^{o}C. It was obtained an inhibition effect of

NaCl=15.00 g/l to *Photobacterium phosphoreum* after 150 min sonication time at 60°C (Table 5.168, SET 3).

Low acute toxicity removals found at high NaCl concentrations could be attributed to their detrimental effect on the *Photobacterium phosphoreum* cells (Table 5.168). High NaCl concentrations caused lysis in *Photobacterium phosphoreum* cells. The high salt concentrations caused plasmolysis in *Photobacterium phosphoreum* cells by increasing the osmotic pressure in the test medium (Table 5.168).

5.17.5.2 Effect of NaCl Concentrations on the Daphnia magna Acute Toxicity Removal Efficiencies in OMI ww at Increasing Sonication Time and Temperature

As seen in Table 5.169 (SET 1), the initial EC_{50} values were observed as 78000 mg/l at 25°C. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{30}=54000 mg/l to EC_{20}=32500 mg/l and to EC_{10}=27000 mg/l in NaCl=2.50 g/l at 30°C (Table 5.169, SET 3). The toxicity removal efficiencies were 40.00%, 60.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 30°C (Table 5.169, SET 3).

The EC_{50} values decreased to EC_{30}=54000 mg/l to EC_{15}=32500 mg/l and to EC_{5}=14000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60°C (Table 5.169, SET 3). The toxicity removal efficiencies were 40.00%, 70.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60°C. 90.00% maximum *Daphnia magna* acute toxicity yield was found in in NaCl=2.50 g/l after 150 min sonication time at 60°C (Table 5.169, SET 3).

The EC_{50} values decreased to EC_{35}=32500 mg/l to EC_{25}=60000 and to EC_{15}=45000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 30°C (Table 5.169, SET 3). The EC_{50} values decreased to EC_{35}=60000 mg/l to EC_{25}=35000 and to EC_{20}=17000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 30°C. The *Daphnia magna* acute toxicity yields were 70.00% and 60.00% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of NaCl=15.00 g/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.169, SET 3).

Table 5.169 Effect of increasing NaCl concentrations on *Daphnia magna* acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	Parameters	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC_{50}**		***EC**		***EC**		***EC**	
1	Raw ww, control	78000		EC_{40}=85000		EC_{30}=55000		EC_{25}=39000	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC_{50}**	***EC**	***EC**	***EC**	***EC_{50}**	***EC**	***EC**	***EC**
2	Raw ww, control	78000	EC_{35}= 70000	EC_{30}= 65000	EC_{25}= 40000	78000	EC_{30}= 60000	EC_{25}= 37000	EC_{20}= 29000
3	NaCl=1.00 g/l	78000	EC_{35}= 32500	EC_{25}= 60000	EC_{15}= 45000	78000	EC_{30}= 65000	EC_{20}= 25000	EC_{10}= 42500
	NaCl=2.50 g/l	78000	EC_{30}= 54000	EC_{20}= 32500	EC_{10}= 27000	78000	EC_{30}= 54000	EC_{15}= 32500	EC_{5}= 14000
	NaCl=15.00 g/l	78000	EC_{35}= 60000	EC_{25}= 35000	EC_{20}= 17000	78000	EC_{30}= 54000	EC_{20}= 30000	EC_{10}= 7000

* EC_{50} values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{30}=65000 mg/l to EC_{20}=25000 and to EC_{10}=42500 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 60°C (Table 5.169, SET 3). The EC_{50} values decreased to EC_{30}=54000 mg/l to EC_{20}=30000 and to EC_{10}=7000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 60°C. The *Daphnia magna* acute toxicity yields were 80.00% and 80.00% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of NaCl=15.00 g/l to *Daphnia magna* in after 150 min sonication time at 60°C (Table 5.169, SET 3).

The maximum acute toxicity removal was 90.00% at the NaCl concentration of 2.50 g/l at 60°C after 150 min sonication time (Table 5.169, SET 3). In this acute toxicity reduction the EC_{50} value of raw OMI ww decreased to EC_5=14000 mg/l. Low acute toxicity removals found at high NaCl concentrations could be attributed to their detrimental effect on the *Daphnia magna* cells. High NaCl caused lysis in *Daphnia magna* cells. The high salt concentrations caused turgor in *Daphnia magna* cells by increasing the osmotic pressure in the test medium (Table 5.169, SET 3).

5.17.5.3 Direct Effects of NaCl Concentrations on the Acute Toxicity of Microtox and Daphnia magna in OMI ww

The acute toxicity test was performed in the samples containing 1.00, 2.50 and 15.00 g/l NaCl concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing NaCl the toxicity test were performed without OMI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing NaCl concentrations after 150 min sonication time. Table 5.170 showed the responses of Microtox and *Daphnia magna* to increasing NaCl concentrations.

Table 5.170 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing NaCl concentrations without OMI ww after 150 min sonication time.

NaCl Conc. (g/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
1.00	EC_{10}=20	-	-	EC_{10}=30	-	-
2.50	EC_{15}=140	1.00	EC_1=4.00	EC_{20}=180	2.00	EC_3=7.00
15.00	EC_{20}=220	4.00	EC_3=8.00	EC_{30}=270	6.00	EC_5=10.00

The acute toxicity originating only from 1.00, 2.50 and 15.00 g/l NaCl were found to be low (Table 5.170). 1.00 g/l NaCl did not exhibited toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 2.50 and 15.00 g/l NaCl were found to be low in the samples without OMI ww for the test organisms mentioned above. The acute toxicity originated from the NaCl decreased significantly to EC_1 and EC_3 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the NaCl is not significant and the real acute toxicity throughout sonication was attributed to the OMI ww, to their metabolites and to the sonodegradation by-products (Table 5.170).

5.17.6 Effect of Fe^{+2} Concentrations on the Removal of Acute Toxicity in OMI ww at Increasing Sonication Time and Temperature

5.17.6.1 Effect of Fe^{+2} Concentrations on the Removal of Microtox Acute Toxicity in OMI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was measured as 100000 mg/l at 25°C (Table 5.171, SET 1). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{60}=67520 mg/l to EC_{25}=50325 mg/l and to EC_{10}=35250 mg/l, in Fe^{+2}=8.00 mg/l at 30°C (Table 5.171, SET 3). The toxicity removal efficiencies were 33.33%, 72.22% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 30°C (Table 5.171, SET 3).

The EC_{90} values decreased to EC_{55}, to EC_{20} and to EC_5 after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C (Table 5.171, SET 3). The EC_{55}, the EC_{20} and the EC_5 values were measured as 63276 mg/l, 49126 and 50840 mg/l, respectively, in Fe^{+2}=8.00 mg/l at 60°C. The toxicity removal efficiencies were 38.89%, 77.78% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C. 94.44% maximum Microtox acute toxicity yield was found in Fe^{+2}=8.00 mg/l after 150 min sonication time at 60°C (Table 5.171, SET 3).

The EC_{50} values decreased to EC_{65}=62098 mg/l to EC_{30}=54330 and to EC_{15}=47882 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=2.00 mg/l at 30°C (Table 5.171, SET 3). The EC_{50} values decreased to EC_{70}=61136 mg/l to EC_{35}=45125 and to EC_{25}=18558 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 30°C. The Microtox acute toxicity yields were 83.33% and 72.22% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of Fe^{+2}=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.171, SET 3).

Table 5.171 Effect of increasing Fe^{+2} concentrations on Microtox acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	Parameters	Microtox Acute Toxicity Values, * EC (mg/l)							
		25°C							
		0. min		60. min		120. min		150. min	
		$*EC_{90}$		$*EC$		$*EC$		$*EC$	
1	Raw ww, control	100000		EC_{80}=90000		EC_{75}=98000		EC_{70}=95000	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
		$*EC_{90}$	$*EC$	$*EC$	$*EC$	$*EC_{90}$	$*EC$	$*EC$	$*EC$
2	Raw ww, control	100000	EC_{75}= 90000	EC_{70}= 94000	EC_{60}= 95000	100000	EC_{70}= 65000	EC_{70}= 65000	EC_{50}= 60000
3	Fe^{+2}=2.00 mg/l	100000	EC_{65}= 62098	EC_{30}= 54330	EC_{15}= 47882	100000	EC_{60}= 60530	EC_{25}= 42755	EC_{10}= 21156
	Fe^{+2}=8.00 mg/l	100000	EC_{60}= 67520	EC_{25}= 50325	EC_{10}= 35250	100000	EC_{55}= 63276	EC_{20}= 49126	EC_{5}= 50840
	Fe^{+2}=20.00 mg/l	100000	EC_{70}= 61136	EC_{35}= 45125	EC_{25}= 18558	100000	EC_{65}= 55390	EC_{30}= 32235	EC_{20}= 3107

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{60}=60530 mg/l to EC_{25}=42755 and to EC_{10}=21156 mg/l after 60 min, 120 and 150 min sonication time, respectively, in Fe^{+2}=2.00 mg/l at 60°C (Table 5.171, SET 3). The EC_{50} values decreased to EC_{65}=55390 mg/l to EC_{30}=32235 and to EC_{20}=3107 mg/l after 60 min, 120 and 150 min sonication time, respectively, in Fe^{+2}=20.00 mg/l at 60°C. The Microtox acute toxicity yields were 88.89% and 77.78% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of Fe^{+2}=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60°C (Table 5.171, SET 3).

Increasing Fe^{+2} concentrations (2.00-8.00-20.00 mg/l) were applied during Microtox acute toxicity test (Table 5.171). And, the maximum acute toxicity yield was found at 8.00 mg/l Fe^{+2} concentrations after 150 min sonication time at 60°C. High acute toxicity removal was obtained low Fe^{+2} concentrations, long sonication time (150 min) and high sonication temperature (60°C). High Fe^{+2} concentrations (> 20.00 mg/l) caused to the inhibition effect on *Photobacterium phosphoreum* cells (Table 5.171).

5.17.6.2 Effect of Fe^{+2} Concentrations on the Removal of Daphnia magna Acute Toxicity in OMI ww at Increasing Sonication Time and Temperature

The initial EC_{50} values were obtained as 78000 mg/l at 25°C (Table 5.172, SET 1). After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{30} to EC_{20} and to EC_{10} in Fe^{+2}=8.00 mg/l at 30°C (Table 5.172, SET 3). The EC_{30}, the EC_{20} and the EC_{10} values were measured as 65000 mg/l, 45000 and 30000 mg/l, respectively, in Fe^{+2}=8.00 mg/l at 30°C. The toxicity removal efficiencies were 40.00%, 60.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 30°C (Table 5.172, SET 3).

The EC_{50} values decreased to EC_{30} to EC_{15} and to EC_{5} after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C (Table 5.172, SET 3). The EC_{30}, the EC_{15} and the EC_{5} values were measured as 60000 mg/l, 44000 and 22500 mg/l, respectively, in Fe^{+2}=8.00 mg/l at 60°C. The toxicity removal efficiencies were 40.00%, 70.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C. 90.00% maximum Microtox acute toxicity yield was found in Fe^{+2}=8.00 mg/l after 150 min sonication time at 60°C (Table 5.172, SET 3).

Table 5.172 Effect of increasing Fe^{+2} concentrations on *Daphnia magna* acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC_{50}**		***EC**		***EC**		***EC**	
1	Raw ww, control	78000		EC_{40}=85000		EC_{30}=55000		EC_{25}=39000	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC_{50}**	***EC**	***EC**	***EC**	***EC_{50}**	***EC**	***EC**	***EC**
2	Raw ww, control	78000	EC_{35}= 70000	EC_{30}= 65000	EC_{25}= 40000	78000	EC_{30}= 60000	EC_{25}= 37000	EC_{20}= 29000
3	Fe^{+2}=2.00 mg/l	78000	EC_{35}= 65000	EC_{20}= 50000	EC_{10}= 37000	78000	EC_{30}= 60000	EC_{15}= 50000	EC_{10}= 35000
	Fe^{+2}=8.00 mg/l	78000	EC_{30}= 65000	EC_{20}= 45000	EC_{10}= 30000	78000	EC_{30}= 60000	EC_{15}= 44000	EC_{5}= 22500
	Fe^{+2}=20.00 mg/l	78000	EC_{35}= 60000	EC_{25}= 44000	EC_{15}= 25000	78000	EC_{30}= 52500	EC_{20}= 34000	EC_{10}= 12500

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{35}=65000 mg/l to EC_{20}=50000 and to EC_{10}=37000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=2.00 mg/l at 30°C (Table 5.172, SET 3). The EC_{50} values decreased to EC_{35}=60000 mg/l to EC_{25}=44000 and to EC_{15}=25000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 30°C. The *Daphnia magna* acute toxicity yields were 80.00% and 70.00% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of Fe^{+2}=20.00 mg/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.172, SET 3).

The EC_{50} values decreased to EC_{30}=60000 mg/l to EC_{15}=50000 and to EC_{10}=35000 mg/l after 60 min, 120 and 150 min sonication time, respectively, in Fe^{+2}=2.00 mg/l at 60°C (Table 5.172, SET 3). The EC_{50} values decreased to EC_{30}=52500 mg/l to EC_{20}=34000 and to EC_{10}=12500 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 60°C. The *Daphnia magna* acute toxicity yields were 80.00% and 80.00% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of Fe^{+2}=20.00 mg/l to *Daphnia magna* in after 150 min sonication time at 60°C (Table 5.172, SET 3).

5.17.6.3 Direct Effects of Fe^{+2} Concentrations on the Acute Toxicity of Microtox and Daphnia magna in OMI ww

The acute toxicity test was performed in the samples containing 2.00, 8.00 and 20.00 mg/l Fe^{+2} concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing Fe^{+2} the toxicity test were performed without OMI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing Fe^{+2} concentrations after 150 min sonication time. Table 5.173 showed the responses of Microtox and *Daphnia magna* to increasing Fe^{+2} concentrations.

Table 5.173 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing Fe^{+2} concentrations without OMI ww after 150 min sonication time.

Fe^{+2} Conc. (mg/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
2.00	EC_{10}=30	-	-	EC_{10}=50	-	-
8.00	EC_{15}=170	2.00	EC_{1}=7.00	EC_{20}=220	4.00	EC_{3}=9.00
20.00	EC_{20}=250	5.00	EC_{3}=10.00	EC_{30}=280	7.00	EC_{5}=16.00

The acute toxicity originating only from 2.00, 8.00 and 20.00 mg/l Fe^{+2} were found to be low (Table 5.173). 2.00 mg/l Fe^{+2} did not exhibit toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 8.00 and 20.00 mg/l Fe^{+2} were found to be low in the samples without OMI ww for the test organisms mentioned above. The acute toxicity originated from the Fe^{+2} decreased significantly to EC_1 and EC_3 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the Fe^{+2} is not significant and the real acute toxicity throughout sonication was attributed to the OMI ww, to their metabolites and to the sonodegradation by-products (Table 5.173).

5.17.7 Effect of Fe^{+3} Concentrations on the Removal of Acute Toxicity in OMI ww at Increasing Sonication Time and Temperature

5.17.7.1 Effect of Fe^{+3} Concentrations on the Removal of Microtox Acute Toxicity in OMI ww at Increasing Sonication Time and Temperature

As seen in Table 5.174 (SET 1), the initial EC_{90} values at pH=7.0 was found as 100000 mg/l at 25°C. The EC_{90} values decreased to EC_{65}, to EC_{30} and to EC_{15} after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 30°C (Table 5.174, SET 3). The EC_{65}, the EC_{30} and the EC_{15} values were measured as 61283 mg/l, 39534 and 26682 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 30°C. The toxicity removal efficiencies were 27.78%, 66.67% and 83.33% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 30°C (Table 5.174, SET 3).

The EC_{90} values decreased to EC_{60}, to EC_{25} and to EC_{10} after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C (Table 5.174, SET 3). The EC_{60}, the EC_{25} and the EC_{10} values were measured as 49152 mg/l, 44460 and 36672 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 60°C. The toxicity removal efficiencies were 33.33%, 72.22% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C. 88.89% maximum

Microtox acute toxicity yield was observed in Fe^{+3}=20.00 mg/l after 150 min sonication time at 60°C (Table 5.174, SET 3).

The EC_{50} values decreased to EC_{70}=63090 mg/l to EC_{35}=61498 and to EC_{25}=59524 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 30°C (Table 5.174, SET 3). The EC_{50} values decreased to EC_{75}=43320 mg/l to EC_{40}=31732 and to EC_{30}=23456 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 30°C. The Microtox acute toxicity yields were 72.22% and 66.67% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of Fe^{+3}=50.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.174, SET 3).

Table 5.174 Effect of increasing Fe^{+3} concentrations on Microtox acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

<table>
<tr><th rowspan="4">No</th><th rowspan="4">Parameters</th><th colspan="8">Microtox Acute Toxicity Values, * EC (mg/l)</th></tr>
<tr><th colspan="8">25°C</th></tr>
<tr><th colspan="2">0. min</th><th colspan="2">60. min</th><th colspan="2">120. min</th><th colspan="2">150. min</th></tr>
<tr><th colspan="2">*EC_{90}</th><th colspan="2">*EC</th><th colspan="2">*EC</th><th colspan="2">*EC</th></tr>
<tr><td>1</td><td>Raw ww, control</td><td colspan="2">100000</td><td colspan="2">EC_{80}=90000</td><td colspan="2">EC_{75}=98000</td><td colspan="2">EC_{70}=95000</td></tr>
<tr><td rowspan="3"></td><td rowspan="3"></td><th colspan="4">30°C</th><th colspan="4">60°C</th></tr>
<tr><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th></tr>
<tr><th>*EC_{90}</th><th>*EC</th><th>*EC</th><th>*EC</th><th>*EC_{90}</th><th>*EC</th><th>*EC</th><th>*EC</th></tr>
<tr><td>2</td><td>Raw ww, control</td><td>100000</td><td>EC_{75}= 90000</td><td>EC_{70}= 94000</td><td>EC_{60}= 95000</td><td>100000</td><td>EC_{70}= 65000</td><td>EC_{70}= 65000</td><td>EC_{50}= 60000</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>3</td><td>Fe^{+3}=10.00 mg/l</td><td>100000</td><td>EC_{70}= 63090</td><td>EC_{35}= 61498</td><td>EC_{25}= 58524</td><td>100000</td><td>EC_{65}= 65412</td><td>EC_{30}= 55815</td><td>EC_{20}= 50217</td></tr>
<tr><td></td><td>Fe^{+3}=20.00 mg/l</td><td>100000</td><td>EC_{65}= 61283</td><td>EC_{30}= 39534</td><td>EC_{15}= 26682</td><td>100000</td><td>EC_{60}= 49152</td><td>EC_{25}= 44460</td><td>EC_{10}= 36672</td></tr>
<tr><td></td><td>Fe^{+3}=50.00 mg/l</td><td>100000</td><td>EC_{75}= 43320</td><td>EC_{40}= 31732</td><td>EC_{30}= 23456</td><td>100000</td><td>EC_{70}= 29335</td><td>EC_{35}= 26811</td><td>EC_{25}= 14716</td></tr>
</table>

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{65}=65412 mg/l to EC_{30}=55815 and to EC_{20}=50217 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 60°C (Table 5.174, SET 3). The EC_{50} values decreased to EC_{70}=29335 mg/l to EC_{35}=26811 and to EC_{25}=14716 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 60°C. The Microtox acute toxicity yields were 77.78% and 72.22% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of Fe^{+3}=50.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60°C (Table 5.174, SET 3).

High Fe^{+3} concentrations (> 50.00 mg/l) caused to hindering effect on *Photobacterium phosphoreum* cells (Table 5.174). Because, high Fe^{+2} concentrations (> 50.00 mg/l) have the more toxic effect than low Fe^{+3} concentrations on *Photobacterium phosphoreum* microorganisms during acute toxicity assay. The maximum acute toxicity removal efficiency was observed at low Fe^{+3} concentrations, long sonication time (150 min) and high sonication temperature (60°C) (Table 5.174).

5.17.7.2 Effect of Fe^{+3} Concentrations on the Removal of Daphnia magna Acute Toxicity in OMI ww at Increasing Sonication Time and Temperature

The initial EC_{50} values were observed as 78000 mg/l at 25°C (Table 5.175, SET 1). After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{30} to EC_{20} and to EC_{15} in Fe^{+3}=20.00 mg/l at 30°C (Table 5.175, SET 3). The EC_{30}, the EC_{20} and the EC_{15} values were measured as 70000 mg/l, 45000 and 32500 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 30°C. The toxicity removal efficiencies were 40.00%, 60.00% and 70.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 30°C (Table 5.175, SET 3).

The EC_{50} values decreased to EC_{30} to EC_{15} and to EC_{10} after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C (Table 5.175, SET 3). The EC_{31}, the EC_{12} and the EC_{6} values were measured as 64000 mg/l, 45000 and 25000 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 60°C. The toxicity removal efficiencies were 40.00%, 70.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C. 80.00% maximum *Daphnia magna* acute toxicity removal was obtained in Fe^{+3}=20.00 mg/l after 150 min sonication time at 60°C (Table 5.175, SET 3).

Table 5.175 Effect of increasing Fe^{+3} concentrations on *Daphnia magna* acute toxicity in OMI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{50}$		***EC**		***EC**		***EC**	
1	Raw ww, control	78000		EC_{40}=85000		EC_{30}=55000		EC_{25}=39000	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{50}$	***EC**	***EC**	***EC**	**$*EC_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	78000	EC_{35}= 70000	EC_{30}= 65000	EC_{25}= 40000	78000	EC_{30}= 60000	EC_{25}= 37000	EC_{20}= 29000
3	Fe^{+3}=10.00 mg/l	78000	EC_{30}= 65000	EC_{25}= 59000	EC_{20}= 35000	78000	EC_{30}= 70000	EC_{20}= 44000	EC_{15}= 27500
	Fe^{+3}=20.00 mg/l	78000	EC_{30}= 70000	EC_{20}= 45000	EC_{15}= 32500	78000	EC_{30}= 64000	EC_{15}= 45000	EC_{10}= 25000
	Fe^{+3}=50.00 mg/l	78000	EC_{35}= 50000	EC_{30}= 45000	EC_{20}= 25000	78000	EC_{30}= 58000	EC_{25}= 35000	EC_{15}= 14000

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{30}=65000 mg/l to EC_{25}=59000 and to EC_{20}=35000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 30°C (Table 5.175, SET 3). The EC_{50} values decreased to EC_{35}=50000 mg/l to EC_{30}=45000 and to EC_{20}=25000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 30°C. The *Daphnia magna* acute toxicity yields were 60.00% and 60.00% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 30^{o}C. It was observed an inhibition effect of Fe^{+3}=50.00 mg/l to *Daphnia magna* after 150 min sonication time at 30^{o}C (Table 5.175, SET 3).

The EC_{50} values decreased to EC_{30}=70000 mg/l to EC_{20}=44000 and to EC_{15}=27500 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 60^{o}C (Table 5.175, SET 3). The EC_{50} values decreased to EC_{30}=58000 mg/l to EC_{25}=35000 and to EC_{15}=14000 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 60^{o}C. The *Daphnia magna* acute toxicity yields were 70.00% and 70.00% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 60^{o}C. It was obtained an inhibition effect of Fe^{+3}=50.00 mg/l to *Daphnia magna* after 150 min sonication time at 60^{o}C (Table 5.175, SET 3).

5.17.7.3 Direct Effects of Fe^{+3} Concentrations on the Acute Toxicity of Microtox and Daphnia magna in OMI ww

The acute toxicity test was performed in the samples containing 10.00, 20.00 and 50.00 mg/l Fe^{+3} concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing Fe^{+3} the toxicity test were performed without OMI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing Fe^{+3} concentrations after 150 min sonication time. Table 5.176 showed the responses of Microtox and *Daphnia magna* to increasing Fe^{+3} concentrations.

Table 5.176 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing Fe^{+3} concentrations without OMI ww after 150 min sonication time.

Fe^{+3} Conc. (mg/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
10.00	EC_{10}=35	-	-	EC_{10}=45	-	-
20.00	EC_{15}=170	3.00	EC_1=9.00	EC_{20}=210	5.00	EC_3=15.00
50.00	EC_{20}=230	6.00	EC_4=12.00	EC_{30}=290	10.00	EC_6=20.00

The acute toxicity originating only from 10.00, 20.00 and 50.00 mg/l Fe^{+3} were found to be low (Table 5.176). 10.00 mg/l Fe^{+3} did not exhibit toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 20.00 and 50.00 mg/l Fe^{+3} were found to be low in the samples without OMI ww for the test organisms mentioned above. The acute toxicity originated from the Fe^{+3} decreased significantly to EC_1 and EC_4 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the Fe^{+3} is not significant and the real acute toxicity throughout sonication was attributed to the OMI ww, to their metabolites and to the sonodegradation by-products (Table 5.176).

5.17.8 OMI ww Toxicities, Interspecies Correlation and Sensitivities

The EC_{50} value of OMI ww increased from EC_{50}=55555.56 mg/l (converted from EC_{90}=100000.00 mg/l in OMI ww for Microtox acute toxicity assay before sonication) to EC_{50}=78000.00 mg/l as the trophic level increased from bacteria in Microtox test to water flea in *Daphnia magna* test in the influent samples. To verify the relationships between the acute toxicity data of two organisms the EC_{50} values of *Photobacterium phosphoreum* were correlated to those of *Daphnia magna* by statistical analysis using their EC_{50} values in the influent of OMI ww. It was found that the EC_{50} values differed in both test organisms for the OMI ww before sonication samples. The coefficient of correlation and t-test statistics (R^2=0.22, $p \leq 0.01$, t-test statistics=0.35) did not show a significant linear relationship between the acute toxicities of OMI ww to *Photobacterium phosphoreum* and to *Daphnia magna* in the influent OMI ww samples. This result verifies the sensitivity of *Photobacterium phosphoreum* and the resistance of *Daphnia magna* to OMI ww by taken into consideration the data obtained with sensitivity scores. This indicated that the water fleas exhibited less acute toxicity to OMI ww. The differences in test sensitivities can be attributed to the differences in the responses of the two different trophic organisms in OMI ww. In this study showed that the Microtox acute toxicity test is more sensitive than that *Daphnia magna* in the OMI ww samples before sonication process.

Table 5.177 shows the sensitivity ranking and the EC_{50} values of OMI ww in *Photobacterium phosphoreum* and *Daphnia magna* in sonicated samples containing some additives after 150 min sonication time at 60°C. The EC_{50} value of OMI ww increased from 2.78 mg/l (converted from 5.00 mg/l at original EC values in OMI ww for Microtox acute toxicity assay after 150 min sonication time) to 20.00 mg/l as the trophic level increased from bacteria in Microtox test to water flea in *Daphnia* *magna* test in the sonicated OMI ww samples containing some additives after 150 min sonication time at 60°C (Table 5.177). To verify the relationships between the acute toxicity data of two organisms the EC_{50} values of *Photobacterium phosphoreum* were correlated to those of *Daphnia magna* by statistical analysis using their EC_{50} values in the effluent of OMI ww. It was found that the EC_{50} values differed in both test organisms for the sonicated samples containing some additives after 150 min sonication time at 60°C. The coefficient of correlation and t-test statistics (R^2=0.92, p=0.01, t-test statistics=10.56) show a significant linear relationship between the acute toxicities of OMI ww to *Photobacterium phosphoreum* and to *Daphnia magna* in the after 150 min sonication samples (Table 5.177). This indicated that the water fleas exhibited less acute toxicity to OMI ww. The differences in test sensitivities can be attributed to the differences in the responses of the two different trophic organisms in OMI ww. As a conclusion, this study showed that the Microtox acute toxicity test is more sensitive than that *Daphnia magna* in the sonicated OMI ww samples containing some additives after 150 min sonication time at 60°C (Table 5.177).

Table 5.177 Sensitivity ranking and EC_{50} values of OMI ww in *Photobacterium phosphoreum* and *Daphnia magna* in sonicated samples containing some additives after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

Parameters	***Photobacterium phosphoreum***		***Daphnia magna***	
	EC_{50} value and 95.00% Confidence Limits (mg/l) 48 h	**Sensitivity Ranking**	**EC_{50} value and 95.00% Confidence Limits (mg/l) 48 h**	**Sensitivity Ranking**
Raw ww, control	17.78 (17.53 – 18.03)	1	20.00 (19.74 – 20.26)	2
1 h aeration	4.33 (4.21 – 4.45)	1	5.00 (4.87 – 5.13)	2
30 min N_2(g) (6.00 mg/l N_2)	4.33 (4.21 – 4.45)	1	5.00 (4.87 – 5.13)	2
pH=10.0	12.22 (12.02 – 12.42)	1	15.00 (14.78 – 15.22)	2
DO=10.00 mg/l	4.11 (3.99 – 4.23)	1	5.00 (4.87 – 5.13)	2
H_2O_2=500 mg/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
TiO_2=10.00 mg/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
NaCl=2.50 g/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
Fe^{+2}=8.00 mg/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
Fe^{+3}=20.00 mg/l	5.56 (5.42 – 5.70)	1	10.00 (9.82 – 10.18)	2
HCO_3^{-1}=1.00 g/l	8.33 (8.16 – 8.50)	1	10.00 (9.82 – 10.18)	2
C_4H_9OH=0.50 g/l	8.33 (8.16 – 8.50)	1	10.00 (9.82 – 10.18)	2

5.18 Acute Toxicity Evaluations in TI ww

5.18.1 Effect of Increasing Sonication Time on the Acute Toxicity Removal Efficiencies in TI ww at Ambient Conditions

5.18.1.1 Effect of Increasing Sonication Time on the Microtox Acute Toxicity Removal Efficiencies in TI ww at Ambient Conditions

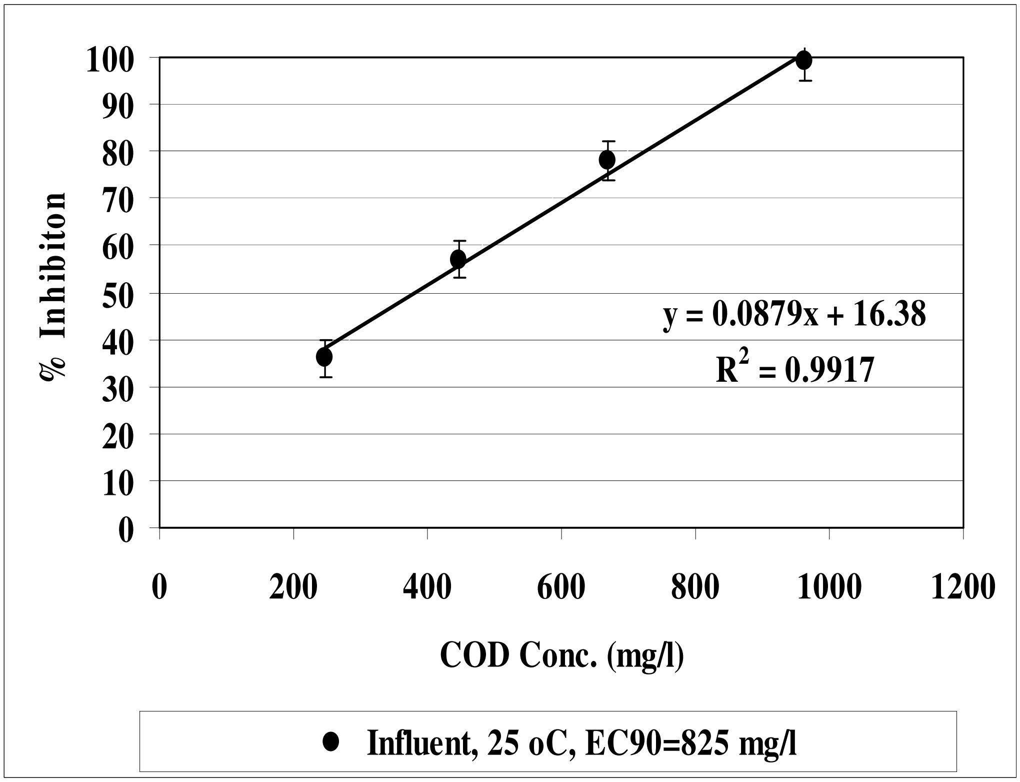
Microtox test is an acute toxicity test. Toxicity was estimated in terms of EC_{50}, defined as the concentration of the toxicant causing 50.00% reduction in activity of the *Photobacterium phosphoreum*. Figure 5.148 was shown the acute toxicity test results obtained from the Microtox acute toxicity test through sonication with increasing sonication time (60 min, 120 and 150 min) at pH=7.0 and at 25^{o}C ambient condition.

All TI ww samples were serially diluted in 2.00% NaCI (w/v) and each assay was performed at pH=7.0 and a temperature of 15°C. NaCl (2.00%) was used as the control. The initial EC_{90} values at pH=7.0 was found as 825 mg/l at 25^{o}C ambient conditions (Table 5.178; Figure 5.148a). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{70}, to EC_{60} and to EC_{50} at 25^{o}C. The EC_{70}, the EC_{60} and the EC_{50} values were measured as 510 mg/l, 650 and 640 mg/l, respectively, at 25^{o}C (Table 5.178; Figure 5.148b-c-d). The toxicity removal efficiencies were 22.22%, 33.33% and 44.44% after 60 min, 120 and 150 min sonication times, respectively, at 25^{o}C. 44.44% maximum Microtox acute toxicity removal was found after 150 min sonication time at 25^{o}C (Table 5.178; Figure 5.148d).

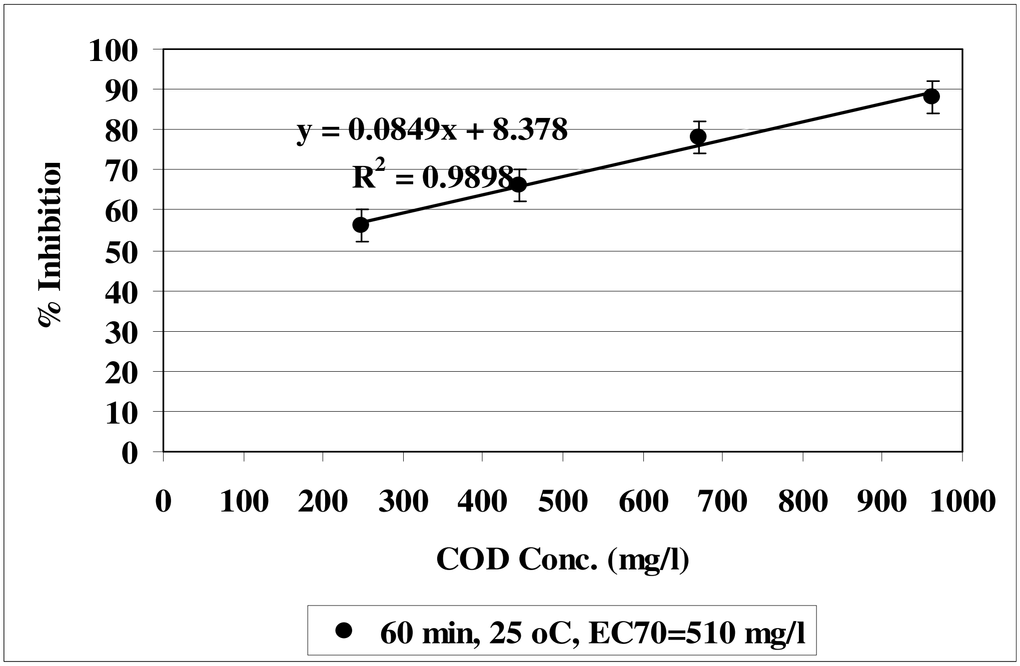
Table 5.178 Effect of increasing sonication time on Microtox acute toxicity in TI ww at 25°C ambient conditions (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**			
		25°C			
		0. min	**60. min**	**120. min**	**150. min**
		$^*EC_{90}$	**$^*EC$**	**$^*EC$**	**$^*EC$**
1	Raw ww, control	825	EC_{70}=510	EC_{60}=650	EC_{50}=640

* EC values were calculated based on COD_{dis} (mg/l).

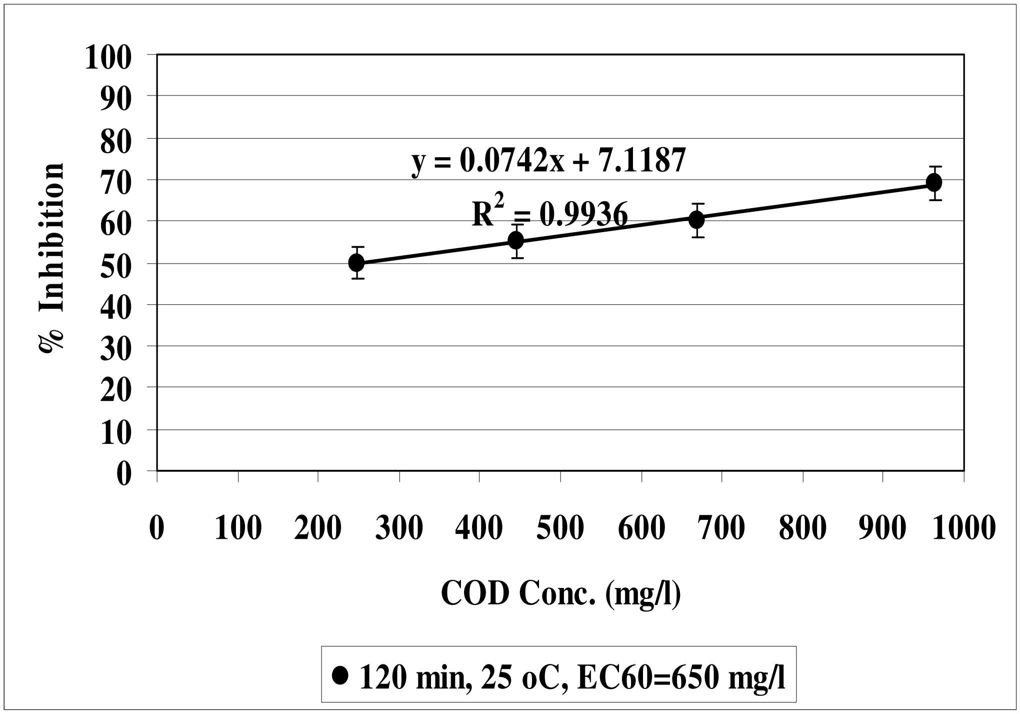


(a)

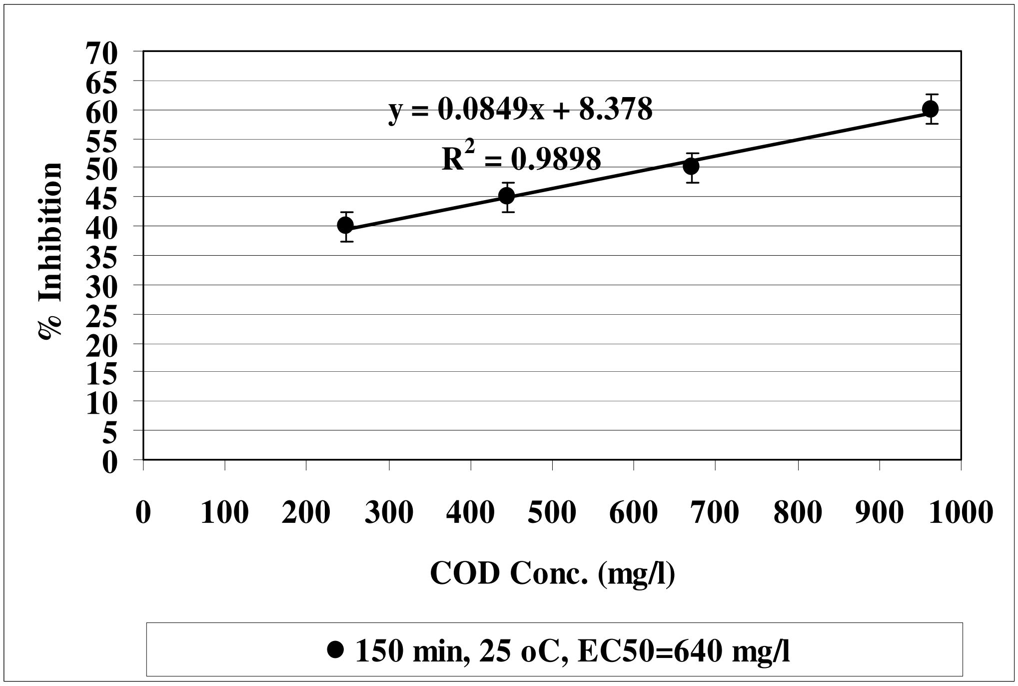


(b)

Figure 5.148 Effect of increasing sonication time on Microtox acute toxicity in TI ww for (a) influent at 25°C and (b) after 60 min sonication time at 25°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.148 Effect of increasing sonication time on Microtox acute toxicity in TI ww for (c) after 120 min sonication time at 25^{o}C and (d) after 150 min sonication time at 25^{o}C (640 W power, 35 kHz frequency).

5.18.1.2 Effect of Increasing Sonication Time on the Daphnia magna Acute Toxicity Removal Efficiencies in TI ww at Ambient Conditions

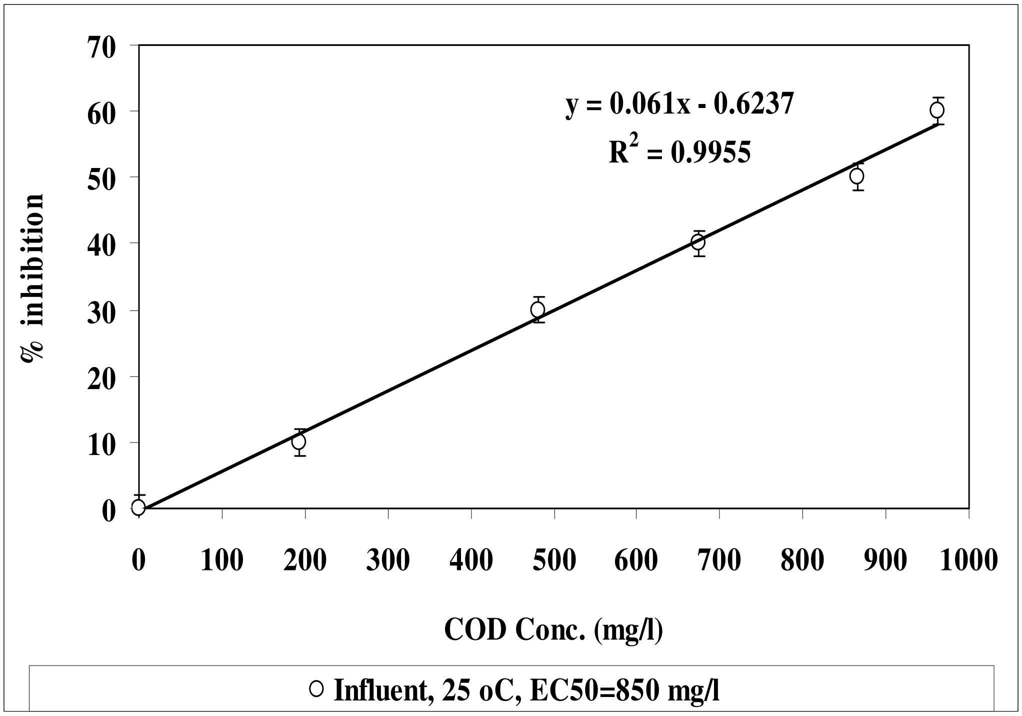
The *Daphnia magna* test is accepted as an acute toxicity test. Toxicity was estimated in terms of EC_{50}, defined as the concentration of the toxicant causing 50.00% reduction in activity of the water flea. The effective COD_{dis} concentrations caused 50.00% mortality in *Daphnia magna* cells EC_{50} (mg/l) in raw and sonicated wastewater samples which were monitored based on COD_{dis} (mg/l) concentrations. The EC_{50} values and the other EC values were calculated by taking into consideration the dilution ratios and the inhibitory concentrations. Figure 5.149 was shown the acute toxicity test results obtained from the *Daphnia magna* test through sonication with increasing sonication time**s** (60 min, 120 and 150 min) at pH=7.0 and at 25^{o}C.

The test samples containing an initial COD_{dis} concentration of 962.99 mg/l were diluted at 1/1, 1/2, 1/8, 1/16 and 1/24 ratios after sonication experiments. The young 10 *Daphnids* (< 24 h old) were added to each test vessel at the initiation time (t=0). After 24 h of exposure, the EC values of COD_{dis} concentrations were calculated. The initial EC_{50} values were obtained as 850 mg/l at 25^{o}C (Table 5.179, SET 1; Figure 5.149a). After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{45}=625 mg/l to EC_{40}=370 mg/l and to EC_{30}=155 mg/l at 25^{o}C (Table 5.179, SET 3; Figure 5.149b-c-d). The toxicity removal efficiencies were 10.00%, 20.00% and 40.00% after 60 min, 120 and 150 min sonication times, respectively, at 25^{o}C. 40.00% maximum *Daphnia magna* acute toxicity removal was found after 150 min sonication time at 25^{o}C (Table 5.179, SET 3; Figure 5.149d).

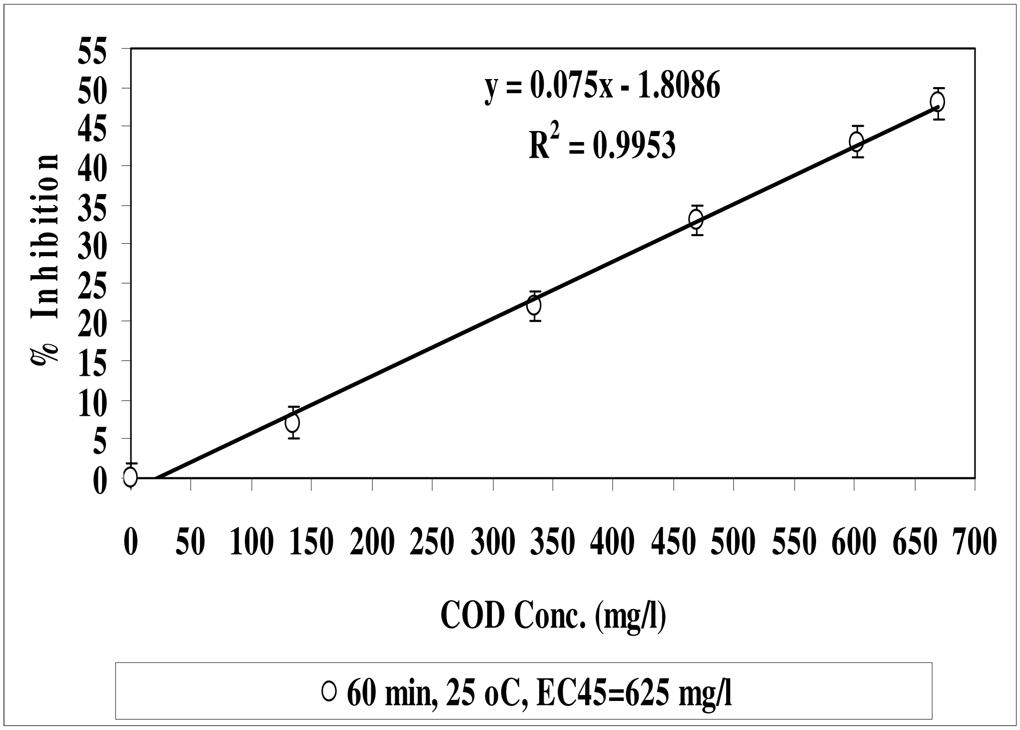
Table 5.179 Effect of increasing sonication time on *Daphnia magna* acute toxicity in TI ww at 25°C ambient conditions (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**			
		25°C			
		0. min	**60. min**	**120. min**	**150. min**
		***EC$_{50}$**	***EC**	***EC**	***EC**
1	Raw ww, control	850	EC$_{45}$=625	EC$_{40}$=370	EC$_{30}$=155

* EC values were calculated based on COD (mg/l).

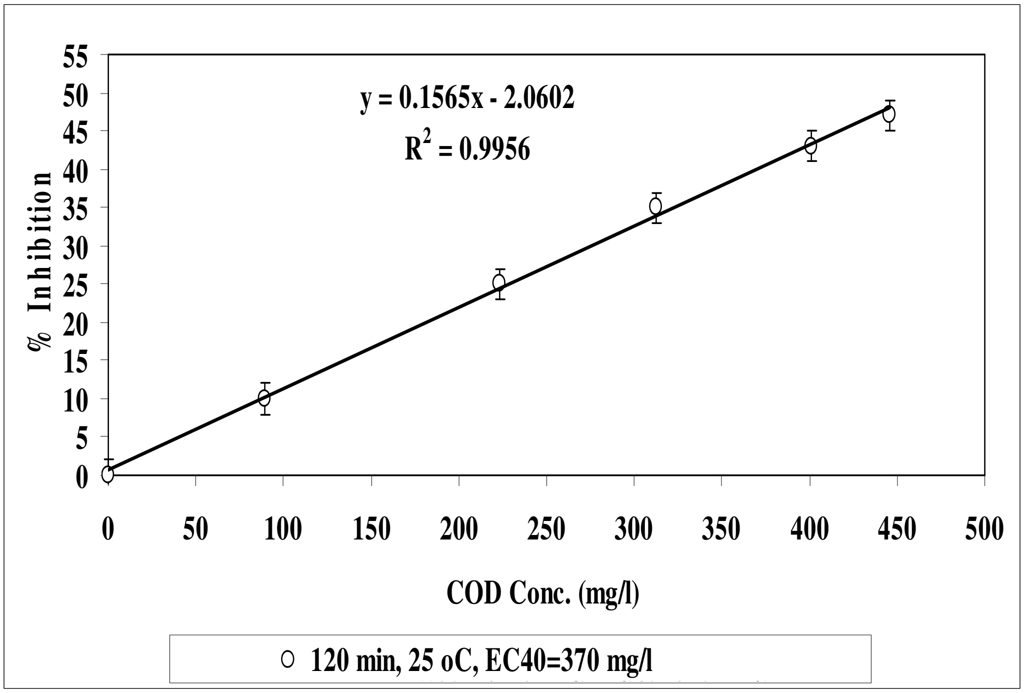


(a)

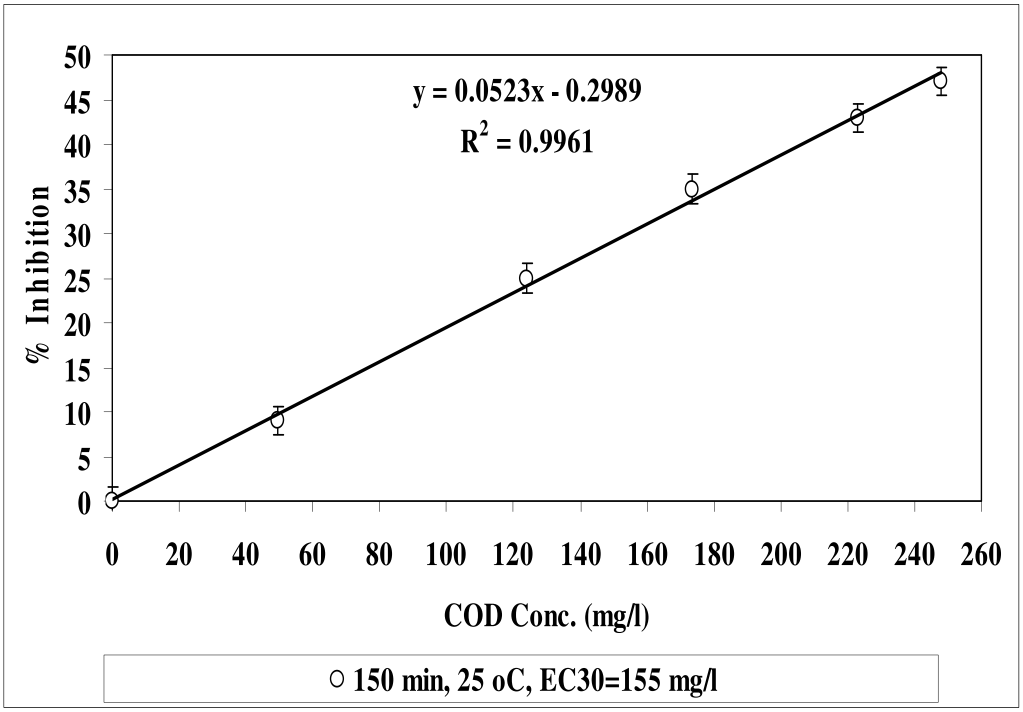


(b)

Figure 5.149 Effect of increasing sonication time on *Daphnia magna* acute toxicity in TI ww for (a) influent at 25°C and (b) after 60 min sonication time at 25°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.149 Effect of increasing sonication time on *Daphnia magna* acute toxicity in TI ww for (c) after 120 min a sonication time t 25^{o}C and (d) after 150 min sonication time at 25^{o}C (640 W power, 35 kHz frequency).

5.18.2 Effect of Increasing Temperature on the Removal of Acute Toxicity in TI ww at Increasing Sonication Time

5.18.2.1 Effect of Increasing Temperature on the Removal of Microtox Acute Toxicity in TI ww at Increasing Sonication Time

The initial EC$_{90}$ values at pH=7.0 was found as 825 mg/l at 25°C (Table 5.180, SET 1; Figure 5.150a). After 60 min, 120 and 150 min of sonication the EC$_{90}$ values decreased to EC$_{70}$, to EC$_{50}$ and to EC$_{40}$ at 30°C. The EC$_{70}$, the EC$_{50}$ and the EC$_{40}$ values were measured as 580 mg/l, 580 and 550 mg/l, respectively, at 30°C (Table 5.180, SET 2). The toxicity removal efficiencies were 22.22%, 44.44% and 55.56% after 60 min, 120 and 150 min sonication times, respectively, at 30°C (Table 5.180, SET 2).

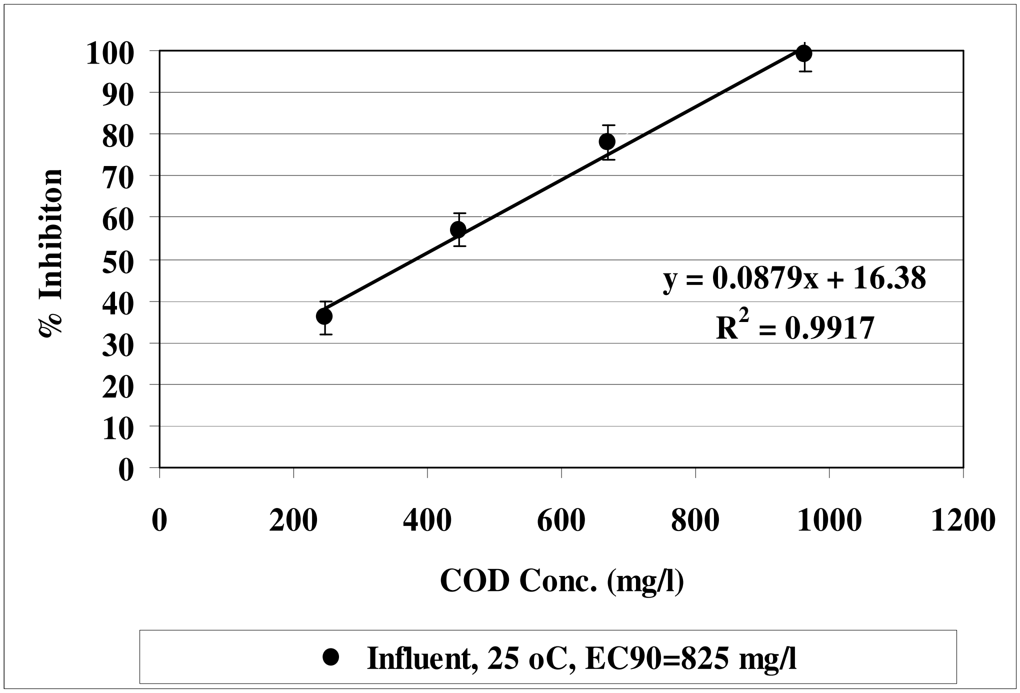
Table 5.180 Effect of increasing sonication temperature on Microtox acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

<table>
<tr><th rowspan="4">No</th><th rowspan="4">Parameters</th><th colspan="8">Microtox Acute Toxicity Values, * EC (mg/l)</th></tr>
<tr><th colspan="8">25°C</th></tr>
<tr><th colspan="2">0. min</th><th colspan="2">60. min</th><th colspan="2">120. min</th><th colspan="2">150. min</th></tr>
<tr><th colspan="2">*EC$_{90}$</th><th colspan="2">*EC</th><th colspan="2">*EC</th><th colspan="2">*EC</th></tr>
<tr><td>1</td><td>Raw ww, control</td><td colspan="2">825</td><td colspan="2">EC$_{70}$=510</td><td colspan="2">EC$_{60}$=650</td><td colspan="2">EC$_{50}$=640</td></tr>
<tr><td rowspan="3"></td><td rowspan="3"></td><th colspan="4">30°C</th><th colspan="4">60°C</th></tr>
<tr><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th></tr>
<tr><th>*EC$_{90}$</th><th>*EC</th><th>*EC</th><th>*EC</th><th>*EC$_{90}$</th><th>*EC</th><th>*EC</th><th>*EC</th></tr>
<tr><td>2</td><td>Raw ww, control</td><td>825</td><td>EC$_{70}$ =580</td><td>EC$_{50}$= 580</td><td>EC$_{40}$= 550</td><td>825</td><td>EC$_{55}$= 550</td><td>EC$_{40}$= 590</td><td>EC$_{30}$ =690</td></tr>
</table>

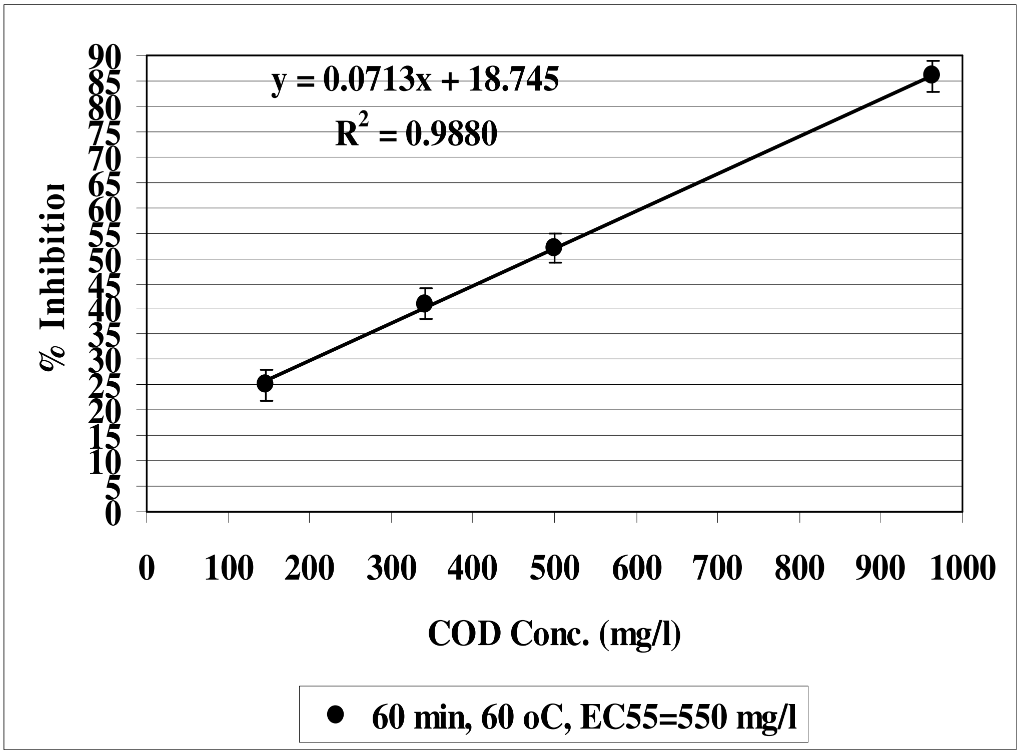
* EC values were calculated based on COD$_{dis}$ (mg/l).

The EC_{90} values decreased to EC_{55}, to EC_{40} and to EC_{30} after 60 min, 120 and 150 min of sonication, respectively, at 60°C (Table 5.180, SET 2; Figure 5.150b-c-d). The EC_{55}, the EC_{40} and the EC_{30} values were measured as 550 mg/l, 590 and 690 mg/l, respectively, at 60°C. The toxicity removal efficiencies were 38.89%, 55.56% and 66.67% after 60 min, 120 and 150 min sonication times, respectively, at 60°C (Table 5.180, SET 2; Figure 5.150b-c-d). 66.67% maximum Microtox acute toxicity removal was observed at 60°C after 150 min sonication time (Table 5.180, SET 2; Figure 5.150d).

The results of the study showed that as the sonication temperature and sonication time increased from 25°C to 30°C and 60°C; from 60 to 150 min, respectively, the Microtox acute toxicity decreased.

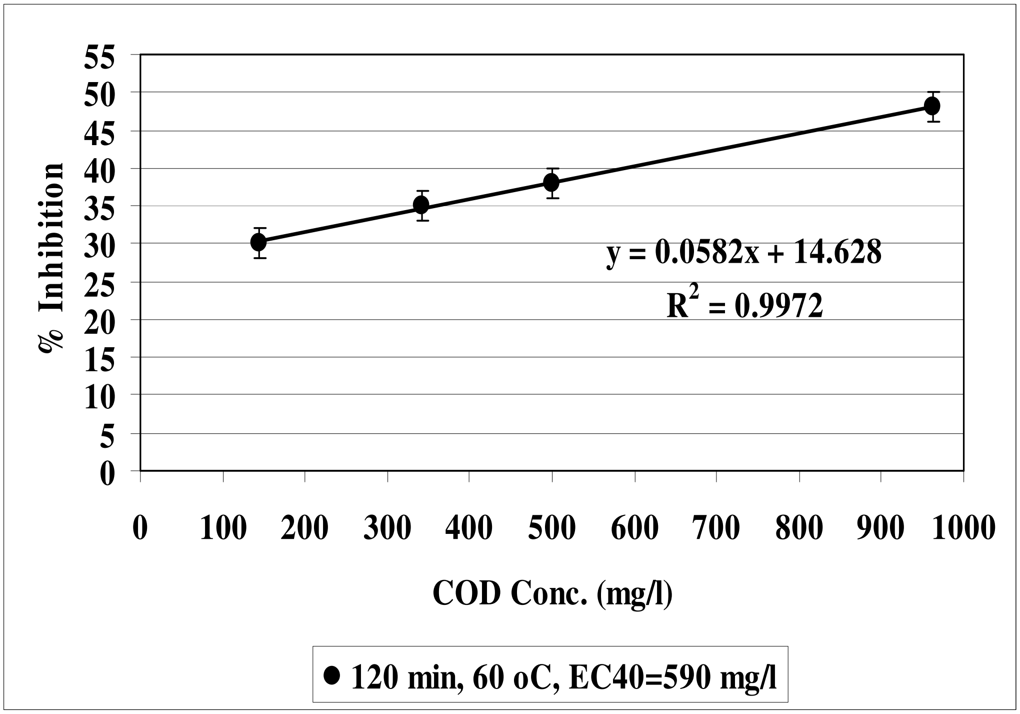


(a)

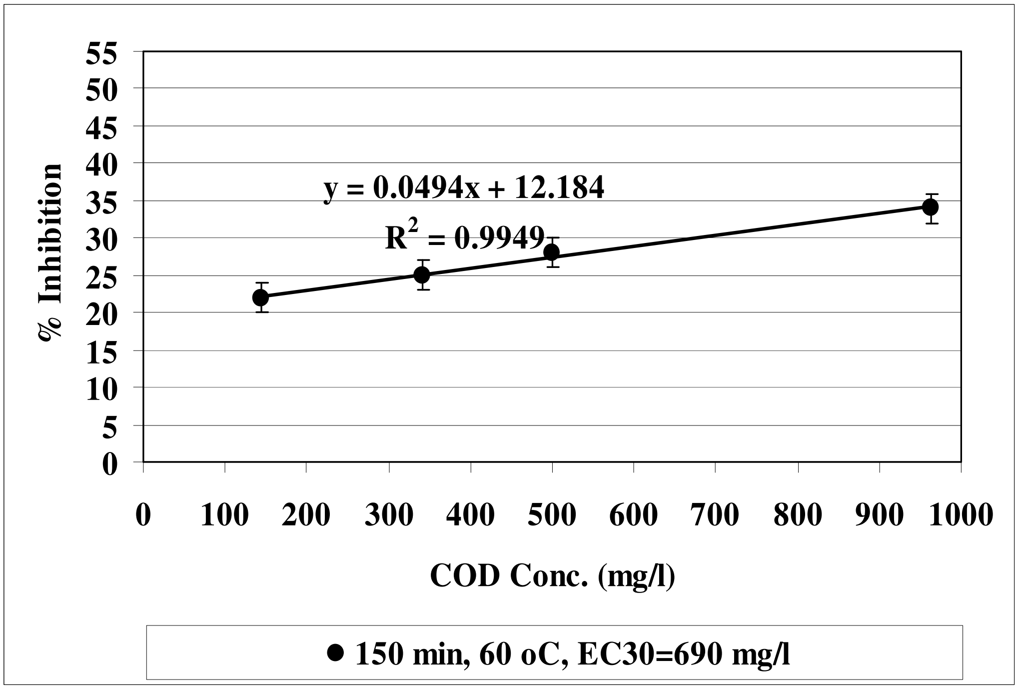


(b)

Figure 5.150 Effect of increasing temperature on Microtox acute toxicity in TI ww for (a) influent at 25°C and (b) after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.150 Effect of increasing temperature on Microtox acute toxicity in TI ww for (c) after 120 min sonication time at 60°C and (d) after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.18.2.2 Effect of Increasing Temperature on the Removal of Daphnia magna Acute Toxicity in TI ww at Increasing Sonication Time

As seen in Table 5.181 (SET 1) and Figure 5.151a, the initial EC_{50} values were obtained as 850 mg/l at 25°C. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{40} to EC_{35} and to EC_{25} at 30°C (Table 5.181, SET 2). The EC_{40}, the EC_{35} and the EC_{25} values were measured as 470 mg/l, 230 and 115 mg/l, respectively, at 30°C. The toxicity removal efficiencies were 20.00%, 30.00% and 50.00% after 60 min, 120 and 150 min sonication times, respectively, at 30°C (Table 5.181, SET 2).

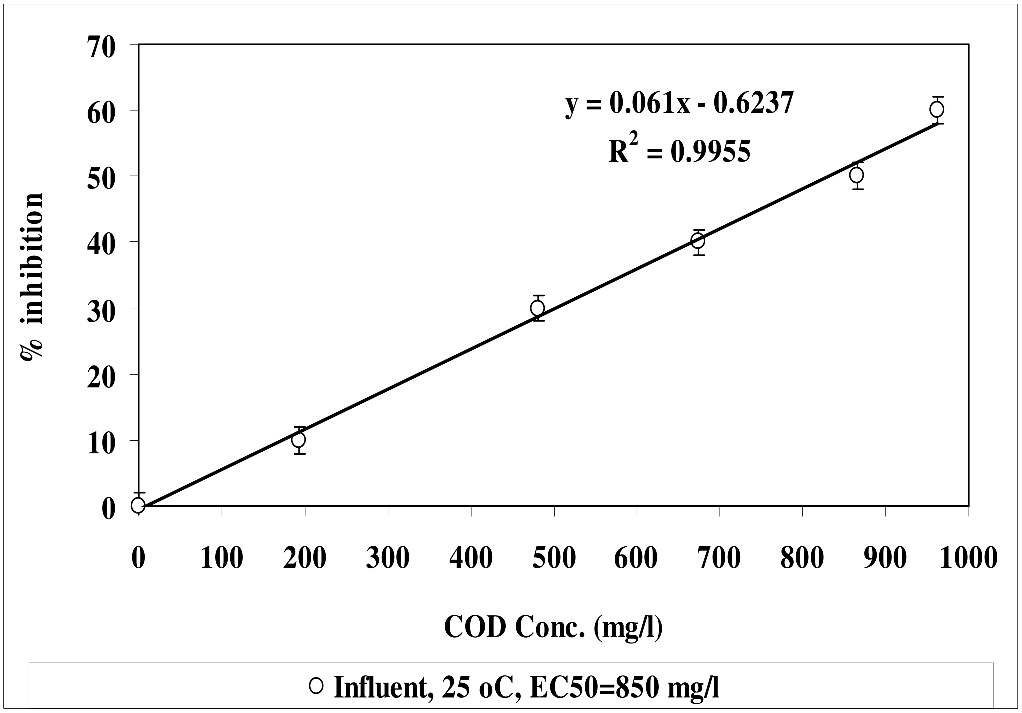
Table 5.181 Effect of increasing sonication temperature on *Daphnia magna* acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

<table>
<tr><th rowspan="4">No</th><th rowspan="4">Parameters</th><th colspan="8">*Daphnia magna* Acute Toxicity Values, * EC (mg/l)</th></tr>
<tr><th colspan="8">25°C</th></tr>
<tr><th colspan="2">0. min</th><th colspan="2">60. min</th><th colspan="2">120. min</th><th colspan="2">150. min</th></tr>
<tr><th colspan="2">*EC_{50}</th><th colspan="2">*EC</th><th colspan="2">*EC</th><th colspan="2">*EC</th></tr>
<tr><td>1</td><td>Raw ww, control</td><td colspan="2">850</td><td colspan="2">EC_{45}=625</td><td colspan="2">EC_{40}=370</td><td colspan="2">EC_{30}=155</td></tr>
<tr><td rowspan="3"></td><td rowspan="3"></td><th colspan="4">30°C</th><th colspan="4">60°C</th></tr>
<tr><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th></tr>
<tr><th>*EC_{50}</th><th>*EC</th><th>*EC</th><th>*EC</th><th>*EC_{50}</th><th>*EC</th><th>*EC</th><th>*EC</th></tr>
<tr><td>2</td><td>Raw ww, control</td><td>850</td><td>EC_{40} =470</td><td>EC_{35}= 230</td><td>EC_{25}= 115</td><td>850</td><td>EC_{35} =375</td><td>EC_{30} =212</td><td>EC_{20} =75</td></tr>
</table>

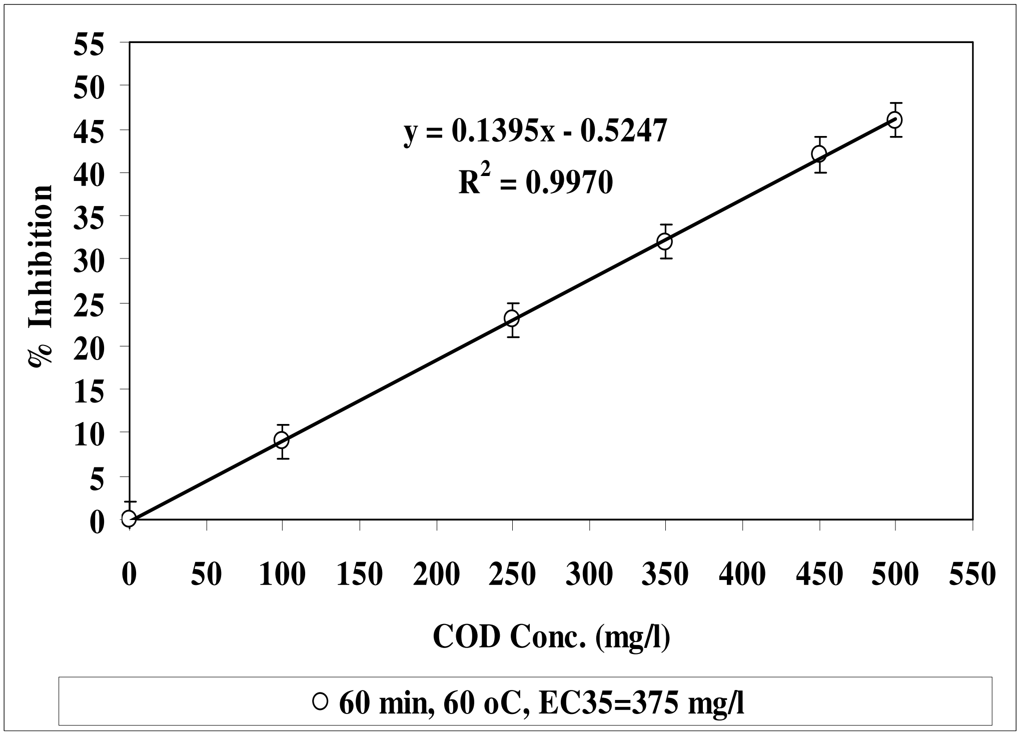
* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{35} to EC_{30} and to EC_{20} after 60 min, 120 and 150 min of sonication, respectively, at 60°C (Table 5.181, SET 2; Figure 5.151b-c-d). The EC_{35}, the EC_{30} and the EC_{20} values were observed as 375 mg/l, 212 and 75 mg/l, respectively, at 60°C. The toxicity removal efficiencies were 30.00%, 40.00% and 60.00% after 60 min, 120 and 150 min sonication times, respectively, at 60°C (Table 5.181, SET 2; Figure 5.151b-c-d). 60.00% maximum *Daphnia magna* acute toxicity yield was measured to 60^{o}C after 150 min sonication time (Table 5.181, SET 2; Figure 5.151d).

As the temperature increased from 25 to 30 and 60^{o}C the acute toxicity removals increased from 40.00% to 50.00% and to 60.00% after 150 min sonication time.

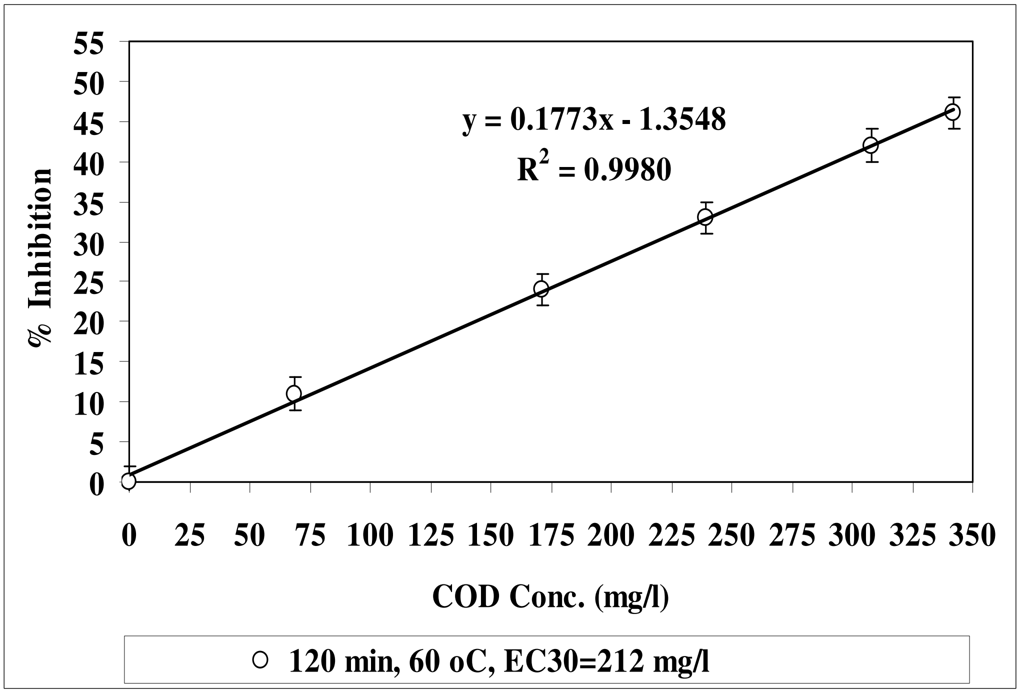


(a)

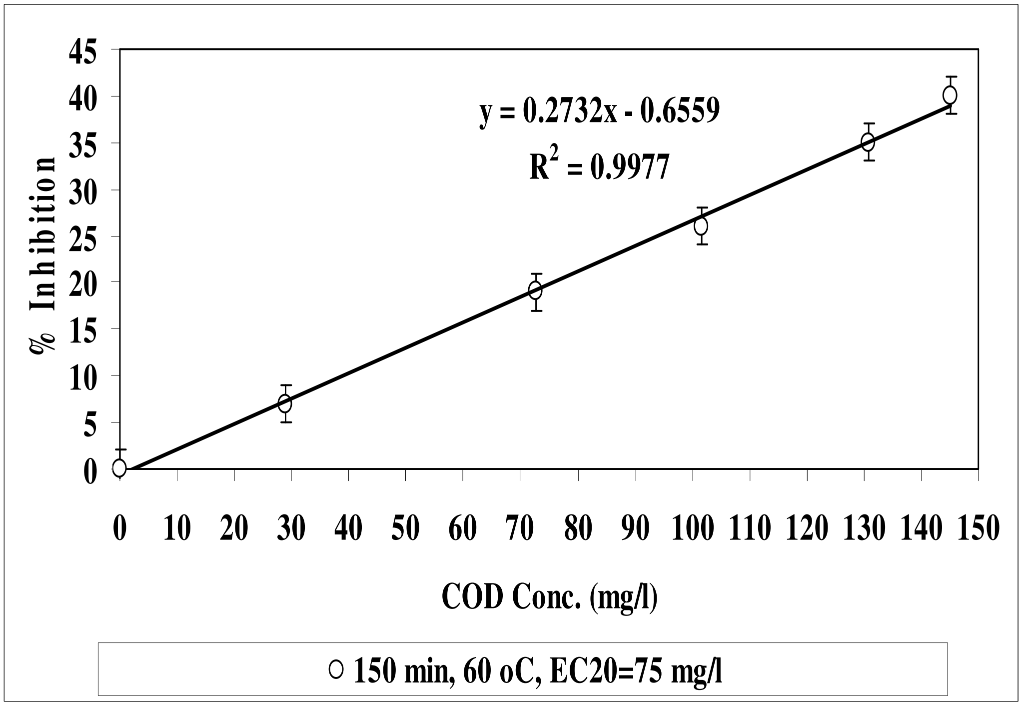


(b)

Figure 5.151 Effect of increasing temperature on *Daphnia magna* acute toxicity in TI ww for (a) influent at 25°C and (b) after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.151 Effect of increasing temperature on *Daphnia magna* acute toxicity in TI ww for (c) after 120 min sonication time at 60°C and (d) after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.18.3 Effect of H_2O_2 Concentrations on the Removal of Acute Toxicity at Increasing Sonication Time and Temperature

5.18.3.1 Effect of H_2O_2 Concentrations on the Removal of Microtox Acute Toxicity in TI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was found as 825 mg/l at 25°C (Table 5.182, SET 1; Figure 5.152a). After 60 min, 120 and 150 min of sonication the EC_{99} values decreased to EC_{55}, to EC_{25} and to EC_{10} in H_2O_2=500 mg/l at 30°C (Table 5.182, SET 3). The EC_{55}, the EC_{25} and the EC_{10} values were measured as 416 mg/l, 342 and 264 mg/l, respectively, in H_2O_2=500 mg/l at 30°C. The toxicity removal efficiencies were 38.89%, 72.22% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 30°C (Table 5.182, SET 3).

The EC_{90} values decreased to EC_{45}, to EC_{15} and to EC_5 after 60 min, 120 and 150 min sonication, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.182, SET 3; Figure 5.152b-c-d). The EC_{45}, the EC_{15} and the EC_5 values were measured as 500 mg/l, 550 and 560 mg/l, respectively, in H_2O_2=500 mg/l at 60°C. The toxicity removal efficiencies were 50.00%, 83.33% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 60°C (Table 5.182, SET 3; Figure 5.152b-c-d). 94.44% maximum Microtox acute toxicity removal was obtained in H_2O_2=500 mg/l after 150 min sonication time at 60°C (Table 5.182, SET 3; Figure 5.152d).

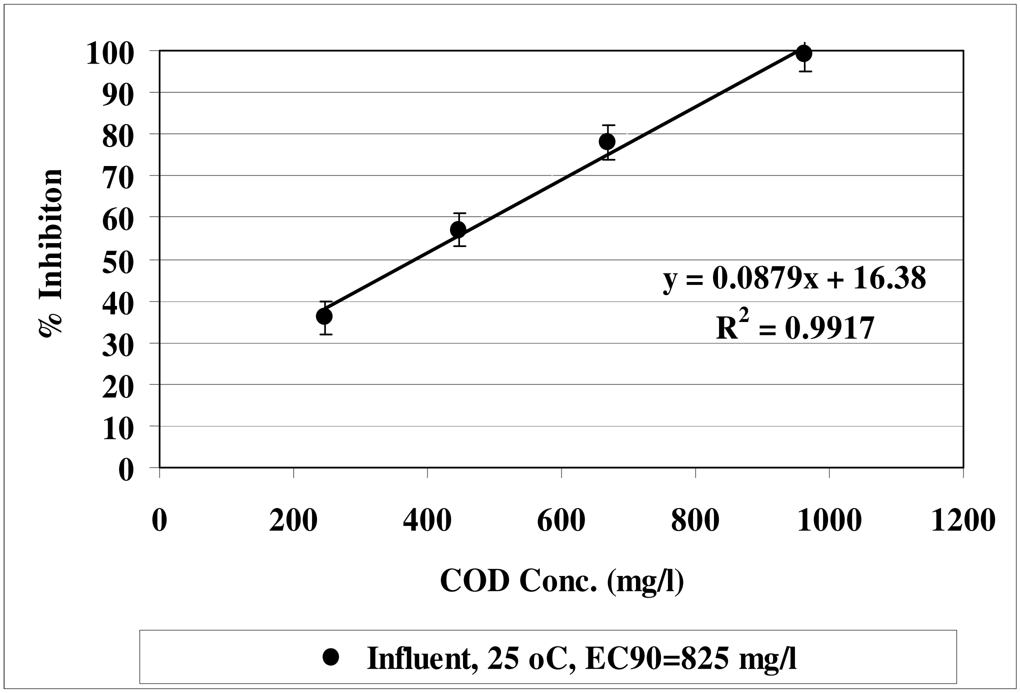
The EC_{90} values decreased to EC_{60}=419 mg/l to EC_{30}=350 and to EC_{15}=271 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 30°C (Table 5.182, SET 3). The EC_{90} values decreased to EC_{60}=470 mg/l to EC_{30}=325 and to EC_{20}=240 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 30°C. The toxicity removal efficiencies were 83.33% and 77.78% in 500 and 2000 mg/l H_2O_2 concentrations, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of H_2O_2=2000 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.182, SET 3).

Table 5.182 Effect of increasing H_2O_2 concentrations on Microtox acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

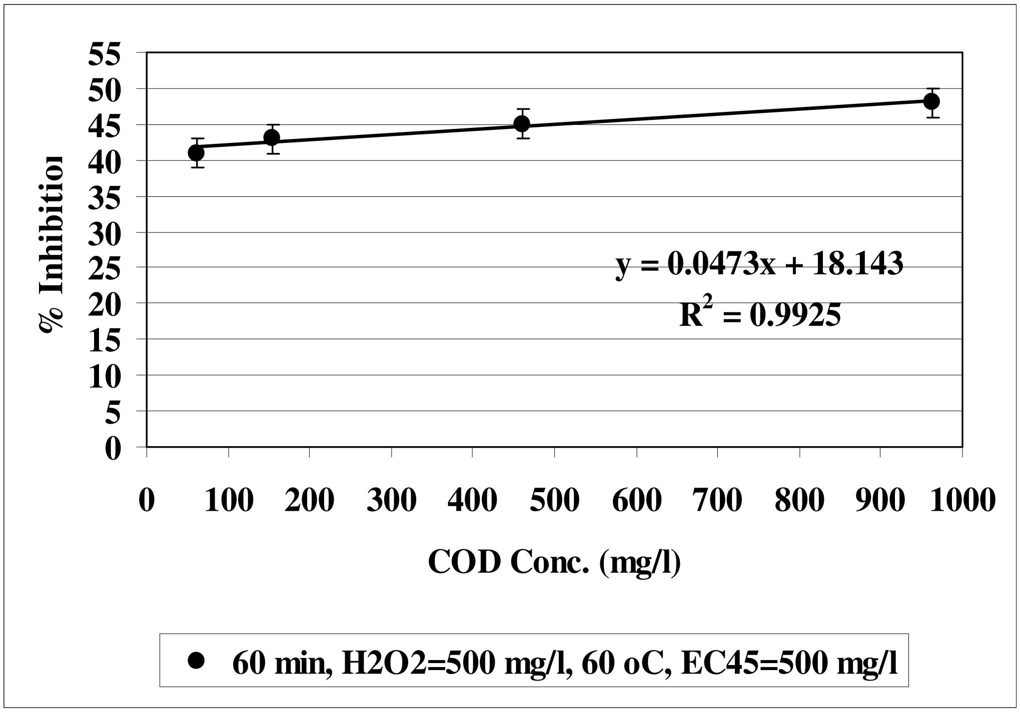
No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{90}$		***EC**		***EC**		***EC**	
1	Raw ww, control	825		$EC_{70}=510$		$EC_{60}=650$		$EC_{50}=640$	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{90}$	***EC**	***EC**	***EC**	**$*EC_{90}$**	***EC**	***EC**	***EC**
2	Raw ww, control	825	$EC_{70}=580$	$EC_{50}=580$	$EC_{40}=550$	825	$EC_{55}=550$	$EC_{40}=590$	$EC_{30}=690$
3	$H_2O_2=100$ mg/l	825	$EC_{60}=419$	$EC_{30}=350$	$EC_{15}=271$	825	$EC_{55}=417$	$EC_{20}=235$	$EC_{10}=264$
	$H_2O_2=500$ mg/l	825	$EC_{55}=416$	$EC_{25}=342$	$EC_{10}=264$	825	$EC_{45}=500$	$EC_{15}=550$	$EC_{5}=560$
	$H_2O_2=2000$ mg/l	825	$EC_{60}=470$	$EC_{30}=325$	$EC_{20}=240$	825	$EC_{55}=403$	$EC_{25}=216$	$EC_{15}=153$

* EC values were calculated based on COD (mg/l).

The EC_{90} values decreased to $EC_{55}=417$ mg/l to $EC_{20}=235$ and to $EC_{10}=264$ mg/l after 60 min, 120 and 150 min sonication times, respectively, in $H_2O_2=100$ mg/l at 60°C (Table 5.152, SET 3). The EC_{90} values decreased to $EC_{55}=403$ mg/l to $EC_{25}=216$ and to $EC_{15}=153$ mg/l after 60 min, 120 and 150 min sonication times, respectively, in $H_2O_2=2000$ mg/l at 60°C. The toxicity removal efficiencies were 88.89% and 83.33% in 500 and 2000 mg/l H_2O_2 concentrations, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of $H_2O_2=2000$ mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60°C (Table 5.152, SET 3).

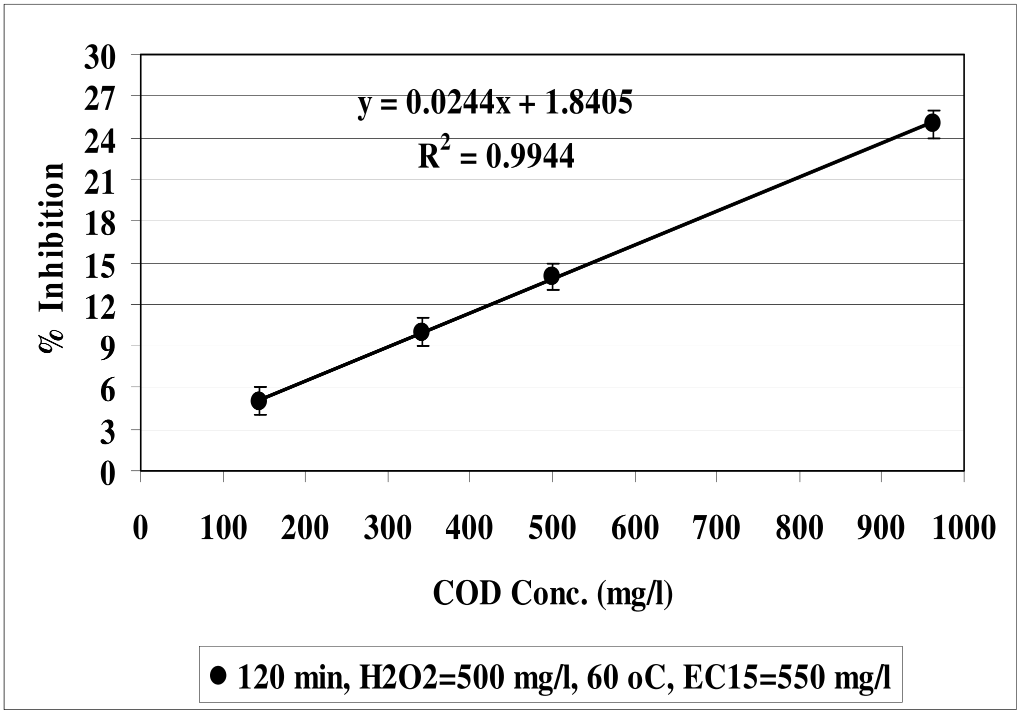


(a)

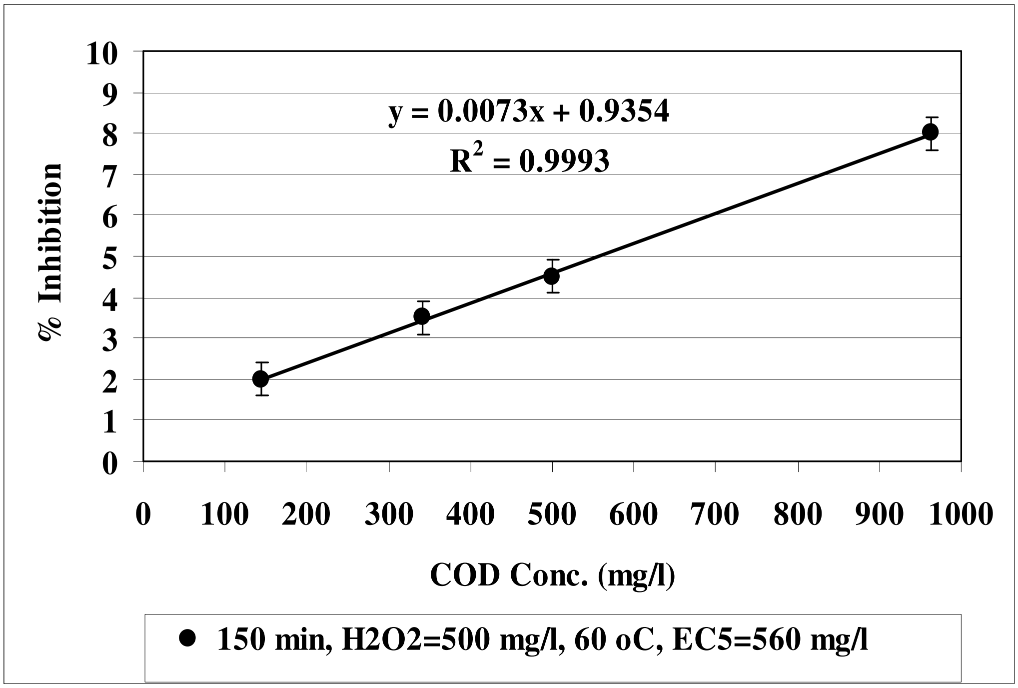


(b)

Figure 5.152 Effect of 500 mg/l H_2O_2 concentration on Microtox acute toxicity in TI ww for (a) influent at 25°C and (b) H_2O_2=500 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.152 Effect of 500 mg/l H_2O_2 concentration on Microtox acute toxicity in TI ww for (c) H_2O_2=500 mg/l after 120 min sonication time at 60°C and (d) H_2O_2=500 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.18.3.2 Effect of H_2O_2 Concentrations on the Removal of Daphnia magna Acute Toxicity in TI ww at Increasing Sonication Time and Temperature

As seen in Table 5.183 (SET 1) and in Figure 5.153a, the initial EC_{50} values were obtained as 850 mg/l at 25°C. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{30}=450 mg/l to EC_{15}=100 mg/l and to EC_{10}=280 mg/l in H_2O_2=500 mg/l at 30°C (Table 5.183, SET 3). The toxicity removal efficiencies were 40.00%, 70.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 30°C (Table 5.183, SET 3).

Table 5.183 Effect of increasing H_2O_2 concentrations on *Daphnia magna* acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

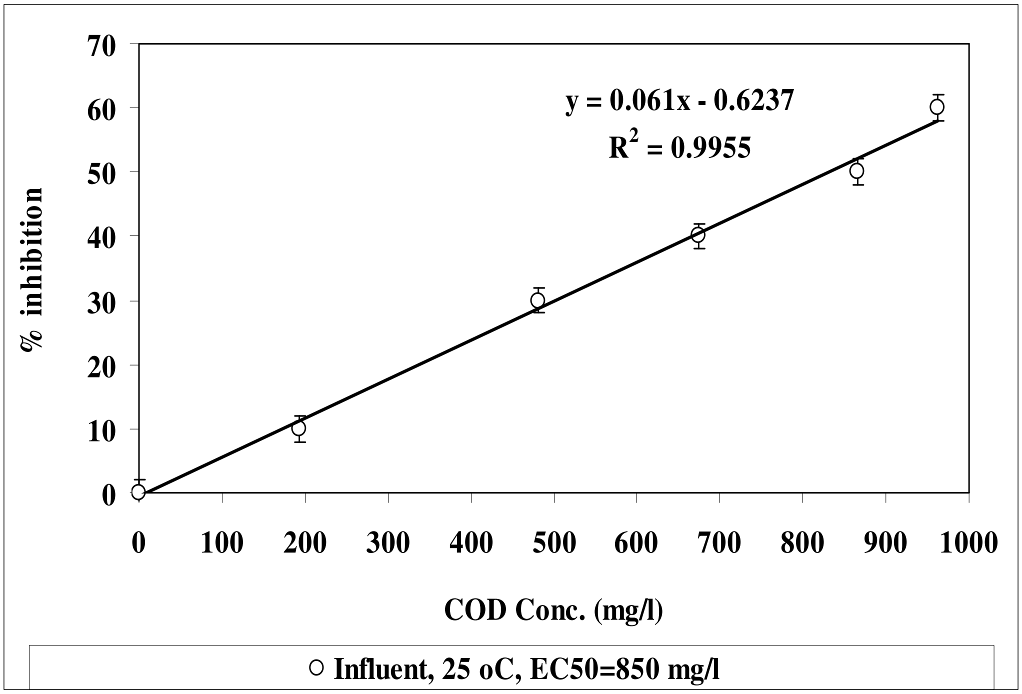
No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{50}$		***EC**		***EC**		***EC**	
1	Raw ww, control	850		EC_{45}=625		EC_{40}=370		EC_{30}=155	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{50}$	***EC**	***EC**	***EC**	**$*EC_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	850	EC_{40}=470	EC_{35}=230	EC_{25}=115	850	EC_{35}=375	EC_{30}=212	EC_{20}=75
3	H_2O_2=100 mg/l	850	EC_{35}=130	EC_{20}=450	EC_{15}=340	850	EC_{30}=105	EC_{15}=440	EC_{10}=230
	H_2O_2=500 mg/l	850	EC_{30}=450	EC_{15}=100	EC_{10}=280	850	EC_{25}=55	EC_{10}=400	EC_{5}=140
	H_2O_2=2000 mg/l	850	EC_{40}=240	EC_{25}=100	EC_{20}=27	850	EC_{35}=200	EC_{20}=70	EC_{15}=12

* EC values were calculated based on COD (mg/l).

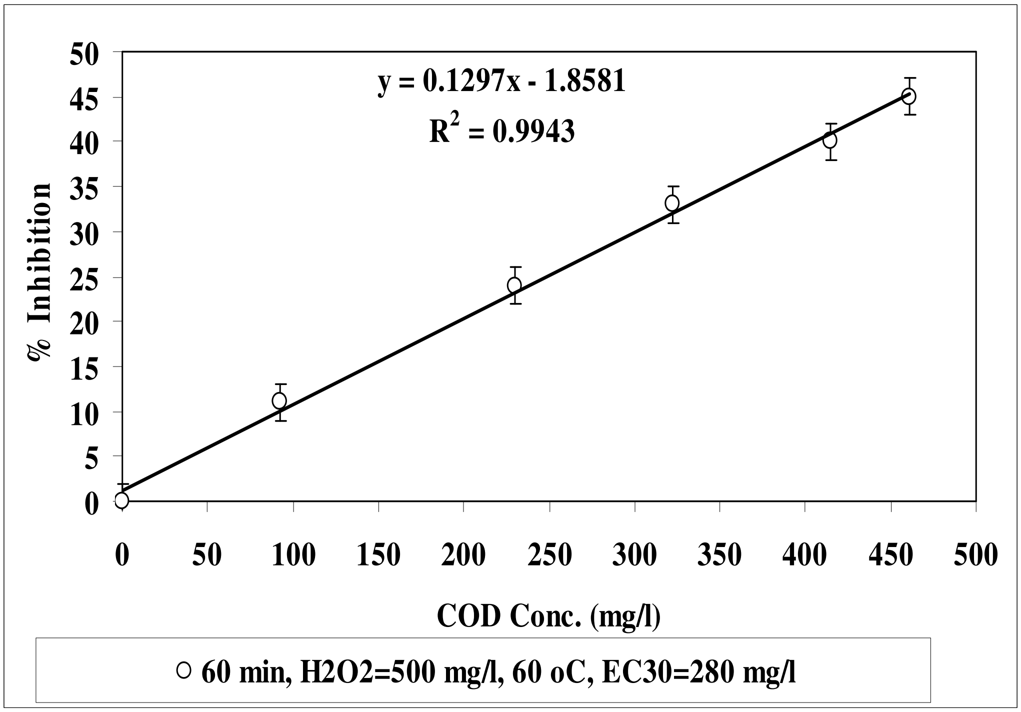
The EC_{50} values decreased to EC_{25} to EC_{10} and to EC_5 after 60 min ,120 and 150 min sonication, respectively, in H_2O_2=500 mg/l at 60^{o}C (Table 5.183, SET 3; Figure 5.153b-c-d). The EC_{25}, the EC_{10} and the EC_5 values were measured as 55 mg/l, 400 and 140 mg/l, respectively, in H_2O_2=500 mg/l at 60^{o}C. The toxicity removal efficiencies were 50.00%, 80.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=500 mg/l at 60^{o}C (Table 5.183, SET 3; Figure 5.153b-c-d). 90.00% maximum acute toxicity removal was observed in *Daphnia magna* for H_2O_2=500 mg/l after 150 min sonication time at 60^{o}C (Table 5.183, SET 3; Figure 5.153d).

The EC_{50} values decreased to EC_{35}=130 mg/l to EC_{20}=450 and to EC_{15}=340 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 30^{o}C (Table 5.183, SET 3). The EC_{90} values decreased to EC_{40}=240 mg/l to EC_{25}=100 and to EC_{20}=27 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 30^{o}C. The toxicity removal efficiencies were 70.00% and 60.00% in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at 30^{o}C. It was obtained an inhibition effect of H_2O_2=2000 mg/l to *Daphnia magna* after 150 min sonication time at 30^{o}C (Table 5.183, SET 3).

The EC_{50} values decreased to EC_{30}=105 mg/l to EC_{15}=440 and to EC_{10}=230 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=100 mg/l at 60^{o}C (Table 5.183, SET 3). The EC_{90} values decreased to EC_{35}=200 mg/l to EC_{20}=70 and to EC_{15}=12 mg/l after 60 min, 120 and 150 min sonication times, respectively, in H_2O_2=2000 mg/l at 60^{o}C. The toxicity removal efficiencies were 80.00% and 70.00% in 500 and 2000 mg/l H_2O_2, respectively, after 150 min sonication time at 60^{o}C. It was observed an inhibition effect of H_2O_2=2000 mg/l to *Daphnia magna* after 150 min sonication time at 60^{o}C (Table 5.183, SET 3).

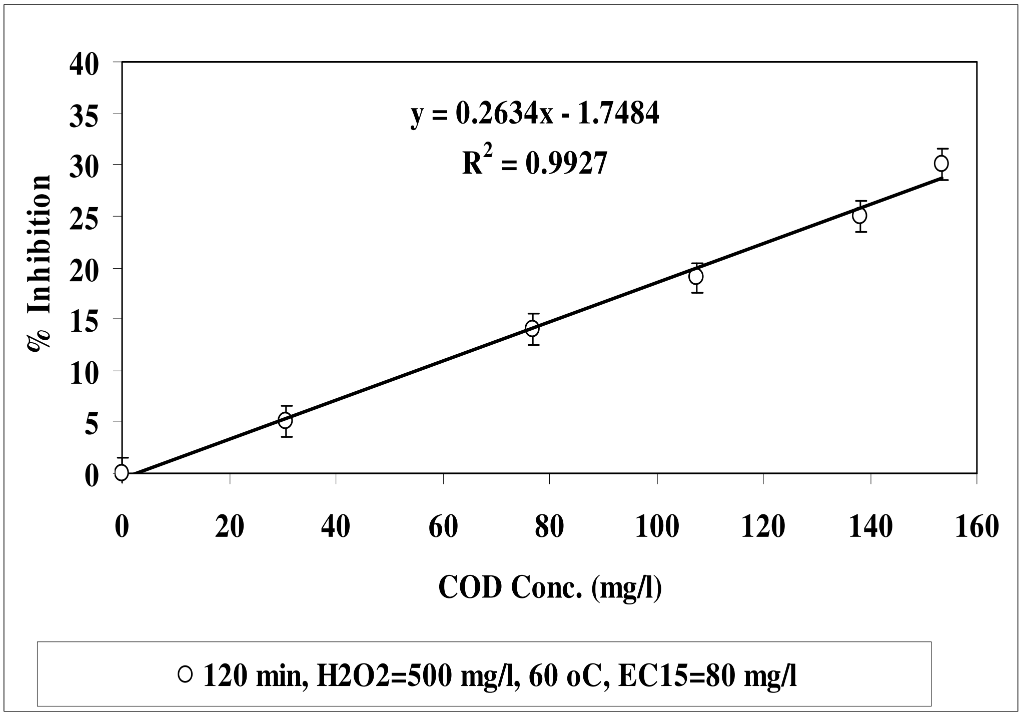


(a)

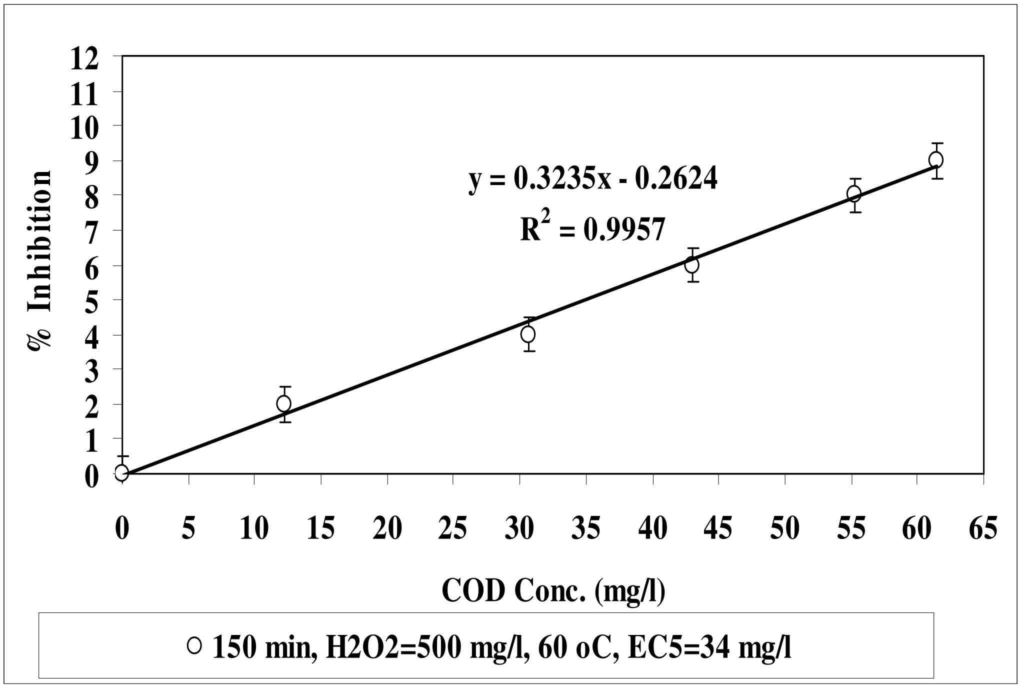


(b)

Figure 5.153 Effect of 500 mg/l H_2O_2 concentration on *Daphnia magna* acute toxicity in TI ww for (a) influent at 25°C and (b) H_2O_2=500 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.153 Effect of 500 mg/l H_2O_2 concentration on *Daphnia magna* acute toxicity in TI ww for (c) H_2O_2=500 mg/l after 120 min sonication time at 60°C and (d) H_2O_2=500 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

H_2O_2 concentrations above 500 mg/l decreased the acute toxicity removals by hindering the sonication process (Table 5.183, SET 3). In other words, the maximum acute toxicity removal was obtained in the samples containing 500 mg/l H_2O_2 concentration at a temperature of 60°C after 150 min of sonication time (Table 5.183, SET 3; Figure 5.153d).

5.18.3.3 Direct Effects of H_2O_2 Concentrations on the Acute Toxicity of Microtox and Daphnia magna in TI ww

The acute toxicity tests were performed in the samples containing some additives such as H_2O_2, TiO_2, NaCl, Fe^{+2} and Fe^{+3}. In order to detect the direct responses of Microtox and *Daphnia magna* to the additives mentioned above the toxicity test were performed without TI ww. The initial EC values and the EC_{50} values were measured in the samples containing different additive concentrations after 150 min sonication time. Table 5.184 showed the responses of Microtox and *Daphnia magna* to increasing H_2O_2 concentrations.

Table 5.184 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing H_2O_2 concentrations without TI ww after 150 min sonication time.

H_2O_2 Conc. (mg/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
100	EC_{10}=25	-	-	EC_{10}=30	-	-
500	EC_{15}=120	4.00	EC_1=3.00	EC_{20}=150	6.00	EC_4=8.00
2000	EC_{20}=210	7.00	EC_4=6.00	EC_{30}=250	9.00	EC_6=14.00

The acute toxicity originating only from 100, 500 and 2000 mg/l H_2O_2 were found to be low (Table 5.184). 100 mg/l H_2O_2 did not exhibited toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity attributed to the 500 and 2000 mg/l H_2O_2 were found to be low in the samples without TI ww for the test organisms mentioned above. The acute toxicity originated from the H_2O_2 decreased significantly to EC_1 and EC_4 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the H_2O_2 is not significant and the real acute toxicity throughout sonication was attributed to the TI ww, to their metabolites and to the sonodegradation by-products (Table 5.184).

5.18.4 Effect of TiO_2 Concentrations on the Acute Toxicity Removal Efficiencies in TI ww at Increasing Sonication Time and Temperature

5.18.4.1 Effect of TiO_2 Concentrations on the Microtox Acute Toxicity Removal Efficiencies in TI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was found as 825 mg/l at 25°C (Table 5.185, SET 1; Figure 5.154a). After 60 min, 120 and 150 min of sonication the EC_{90} values decreased to EC_{55}=414 mg/l to EC_{20}=236 mg/l and to EC_{10}=165 mg/l in TiO_2=10.00 mg/l at 30°C (Table 5.185, SET 3). The toxicity removal efficiencies were 38.89%, 77.78% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 30°C (Table 5.185, SET 3).

The EC_{90} values decreased to EC_{50}, to EC_{15} and to EC_5 after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.185, SET 3; Figure 5.154b-c-d). The EC_{50}, the EC_{15} and the EC_5 values were measured as 550 mg/l, 540 and 500 mg/l, respectively, in TiO_2=10.00 mg/l at 60°C. The toxicity removal efficiencies were 44.44%, 83.33% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.185, SET 3; Figure 5.154b-c-d). 94.44% maximum Microtox acute toxicity yield was found in TiO_2=10.00 mg/l after 150 min sonication time at 60°C (Table 5.185, SET 3; Figure 5.154d).

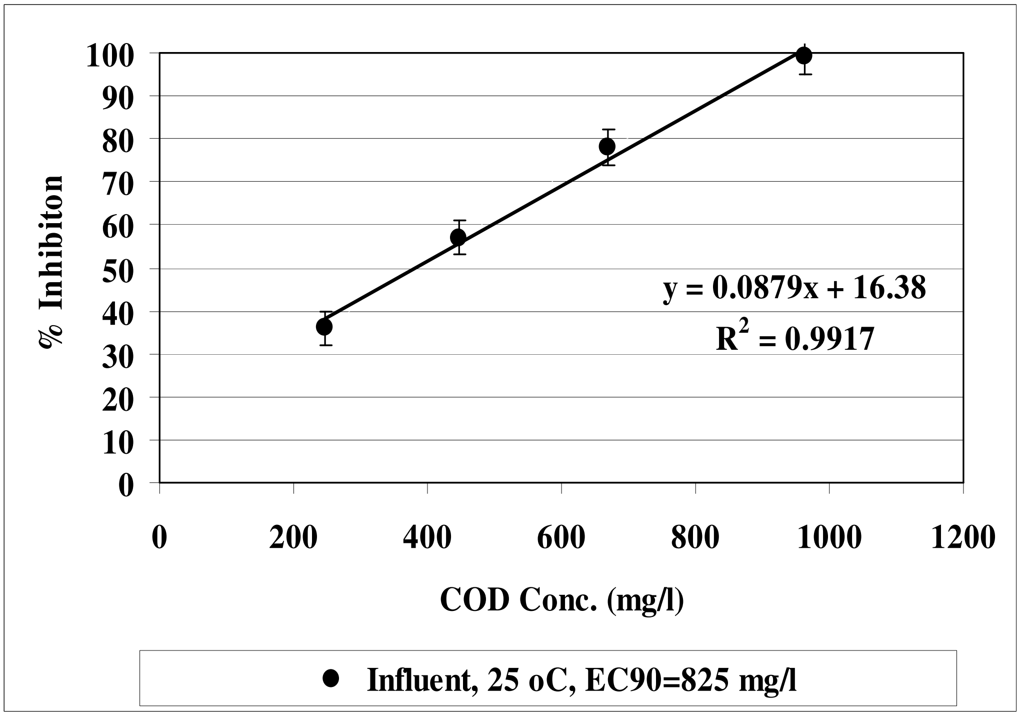
Table 5.185 Effect of increasing TiO_2 concentrations on Microtox acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{90}$		**$*EC$**		**$*EC$**		**$*EC$**	
1	Raw ww, control	825		EC_{70}=510		EC_{60}=650		EC_{50}=640	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{90}$	**$*EC$**	**$*EC$**	**$*EC$**	**$*EC_{90}$**	**$*EC$**	**$*EC$**	**$*EC$**
2	Raw ww, control	825	EC_{70} =580	EC_{50}= 580	EC_{40}= 550	825	EC_{55}= 550	EC_{40}= 590	EC_{30} =690
3	TiO_2=0.10 mg/l	825	EC_{60} =422	EC_{25}= 241	EC_{15}= 168	825	EC_{55}= 419	EC_{20}= 266	EC_{10} =150
	TiO_2=0.50 mg/l	825	EC_{60} =421	EC_{25}= 239	EC_{15}= 167	825	EC_{55}= 414	EC_{20}= 232	EC_{10} =161
	TiO_2=10.00 mg/l	825	EC_{5} =414	EC_{20}= 236	EC_{10}= 165	825	EC_{50}= 550	EC_{15}= 540	EC_{5}= 500
	TiO_2=20.00 mg/l	825	EC_{65} =408	EC_{30}= 230	EC_{20}= 162	825	EC_{60}= 403	EC_{25}= 218	EC_{15} =148

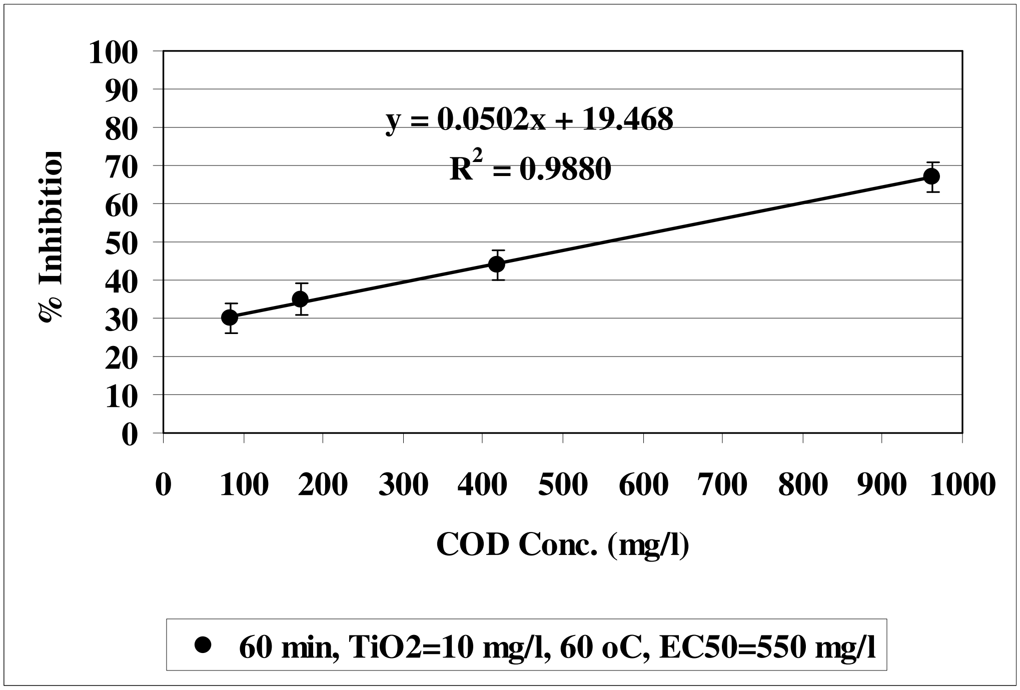
* EC values were calculated based on COD_{dis} (mg/l).

The EC_{90} values decreased to EC_{60}=422 mg/l to EC_{25}=241 and to EC_{15}=168 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 30°C (Table 5.185, SET 3). The EC_{90} values decreased to EC_{60}=421 mg/l to EC_{25}=239 and to EC_{15}=167 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 30°C. The EC_{90} values decreased to EC_{65}=408 mg/l to EC_{30}=230 and to EC_{20}=162 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 30°C. The Microtox acute toxicity removals were 83.33%, 83.33% and 77.78% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 30^{o}C. It was obtained an inhibition effect of TiO_2=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30^{o}C (Table 5.185, SET 3).

The EC_{90} values decreased to EC_{55}=419 mg/l to EC_{20}=266 and to EC_{10}=150 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 60^{o}C (Table 5.185, SET 3). The EC_{90} values decreased to EC_{55}=414 mg/l to EC_{20}=232 and to EC_{10}=161 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 60^{o}C. The EC_{90} values decreased to EC_{60}=403 mg/l to EC_{25}=218 and to EC_{15}=148 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 60^{o}C. The Microtox acute toxicity removals were 88.89%, 88.89% and 83.33% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 60^{o}C. It was observed an inhibition effect of TiO_2=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60^{o}C (Table 5.185, SET 3).

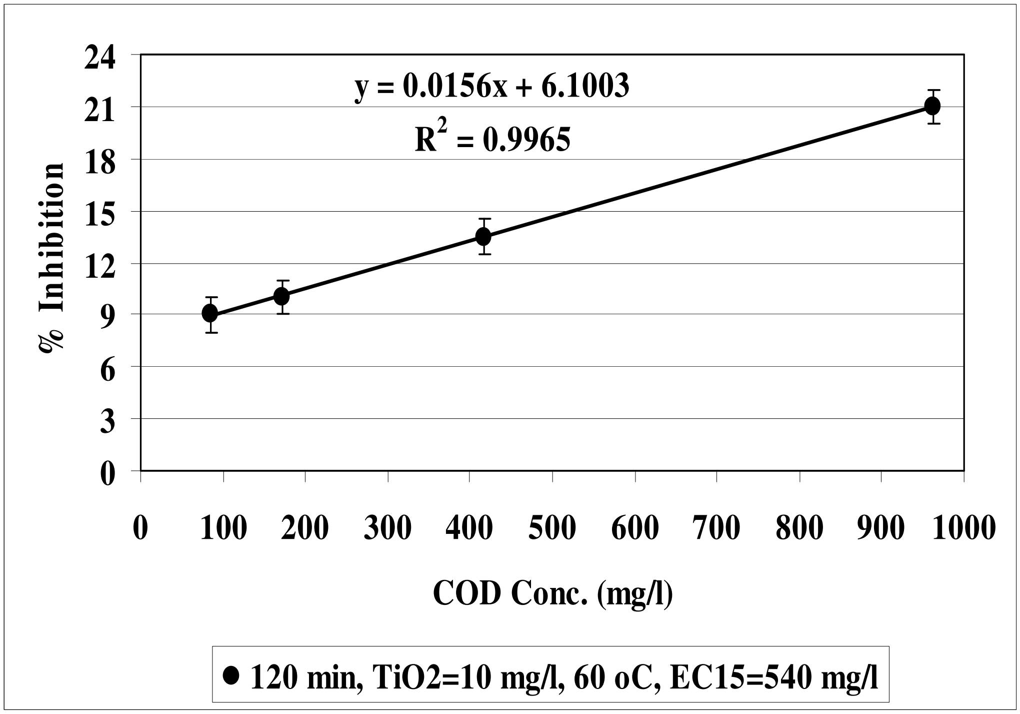


(a)

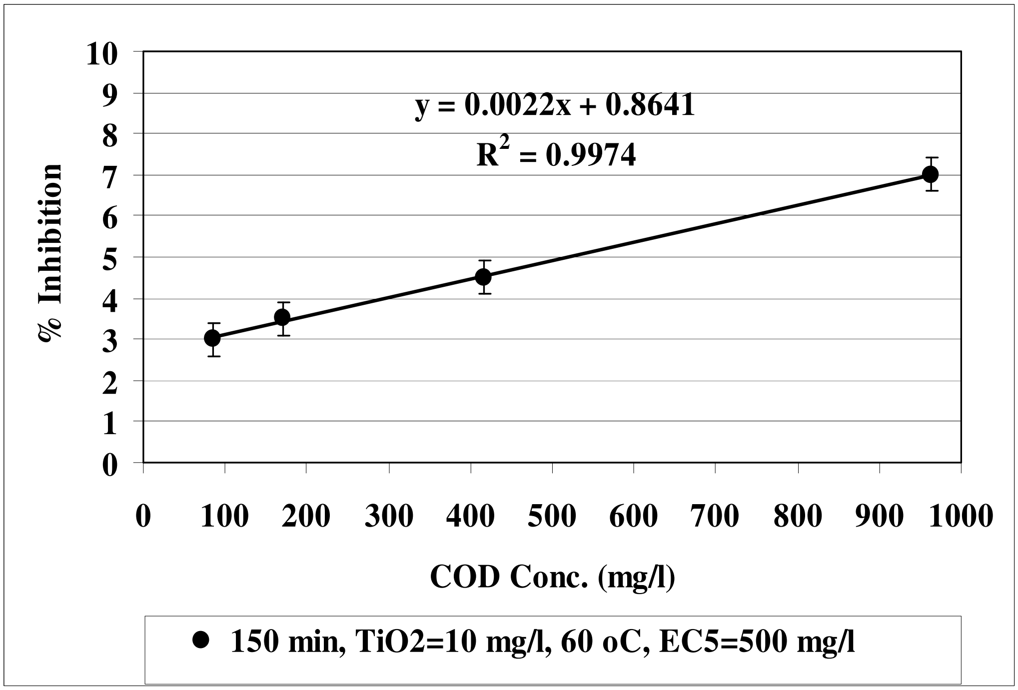


(b)

Figure 5.154 Effect of 10.00 mg/l TiO_2 concentration on Microtox acute toxicity in TI ww for (a) influent at 25°C and (b) TiO_2=10.00 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.154 Effect of 10.00 mg/l TiO_2 concentration on Microtox acute toxicity in TI ww for (c) TiO_2=10.00 mg/l after 120 min sonication time at 60°C and (d) TiO_2=10.00 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

5.18.4.2 Effect of TiO_2 Concentrations on the Daphnia magna Acute Toxicity Removal Efficiencies in TI ww at Increasing Sonication Time and Temperature

The initial EC_{50} values were observed as 850 mg/l at 25°C (Table 5.186, SET 1; Figure 5.155a). After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{30}=350 mg/l to EC_{15}=240 mg/l and to EC_{10}=90 mg/l in TiO_2=10.00 mg/l at 30°C (Table 5.186, SET 3). The toxicity removal efficiencies were 40.00%, 70.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 30°C (Table 5.186, SET 3).

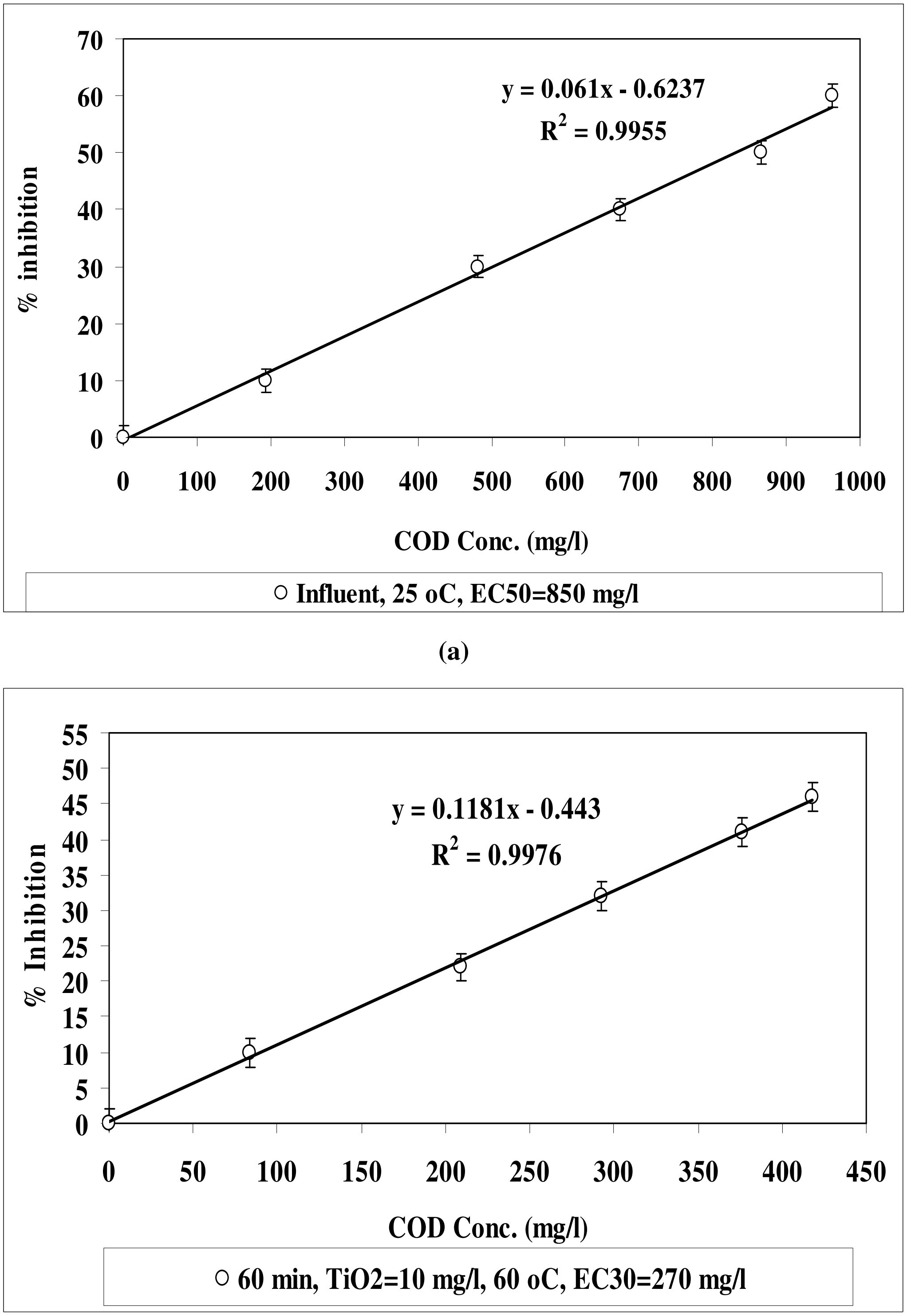
The EC_{50} values decreased to EC_{25} to EC_{10} and to EC_5 after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.186, SET 3; Figure 5.155b-c-d). The EC_{25}, the EC_{10} and the EC_5 values were measured as 150 mg/l, 60 and 375 mg/l, respectively, in TiO_2=10.00 mg/l at 60°C. The toxicity removal efficiencies were 50.00%, 80.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=10.00 mg/l at 60°C (Table 5.186, SET 3; Figure 5.155b-c-d). 90.00% maximum *Daphnia magna* acute toxicity removal was obtained in TiO_2=10.00 mg/l after 150 min sonication time at 60°C (Table 5.186, SET 3; Figure 5.155d).

The EC_{50} values decreased to EC_{35}=450 mg/l to EC_{20}=145 and to EC_{15}=260 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 30°C (Table 5.186, SET 3). The EC_{50} values decreased to EC_{35}=450 mg/l to EC_{20}=175 and to EC_{15}=100 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 30°C. The EC_{50} values decreased to EC_{40}=300 mg/l to EC_{25}=170 and to EC_{20}=52 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 30°C. The *Daphnia magna* acute toxicity removals were 70.00%, 70.00% and 60.00% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of TiO_2=20.00 mg/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.186, SET 3).

Table 5.186 Effect of increasing TiO_2 concentrations on *Daphnia magna* acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC_{50}**		***EC**		***EC**		***EC**	
1	Raw ww, control	850		EC_{45}=625		EC_{40}=370		EC_{30}=155	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC_{50}**	***EC**	***EC**	***EC**	***EC_{50}**	***EC**	***EC**	***EC**
2	Raw ww, control	850	EC_{40} =470	EC_{35}= 230	EC_{25}= 115	850	EC_{35} =375	EC_{30} =212	EC_{20} =75
3	TiO_2=0.10 mg/l	850	EC_{35} =450	EC_{20}= 145	EC_{15}= 260	850	EC_{30} =130	EC_{15} =425	EC_{10} =340
	TiO_2=0.50 mg/l	850	EC_{35} =450	EC_{20}= 175	EC_{15}= 100	850	EC_{30} =425	EC_{15} =140	EC_5= 90
	TiO_2=10.00 mg/l	850	EC_{30} =350	EC_{15}= 240	EC_{10}= 90	850	EC_{25} =150	EC_{10} =60	EC_5= 375
	TiO_2=20.00 mg/l	850	EC_{40} =300	EC_{25}= 170	EC_{20}= 52	850	EC_{35} =250	EC_{20} =110	EC_{15} =11

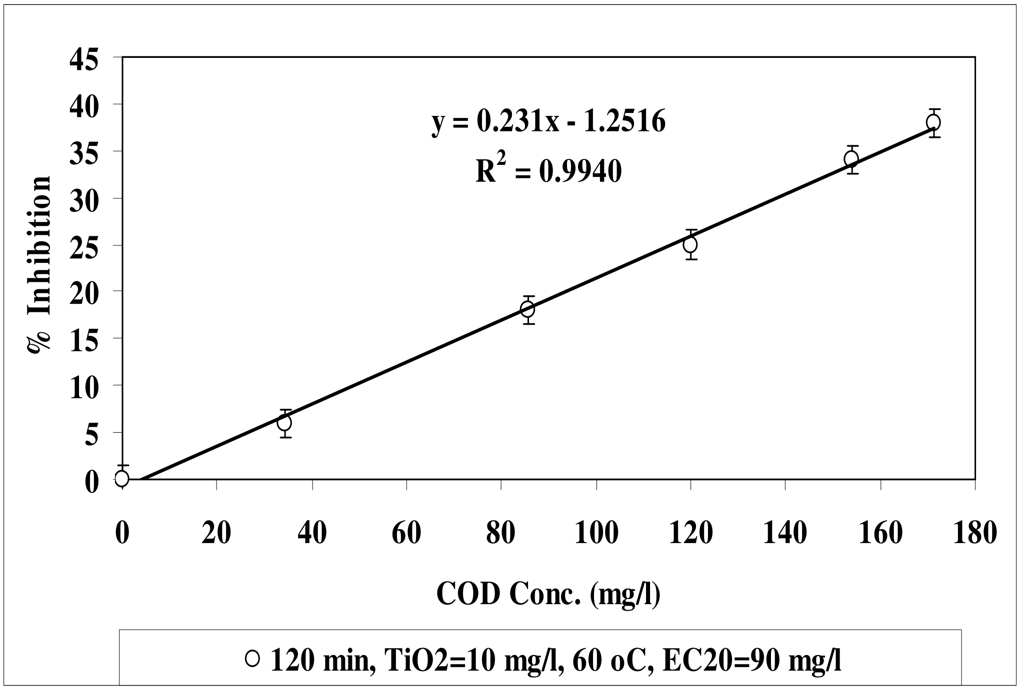
* EC values were calculated based on COD_{dis} (mg/l).



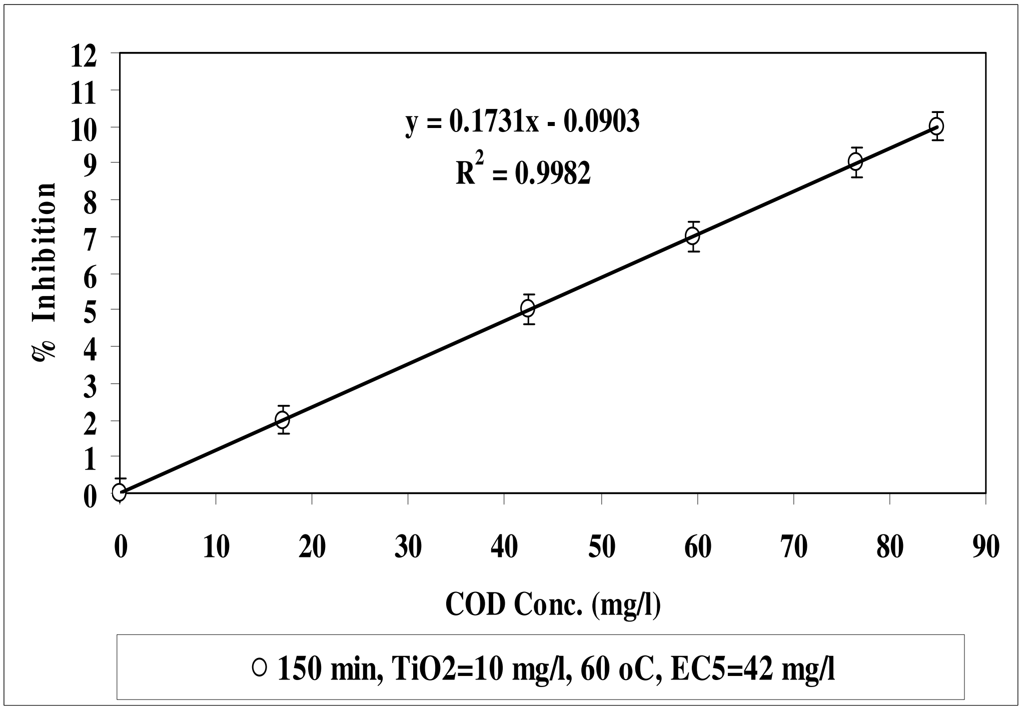
(a)

(b)

Figure 5.155 Effect of 10.00 mg/l TiO_2 concentration on *Daphnia magna* acute toxicity in TI ww for (a) influent at 25°C and (b) TiO_2=10.00 mg/l after 60 min sonication time at 60°C (640 W power, 35 kHz frequency).



(c)



(d)

Figure 5.155 Effect of 10.00 mg/l TiO_2 concentration on *Daphnia magna* acute toxicity in TI ww for (c) TiO_2=10.00 mg/l after 120 min sonication time at 60°C and (d) TiO_2=10.00 mg/l after 150 min sonication time at 60°C (640 W power, 35 kHz frequency).

The EC_{50} values decreased to EC_{30}=130 mg/l to EC_{15}=425 and to EC_{10}=340 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.10 mg/l at 60°C (Table 5.186, SET 3). The EC_{50} values decreased to EC_{30}=425 mg/l to EC_{15}=140 and to EC_5=90 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=0.50 mg/l at 60°C. The EC_{50} values decreased to EC_{35}=250 mg/l to EC_{20}=110 and to EC_{15}=11 mg/l after 60 min, 120 and 150 min sonication times, respectively, in TiO_2=20.00 mg/l at 60°C. The *Daphnia magna* acute toxicity removals were 80.00%, 90.00% and 70.00% in 0.10, 0.50 and 20.00 mg/l TiO_2, respectively, after 150 min sonication time at 60°C. It was observed an inhibition effect of TiO_2=20.00 mg/l to *Daphnia magna* after 150 min sonication time at 60°C (Table 5.186, SET 3).

Increasing the TiO_2 concentrations from 0.10 to 20.00 mg/l did not have a positive effect on the decrease of EC_{50} values as shown in Table 5.186 at SET 3. TiO_2 concentrations > 10.00 mg/l decreased the acute toxicity removals by hindering the sonication process. Similarly, a significant contribution of increasing TiO_2 concentration to acute toxicity removal at 60°C after 150 min of sonication time was not observed. Low toxicity removals found at high TiO_2 concentrations could be attributed to their detrimental effect on the *Daphnia magna* (Table 5.186, SET 3).

5.18.4.3 Direct Effects of TiO_2 Concentrations on the Acute Toxicity of Microtox and Daphnia magna in TI ww

The acute toxicity test was performed in the samples containing 0.10, 0.50, 10.00 and 20.00 mg/l TiO_2 concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing TiO_2 concentrations the toxicity test were performed without TI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing TiO_2 concentrations after 150 min sonication time. Table 5.187 showed the responses of Microtox and *Daphnia magna* to increasing TiO_2 concentrations.

Table 5.187 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing TiO_2 concentrations without TI ww after 150 min sonication time.

TiO_2 Conc. (mg/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
0.10	EC_{10}=25	-	-	EC_{10}=40	-	-
0.50	EC_{15}=80	4.00	EC_1=4.00	EC_{20}=100	6.00	EC_3=6.00
10.00	EC_{20}=150	6.00	EC_4=7.00	EC_{30}=200	7.00	EC_6=12.00
20.00	EC_{25}=220	8.00	EC_6=10.00	EC_{40}=300	10.00	EC_8=16.00

The acute toxicity originating only from 0.10, 0.50, 10.00 and 20.00 mg/l TiO_2 were found to be low (Table 5.187). 0.10 mg/l TiO_2 did not exhibited toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication. The toxicity atributed to the 0.50, 10.00 and 20.00 mg/l TiO_2 were found to be low in the samples without TI ww for the test organisms mentioned above. The acute toxicity originated from the TiO_2 decreased significantly to EC_1, EC_4 and EC_6 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the TiO_2 is not significant and the real acute toxicity throughout sonication was attributed to the TI ww, to their metabolites and to the sonodegradation by-products (Table 5.187).

5.18.5 Effect of NaCl Concentrations on the Acute Toxicity Removal Efficiencies in TI ww at Increasing Sonication Time and Temperature

5.18.5.1 Effect of NaCl Concentrations on the Microtox Acute Toxicity Removal Efficiencies in TI ww Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was found as 825 mg/l at 25°C (Table 5.188, SET 1). After 60 min, 120 and 150 min of sonication the EC_{99} values decreased to EC_{55}=314 mg/l to EC_{25}=133 mg/l and to EC_{10}=62 mg/l in NaCl=2.50 g/l at 30°C (Table 5.188, SET 3). The toxicity removal efficiencies were 38.89%, 72.22% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 30°C (Table 5.188, SET 3).

The EC_{90} values decreased to EC_{50}, to EC_{20} and to EC_5 after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60°C (Table 5.188, SET 3). The EC_{50}, the EC_{20} and the EC_5 values were measured as 307 mg/l, 143 and 22 mg/l, respectively, in NaCl=2.50 g/l at 60°C. The toxicity removal efficiencies were 44.44%, 77.78% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60°C. 94.44% maximum Microtox acute toxicity yield was observed in NaCl=2.50 g/l after 150 min sonication time at 60°C (Table 5.188, SET 3).

The EC_{50} values decreased to EC_{60}=320 mg/l to EC_{30}=140 and to EC_{15}=67 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 30°C (Table 5.188, SET 3). The EC_{50} values decreased to EC_{65}=310 mg/l to EC_{35}=127 and to EC_{20}=59 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 30°C. The Microtox acute toxicity yields were 83.33% and 77.78% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of NaCl=15.00 g/l to *Photobacterium phosphoreum* in after 150 min sonication time at 30°C (Table 5.188, SET 3).

Table 5.188 Effect of increasing NaCl concentrations on Microtox acute toxicity in TI ww at 30^{o}C and at 60^{o}C (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25^{o}C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC_{90}**		***EC**		***EC**		***EC**	
1	Raw ww, control	825		EC_{70}=510		EC_{60}=650		EC_{50}=640	
		30^{o}C				**60^{o}C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC_{90}**	***EC**	***EC**	***EC**	***EC_{90}**	***EC**	***EC**	***EC**
2	Raw ww, control	825	EC_{70}= 580	EC_{50}= 580	EC_{40}= 550	825	EC_{55} =550	EC_{40}= 590	EC_{30}= 690
3	NaCl=1.00 g/l	825	EC_{60}= 320	EC_{30}= 140	EC_{15}= 67	825	EC_{55} =315	EC_{25}= 137	EC_{10}= 54
	NaCl=2.50 g/l	825	EC_{55}= 314	EC_{25}= 133	EC_{10}= 62	825	EC_{50} =307	EC_{20}= 143	EC_{5}= 22
	NaCl=15.00 g/l	825	EC_{65}= 310	EC_{35}= 127	EC_{20}= 59	825	EC_{60} =304	EC_{30}= 121	EC_{15}= 42

* EC values were calculated based on COD_{dis} (mg/l).

The EC_{50} values decreased to EC_{55}=315 mg/l to EC_{25}=137 and to EC_{10}=54 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 60^{o}C (Table 5.188, SET 3). The EC_{50} values decreased to EC_{60}=304 mg/l to EC_{30}=121 and to EC_{15}=42 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 60^{o}C. The Microtox acute toxicity yields were 88.89% and 83.33% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 60^{o}C. It was obtained an inhibition effect of NaCl=15.00 g/l to *Photobacterium phosphoreum* after 150 min sonication time at 60^{o}C (Table 5.188, SET 3).

5.18.5.2 Effect of NaCl Concentrations on the Daphnia magna Acute Toxicity Removal Efficiencies in the Sonication Time and Temperature

As seen in Table 5.189 (SET 1), the initial EC_{50} values were observed as 850 mg/l at 25°C. After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC30=350 mg/l to EC15=190 mg/l and to EC10=85 mg/l in NaCl=2.50 g/l at 30°C (Table 5.189, SET 3). The toxicity removal efficiencies were 40.00%, 70.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 30°C (Table 5.189, SET 3).

Table 5.189 Effect of increasing NaCl concentrations on *Daphnia magna* acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	Parameters	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{50}$		***EC**		***EC**		***EC**	
1	Raw ww, control	850		EC_{45}=625		EC_{40}=370		EC_{30}=155	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{50}$	***EC**	***EC**	***EC**	**$*EC_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	850	EC_{40} =470	EC_{35}= 230	EC_{25}= 115	850	EC_{35}= 375	EC_{30} =212	EC_{20}= 75
3	NaCl=1.00 g/l	850	EC_{35} =140	EC_{20}= 450	EC_{15}= 280	850	EC_{30}= 375	EC_{15} =95	EC_{10}= 250
	NaCl=2.50 g/l	850	EC_{30} =350	EC_{15}= 190	EC_{10}= 85	850	EC_{25}= 275	EC_{10} =160	EC_{5}= 45
	NaCl=15.00 g/l	850	EC_{40} =400	EC_{25}= 170	EC_{20}= 63	850	EC_{35}= 275	EC_{20} =145	EC_{15}= 22

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{25}=275 mg/l to EC_{10}=160 mg/l and to EC_{5}=45 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60°C (Table 5.189, SET 3). The toxicity removal efficiencies were 50.00%, 80.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in NaCl=2.50 g/l at 60°C (Table 5.189, SET 3).

The EC_{50} values decreased to EC_{35}=140 mg/l to EC_{20}=450 and to EC_{15}=280 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 30°C (Table 5.189, SET 3). The EC_{50} values decreased to EC_{40}=400 mg/l to EC_{25}=170 and to EC_{20}=63 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 30°C. The *Daphnia magna* acute toxicity yields were 70.00% and 60.00% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of NaCl=15.00 g/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.189, SET 3).

The EC_{50} values decreased to EC_{30}=375 mg/l to EC_{15}=95 and to EC_{10}=250 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=1.00 g/l at 60°C (Table 5.189, SET 3). The EC_{50} values decreased to EC_{35}=275 mg/l to EC_{20}=145 and to EC_{15}=22 mg/l after 60 min, 120 and 150 min sonication times, respectively, in NaCl=15.00 g/l at 60°C. The *Daphnia magna* acute toxicity yields were 80.00% and 70.00% in 1.00 and 15.00 g/l NaCl, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of NaCl=15.00 g/l to *Daphnia magna* in after 150 min sonication time at 60°C (Table 5.189, SET 3).

The maximum acute toxicity removal was 90.00% at the NaCl concentration of 2.50 g/l at 30°C after 150 min sonication time (Table 5.189, SET 3). In this acute toxicity reduction the EC_{50} value of raw PCI ww decreased to EC_{5}=45 mg/l. Low acute toxicity removals found at high NaCl concentrations could be attributed to their detrimental effect on the *Daphnia magna* cells. High NaCl (> 15.00 g/l) caused lysis in *Daphnia magna* cells. The high salt concentrations caused turgor in *Daphnia magna* cells by increasing the osmotic pressure in the test medium (Table 5.189).

The sonication process decreased the toxicity of wastewater sample to *Daphnia magna* and a significant correlation was observed between *Daphnia magna* and NaCl concentrations after 150 min sonication time according to multiple regression analysis (R^2=0.91, F=12.11, p=0.001).

5.18.5.3 Direct Effects of NaCl Concentrations on the Acute Toxicity of Microtox and Daphnia magna in TI ww

The acute toxicity test was performed in the samples containing 1.00, 2.50 and 15.00 g/l NaCl concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing NaCl the toxicity test were performed without TI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing NaCl concentrations after 150 min sonication time. Table 5.190 showed the responses of Microtox and *Daphnia magna* to increasing NaCl concentrations.

Table 5.190 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing NaCl concentrations without TI ww after 150 min sonication time.

NaCl Conc. (g/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
1.00	EC_{10}=20	-	-	EC_{10}=30	-	-
2.50	EC_{15}=120	3.00	EC_1=7.00	EC_{20}=150	6.00	EC_3=9.00
15.00	EC_{20}=240	7.00	EC_5=12.00	EC_{30}=260	10.00	EC_7=15.00

The acute toxicity originating only from 1.00, 2.50 and 15.00 g/l NaCl were found to be low (Table 5.190). 1.00 g/l NaCl did not exhibited toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 2.50 and 15.00 g/l NaCl were found to be low in the samples without TI ww for the test organisms mentioned above. The acute toxicity originated from the NaCl decreased significantly to EC_1 and EC_5 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the NaCl is not significant and the real acute toxicity throughout sonication was attributed to the TI ww, to their metabolites and to the sonodegradation by-products (Table 5.190).

5.18.6 Effect of Fe^{+2} Concentrations on the Removal of Acute Toxicity in TI ww at Increasing Sonication Time and Temperature

5.18.6.1 Effect of Fe^{+2} Concentrations on the Removal of Microtox Acute Toxicityin TI ww at Increasing Sonication Time and Temperature

The initial EC_{90} values at pH=7.0 was measured as 825 mg/l at 25°C (Table 5.191, SET 1). After 60 min, 120 and 150 min of sonication the EC_{99} values decreased to EC_{60}=312 mg/l to EC_{25}=135 mg/l and to EC_{10}=66 mg/l, in Fe^{+2}=8.00 mg/l at 30°C (Table 5.191, SET 3). The toxicity removal efficiencies were 33.33%, 72.22% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 30°C (Table 5.191, SET 3).

The EC_{90} values decreased to EC_{50}, to EC_{20} and to EC_5 after 60 min, 120 and 150 min sonication, respectively, in Fe^{+2}=8.00 mg/l at 60°C (Table 5.191, SET 3). The EC_{50}, the EC_{20} and the EC_5 values were measured as 307 mg/l, 125 and 53 mg/l, respectively, at 60°C. The toxicity removal efficiencies were 44.44%, 77.78% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C. 94.44% maximum Microtox acute toxicity yield was found in Fe^{+2}=8.00 mg/l after 150 min sonication time at 60°C (Table 5.191, SET 3).

The EC_{50} values decreased to EC_{60}=317 mg/l to EC_{30}=141 and to EC_{15}=69 mg/l after 60 min, 120 and 150 min sonication time, respectively, in Fe^{+2}=2.00 mg/l at 30°C (Table 5.191, SET 3). The EC_{50} values decreased to EC_{65}=305 mg/l to EC_{35}=132 and to EC_{20}=62 mg/l after 60 min, 120 and 150 min sonication time, respectively, in Fe^{+2}=20.00 mg/l at 30°C. The Microtox acute toxicity yields were 83.33% and 77.78% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of Fe^{+2}=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.191, SET 3).

Table 5.191 Effect of increasing Fe^{+2} concentrations on Microtox acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	Parameters	Microtox Acute Toxicity Values, * EC (mg/l)							
		25°C							
		0. min		60. min		120. min		150. min	
		*EC_{90}		*EC		*EC		*EC	
1	Raw ww, control	825		EC_{70}=510		EC_{60}=650		EC_{50}=640	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
		*EC_{90}	*EC	*EC	*EC	*EC_{90}	*EC	*EC	*EC
2	Raw ww, control	825	EC_{70}=580	EC_{50}=580	EC_{40}=550	825	EC_{55}=550	EC_{40}=590	EC_{30}=690
3	Fe^{+2}=2.00 mg/l	825	EC_{60}=317	EC_{30}=141	EC_{15}=69	825	EC_{55}=313	EC_{25}=136	EC_{10}=55
	Fe^{+2}=8.00 mg/l	825	EC_{60}=312	EC_{25}=135	EC_{10}=66	825	EC_{50}=307	EC_{20}=125	EC_{5}=53
	Fe^{+2}=20.00 mg/l	825	EC_{65}=305	EC_{35}=132	EC_{20}=62	825	EC_{60}=301	EC_{30}=115	EC_{15}=41

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{55}=313 mg/l to EC_{25}=136 and to EC_{10}=55 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=2.00 mg/l at 60°C (Table 5.191, SET 3). The EC_{50} values decreased to EC_{60}=301 mg/l to EC_{30}=115 and to EC_{15}=41 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 60°C. The Microtox acute toxicity yields were 88.89% and 83.33% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of Fe^{+2}=20.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60°C (Table 5.191, SET 3).

5.18.6.2 Effect of Fe^{+2} Concentrations on the Removal of Daphnia magna Acute Toxicity in TI ww at Increasing Sonication Time and Temperature

The initial EC_{50} values were obtained as 850 mg/l at 25°C (Table 5.192, SET 1). After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{30} to EC_{15} and to EC_{10} in Fe^{+2}=8.00 mg/l at 30°C (Table 5.192, SET 3). The EC_{30}, the EC_{15} and the EC_{10} values were measured as 450 mg/l, 230 and 80 mg/l, respectively, in Fe^{+2}=8.00 mg/l at 30°C. The toxicity removal efficiencies were 40.00%, 70.00% and 80.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 30°C (Table 5.192, SET 3).

The EC_{50} values decreased to EC_{25} to EC_{10} and to EC_5 after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C (Table 5.192, SET 3). The EC_{25}, the EC_{10} and the EC_5 values were measured as 375 mg/l, 200 and 24 mg/l, respectively, in Fe^{+2}=8.00 mg/l at 60°C. The toxicity removal efficiencies were 40.00%, 80.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=8.00 mg/l at 60°C (Table 5.192, SET 3).

The acute toxicity decreased from an initial 850 mg/l to EC_5=42 mg/l at a Fe^{+2} concentration of 8.00 mg/l at 60°C after a sonication time of 150 min (Table 5.192, SET 3). The maximum acute toxicity removal was approximately 90.00% in the samples containing 8.00 mg/l Fe^{+2} concentrations at a temperature of 60°C after 150 min of sonication time. The acute toxicity removal decreased at Fe^{+2} concentrations above 8.00 mg/l (Table 5.192, SET 3).

The EC_{50} values decreased to EC_{35}=475 mg/l to EC_{20}=270 and to EC_{15}=105 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=2.00 mg/l at 30°C (Table 5.192, SET 3). The EC_{50} values decreased to EC_{40}=425 mg/l to EC_{25}=210 and to EC_{20}=29 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 30°C. The *Daphnia magna* acute toxicity yields were 70.00% and 60.00% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of Fe^{+2}=20.00 mg/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.192, SET 3).

Table 5.192 Effect of increasing Fe^{+2} concentrations on *Daphnia magna* acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC_{50}**		***EC**		***EC**		***EC**	
1	Raw ww, control	850		EC_{45}=625		EC_{40}=370		EC_{30}=155	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC_{50}**	***EC**	***EC**	***EC**	***EC_{50}**	***EC**	***EC**	***EC**
2	Raw ww, control	850	EC_{40} =470	EC_{35}= 230	EC_{25}= 115	850	EC_{35}= 375	EC_{30} =212	EC_{20}= 75
3	Fe^{+2}=2.00 mg/l	850	EC_{35} =475	EC_{20}= 270	EC_{15}= 105	850	EC_{30}= 350	EC_{15} =240	EC_{10}= 80
	Fe^{+2}=8.00 mg/l	850	EC_{30} =450	EC_{15}= 230	EC_{10}= 80	850	EC_{25}= 350	EC_{10} =170	EC_{5}= 42
	Fe^{+2}=20.00 mg/l	850	EC_{40} =425	EC_{25}= 210	EC_{20}= 29	850	EC_{35}= 260	EC_{20} =95	EC_{15}= 6

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{30}=350 mg/l to EC_{15}=240 and to EC_{10}=80 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=2.00 mg/l at 60°C (Table 5.192, SET 3). The EC_{50} values decreased to EC_{35}=260 mg/l to EC_{20}=95 and to EC_{15}=6 mg/l after 60 min, 120 and 150 min sonication times, respectively, in

Fe^{+2}=20.00 mg/l at 60°C. The *Daphnia magna* acute toxicity yields were 80.00% and 70.00% in 2.00 and 20.00 mg/l Fe^{+2}, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of Fe^{+2}=20.00 mg/l to *Daphnia magna* in after 150 min sonication time at 60°C (Table 5.192, SET 3).

5.18.6.3 Direct Effects of Fe^{+2} Concentrations on the Acute Toxicity of Microtox and Daphnia magna in TI ww

The acute toxicity test was performed in the samples containing 2.00, 8.00 and 20.00 mg/l Fe^{+2} concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing Fe^{+2} the toxicity test were performed without TI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing Fe^{+2} concentrations after 150 min sonication time. Table 5.193 showed the responses of Microtox and *Daphnia magna* to increasing Fe^{+2} concentrations.

Table 5.193 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing Fe^{+2} concentrations without TI ww after 150 min sonication time.

Fe^{+2} Conc. (mg/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
2.00	EC_{10}=30	-	-	EC_{10}=40	-	-
8.00	EC_{15}=160	2.00	EC_{1}=7.00	EC_{20}=210	4.00	EC_{3}=10.00
20.00	EC_{20}=240	5.00	EC_{3}=12.00	EC_{30}=270	7.00	EC_{6}=16.00

The acute toxicity originating only from 2.00, 8.00 and 20.00 mg/l Fe^{+2} were found to be low (Table 5.193). 2.00 mg/l Fe^{+2} did not exhibit toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 8.00 and 20.00 mg/l Fe^{+2} were found to be low in the samples without TI ww for the test organisms mentioned above. The acute toxicity originated from the Fe^{+2} decreased significantly to EC_1 and EC_3 after 150 min sonication time. Therefore it can be concluded that the toxicity originating from the Fe^{+2} is not significant and the real acute toxicity throughout sonication was attributed to the TI ww, to their metabolites and to the sonodegradation by-products (Table 5.193).

5.18.7 Effect of Fe^{+3} Concentrations on the Removal of Acute Toxicity in TI ww at Increasing Sonication Time and Temperature

5.18.7.1 Effect of Fe^{+3} Concentrations on the Removal of Microtox Acute Toxicity in TI ww at Increasing Sonication Time and Temperature

As seen in Table 5.194 (SET 1), the initial EC_{90} values at pH=7.0 was found as 825 mg/l at 25°C. The EC_{90} values decreased to EC_{60}, to EC_{25} and to EC_{10} after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 30°C (Table 5.194, SET 3). The EC_{60}, the EC_{25} and the EC_{10} values were measured as 411 mg/l, 237 and 171 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 30°C. The toxicity removal efficiencies were 33.33%, 72.22% and 88.89% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 30°C (Table 5.194, SET 3).

The EC_{90} values decreased to EC_{55}, to EC_{20} and to EC_5 after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C (Table 5.194, SET 3). The EC_{55}, the EC_{20} and the EC_5 values were measured as 405 mg/l, 228 and 154 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 60°C. The toxicity removal efficiencies were 38.89%, 77.78% and 94.44% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C. 94.44% maximum Microtox acute toxicity yield was observed in Fe^{+3}=20.00 mg/l after 150 min sonication time at 30°C (Table 5.194, SET 3).

The EC_{50} values decreased to EC_{60}=415 mg/l to EC_{30}=243 and to EC_{15}=174 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at

30°C (Table 5.194, SET 3). The EC_{50} values decreased to EC_{65}=405 mg/l to EC_{35}=226 and to EC_{20}=160 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 30°C. The Microtox acute toxicity yields were 83.33% and 77.78% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of Fe^{+3}=50.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 30°C (Table 5.194, SET 3).

Table 5.194 Effect of increasing Fe^{+3} concentrations on Microtox acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$^*EC_{90}$		**$^*EC$**		**$^*EC$**		**$^*EC$**	
1	Raw ww, control	825		EC_{70}=510		EC_{60}=650		EC_{50}=640	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$^*EC_{90}$	**$^*EC$**	**$^*EC$**	**$^*EC$**	**$^*EC_{90}$**	**$^*EC$**	**$^*EC$**	**$^*EC$**
2	Raw ww, control	825	EC_{70}= 580	EC_{50}= 580	EC_{40}= 550	825	EC_{55} =550	EC_{40}= 590	EC_{30}= 690
3	Fe^{+3}=10.00 mg/l	825	EC_{60}= 415	EC_{30}= 243	EC_{15}= 174	825	EC_{55} =412	EC_{25}= 234	EC_{10}= 156
	Fe^{+3}=20.00 mg/l	825	EC_{60}= 411	EC_{25}= 237	EC_{10}= 171	825	EC_{55} =405	EC_{20}= 228	EC_{5}= 154
	Fe^{+3}=50.00 mg/l	825	EC_{65}= 405	EC_{35}= 226	EC_{20}= 160	825	EC_{60} =401	EC_{30}= 214	EC_{15}= 151

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{55}=412 mg/l to EC_{25}=234 and to EC_{10}=156 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at

60°C (Table 5.194, SET 3). The EC_{50} values decreased to EC_{60}=401 mg/l to EC_{30}=214 and to EC_{15}=151 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 60°C. The Microtox acute toxicity yields were 88.89% and 83.33% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 60°C. It was obtained an inhibition effect of Fe^{+3}=50.00 mg/l to *Photobacterium phosphoreum* after 150 min sonication time at 60°C (Table 5.194, SET 3).

5.18.7.2 Effect of Fe^{+3} Concentrations on the Removal of Daphnia magna Acute Toxicity in TI ww at Increasing Sonication Time and Temperature

The initial EC_{50} values were observed as 850 mg/l at 25°C (Table 5.195, SET 1). After 60 min, 120 and 150 min of sonication the EC_{50} values decreased to EC_{35} to EC_{20} and to EC_{15} in Fe^{+3}=20.00 mg/l at 30°C (Table 5.195, SET 3). The EC_{35}, the EC_{20} and the EC_{15} values were measured as 500 mg/l, 250 and 65 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 30°C. The toxicity removal efficiencies were 40.00%, 80.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 30°C (Table 5.195, SET 3).

The EC_{50} values decreased to EC_{30} to EC_{10} and to EC_{5} after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C (Table 5.195, SET 3). The EC_{30}, the EC_{10} and the EC_{5} values were measured as 375 mg/l, 200 and 24 mg/l, respectively, in Fe^{+3}=20.00 mg/l at 60°C. The toxicity removal efficiencies were 40.00%, 80.00% and 90.00% after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=20.00 mg/l at 60°C. 90.00% maximum *Daphnia magna* acute toxicity removal was obtained in Fe^{+3}=20.00 mg/l after 150 min sonication time at 60°C (Table 5.195, SET 3).

The EC_{50} values decreased to EC_{35}=480 mg/l to EC_{25}=320 and to EC_{20}=95 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 30°C (Table 5.195, SET 3). The EC_{50} values decreased to EC_{40}=325 mg/l to EC_{30}=180 and to EC_{25}=22 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+2}=20.00 mg/l at 30°C. The *Daphnia magna* acute toxicity yields were 60.00% and 50.00% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at 30°C. It was observed an inhibition effect of Fe^{+3}=50.00 mg/l to *Daphnia magna* after 150 min sonication time at 30°C (Table 5.195, SET 3).

Table 5.195 Effect of increasing Fe^{+3} concentrations on *Daphnia magna* acute toxicity in TI ww at 30°C and at 60°C (640 W power, 35 kHz frequency).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{50}$		***EC**		***EC**		***EC**	
1	Raw ww, control	850		EC_{45}=625		EC_{40}=370		EC_{30}=155	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{50}$	***EC**	***EC**	***EC**	**$*EC_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	850	EC_{40} =470	EC_{35}= 230	EC_{25}= 115	850	EC_{35}= 375	EC_{30} =212	EC_{20}= 75
3	Fe^{+3}=10.00 mg/l	850	EC_{35} =480	EC_{25}= 320	EC_{20}= 95	850	EC_{30}= 390	EC_{20} =230	EC_{10}= 75
	Fe^{+3}=20.00 mg/l	850	EC_{35} =500	EC_{20}= 250	EC_{15}= 65	850	EC_{30}= 375	EC_{10} =200	EC_{5}= 24
	Fe^{+3}=50.00 mg/l	850	EC_{40} =325	EC_{30}= 180	EC_{25}= 22	850	EC_{35}= 350	EC_{25} =90	EC_{15}= 5

* EC values were calculated based on COD (mg/l).

The EC_{50} values decreased to EC_{30}=390 mg/l to EC_{20}=230 and to EC_{10}=75 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=10.00 mg/l at 60°C (Table 5.195, SET 3). The EC_{50} values decreased to EC_{35}=350 mg/l to EC_{25}=90 and to EC_{15}=5 mg/l after 60 min, 120 and 150 min sonication times, respectively, in Fe^{+3}=50.00 mg/l at 60°C. The *Daphnia magna* acute toxicity yields were 80.00% and 70.00% in 10.00 and 50.00 mg/l Fe^{+3}, respectively, after 150 min sonication time at

60^{o}C. It was obtained an inhibition effect of Fe^{+3}=50.00 mg/l to *Daphnia magna* after 150 min sonication time at 60^{o}C (Table 5.195, SET 3).

5.18.7.3 Direct Effects of Fe^{+3} Concentrations on the Acute Toxicity of Microtox and Daphnia magna in TI ww

The acute toxicity test was performed in the samples containing 10.00, 20.00 and 50.00 mg/l Fe^{+3} concentrations. In order to detect the direct responses of Microtox and *Daphnia magna* to the increasing Fe^{+3} the toxicity test were performed without TI ww. The initial EC values and the the EC_{50} values were measured in the samples containing increasing Fe^{+3} concentrations after 150 min sonication time. Table 5.196 showed the responses of Microtox and *Daphnia magna* to increasing Fe^{+3} concentrations.

Table 5.196 The responses of Microtox and *Daphnia magna* acute toxicity tests in addition of increasing Fe^{+3} concentrations without TI ww after 150 min sonication time.

Fe^{+3} Conc. (mg/l)	**Microtox Test**			***Daphnia magna* Test**		
	Initial Acute Toxicity EC_{50} Value (mg/l)	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**	**Initial Acute Toxicity EC_{50} Value (mg/l)**	**Inhibitions after 150 min Sonication**	**EC Values (mg/l)**
10.00	EC_{10}=35	-	-	EC_{10}=40	-	-
20.00	EC_{15}=150	4.00	EC_{2}=9.00	EC_{20}=210	6.00	EC_{4}=12.00
50.00	EC_{20}=240	6.00	EC_{4}=15.00	EC_{30}=280	10.00	EC_{7}=25.00

The acute toxicity originating only from 10.00, 20.00 and 50.00 mg/l Fe^{+3} were found to be low (Table 5.196). 10.00 mg/l Fe^{+3} did not exhibit toxicity to *Photobacterium phosphoreum* and *Daphnia magna* before and after 150 min sonication time. The toxicity atributed to the 20.00 and 50.00 mg/l Fe^{+3} were found to be low in the samples without TI ww for the test organisms mentioned above. The acute toxicity originated from the Fe^{+3} decreased significantly to EC_{2} and EC_{4} after

150 min sonication time. Therefore it can be concluded that the toxicity originating from the Fe^{+3} is not significant and the real acute toxicity throughout sonication was attributed to the OMI ww, to their metabolites and to the sonodegradation by-products (Table 5.196).

5.18.8 TI ww Toxicities, Interspecies Correlation and Sensitivities

To verify the relationships between the acute toxicity data of two organisms the EC_{50} values of *Photobacterium phosphoreum* were correlated to those of *Daphnia magna* by statistical analysis using their EC_{50} values in the influent of TI ww. It was found that the EC_{50} values differed in both test organisms for the TI ww before sonication samples. The EC_{50} value of TI ww increased from 458.33 mg/l (converted from EC_{90}=825.00 mg/l in TI ww for Microtox acute toxicity assay before sonication) to 850.00 mg/l as the trophic level increased from bacteria in Microtox test to water flea in *Daphnia magna* test in the influent samples. The coefficient of correlation and t-test statistics (R^2=0.28, $p \leq 0.01$, t-test statistics=0.41) did not show a significant linear relationship between the acute toxicities of TI ww to *Photobacterium phosphoreum* and to *Daphnia magna* in the influent TI ww samples. This result verifies the sensitivity of *Photobacterium phosphoreum* and the resistance of *Daphnia magna* to TI ww by taken into consideration the data obtained with sensitivity scores. This indicated that the water fleas exhibited less acute toxicity to TI ww. The differences in test sensitivities can be attributed to the differences in the responses of the two different trophic organisms in TI ww. In this study showed that the Microtox acute toxicity test is more sensitive than that *Daphnia magna* in the TI ww samples before sonication process.

Table 5.197 shows the sensitivity ranking and the EC_{50} values of TI ww in *Photobacterium phosphoreum* and *Daphnia magna* in sonicated samples containing some additives after 150 min sonication time at 60°C.

The EC_{50} value of TI ww increased from 2.78 mg/l (converted from 5.00 mg/l at original EC values in TI ww for Microtox acute toxicity assay after 150 min sonication time) to 20.00 mg/l as the trophic level increased from bacteria in

Microtox test to water flea in *Daphnia magna* test in the sonicated TI ww samples containing some additives after 150 min sonication time at 60^{o}C (Table 5.197). To verify the relationships between the acute toxicity data of two organisms the EC_{50} values of *Photobacterium phosphoreum* were correlated to those of *Daphnia magna* by statistical analysis using their EC_{50} values in the effluent of TI ww. It was found that the EC_{50} values differed in both test organisms for the sonicated samples containing some additives after 150 min sonication time at 60^{o}C. The coefficient of correlation and t-test statistics (R^2=0.92, p=0.01, t-test statistics=10.56) show a significant linear relationship between the acute toxicities of TI ww to *Photobacterium phosphoreum* and to *Daphnia magna* in the after 150 min sonication time (Table 5.197). This indicated that the water fleas exhibited less acute toxicity to TI ww. The differences in test sensitivities can be attributed to the differences in the responses of the two different trophic organisms in TI ww. As a conclusion, this study showed that the Microtox acute toxicity test is more sensitive than that *Daphnia magna* in the sonicated TI ww samples containing some additives after 150 min sonication time at 60^{o}C (Table 5.197).

Table 5.197 Sensitivity ranking and EC_{50} values of TI ww in *Photobacterium phosphoreum* and *Daphnia magna* in sonicated samples containing some additives after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

Parameters	***Photobacterium phosphoreum***		***Daphnia magna***	
	EC_{50} value and 95.00% Confidence Limits (mg/l) 48 h	**Sensitivity Ranking**	**EC_{50} value and 95.00% Confidence Limits (mg/l) 48 h**	**Sensitivity Ranking**
Raw ww, control	16.67 (16.43 – 16.91)	1	20.00 (19.74 – 20.26)	2
1 h aeration	4.33 (4.21 – 4.45)	1	5.00 (4.87 – 5.13)	2
30 min $N_2(g)$ (6.00 mg/l N_2)	4.33 (4.21 – 4.45)	1	5.00 (4.87 – 5.13)	2
pH=7.0	13.89 (13.67 – 14.11)	1	15.00 (14.78 – 15.22)	2
DO=10.00 mg/l	8.11 (7.94 – 8.28)	1	10.00 (9.82 – 10.18)	2
H_2O_2=500 mg/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
TiO_2=10.00 mg/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
NaCl=2.50 g/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
Fe^{+2}=8.00 mg/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
Fe^{+3}=20.00 mg/l	2.78 (2.67 – 2.89)	1	5.00 (4.87 – 5.13)	2
HCO_3^{-1}=1.00 g/l	5.56 (5.42 – 5.70)	1	10.00 (9.82 – 10.18)	2
C_4H_9OH=0.50 g/l	5.56 (5.42 – 5.70)	1	10.00 (9.82 – 10.18)	2

5.19 Cost and Specific Energy Estimation

5.19.1 Cost Estimation Methodology

A very simple methodology was developed to arrive at the treatment costs of the various AOPs processes studied. First of all, data were collected from the published literature for all the AOPs involving the use of ultrasound (US) and some standard commercial AOPs. Table 5.198 shows the various studies considered for this investigation along with their operating conditions. From this data, the kinetics of pollutant removal was found. If the kinetics is reported then it was taken from the literature as such; otherwise it was calculated from the data given in the literature using standard methods of finding kinetics (Fogler & Barnes, 1968; Fogler, 2004). By kinetics, we mean the order of degradation and the rate constant. Table 5.199 depicts the kinetic data collected from these studies. These rate constants were then used to calculate the time required for 90.00% degradation of the pollutant from its initial concentration. This time was assumed as the residence time for the reactor for wastewater treatment using the given AOP. The cost estimation was done for the assumed flow rate of 1000 l/min. The reactor capacity was calculated by multiplying the residence time with the design flow rate (1000 l/min). From the treatability study in the literature, the energy consumption data was then collected as energy dissipated per unit volume (W/ml). The total amount of energy required to treat the wastewater at the designed flow rate for given residence time was then calculated. From the quotations, which we had invited from manufacturers, we knew the amount of energy supplied by one commercial unit. Hence, the number of such commercial units required for dissipating the required energy was calculated. From the number of commercial units required, the capital cost of the wastewater treatment unit was calculated (AOP unit cost). This AOP unit cost was used to calculate the total capital cost using certain standard assumptions. These assumptions are described in the next section. Similarly, total annual operating and maintenance cost was also calculated. The total capital cost was amortized at a rate of 7.00% over a period of 30 years to arrive at total amortized annual capital cost. Sum of the annual operating and maintenance cost and annual capital cost gave the total annual operating cost. Dividing this cost with the amount of liters of wastewater treated in a year gave us the cost of wastewater treatment per 3.79 l of water treated. It was assumed that the plant is running throughout the year continuously.

The cost estimation of various ultrasonic AOPs for the elimination of phenol and reactive dyes was performed on the basis of the rate constants. Since the rate of degradation changes significantly with the experimental system, the reactor configuration and the operating conditions such as pH, ultraviolet (UV) intensity or US intensity etc., limited number of sources having similar operating conditions were considered. Kinetic data was collected from a limited number of sources in the literature (Table 5.199). Five sources were considered for phenol and three sources were considered for reactive dyes. The collected data was then compared with the kinetic data available for a number of other similar treatability studies in the literature to make sure that it is comparable with the reported values.

Adewuyi (2001) has summarized results of a number of studies of wastewater treatment using ultrasonic processes. They have reported the rates of degradation for phenol, reactive dyes and a number of other hazardous compounds. Kidak & Ince (2006) have recently reviewed the subject of phenol degradation using ultrasonic processes. Beckett et al. (2001) have described the degradation of phenols and chlorinated compounds and their mixtures using ultrasonic cavitation. Destaillats et al. (2001a) and Destaillats et al. (2001b) have reported the scale up of sonochemical reactors for wastewater treatment. They have also reported the rates of degradation for reactive dyes. It lies in the range of 0.002–0.045 1/min. Lesko (2006) have reported the rates of degradation of phenol using a pilot station sonochemical reactor. The authors found that the rate of phenol degradation was in the range of 0.0011–0.063 1/min. Zheng et al. (2005) have reported the rates of sonochemical degradation of phenol in the range of 0.014–0.061 1/min. Lesko et al. (2006) have reported the rate of phenol degradation in the presence of ozone (O_3) and US to be in the range of 0.137 1/min. One can observe from Table 5.199 that the reported rates of degradation of phenol and reactive dyes are in the same range as are considered in this study. Hence, it can safely be said that the results of cost estimation of this study can at least provide an order of magnitude glimpse of the economics involved in the wastewater treatment using ultrasonic processes.

Table 5.198 Operating conditions for different wastewaters and different AOPs.

Process	Wastewater	Pollutant Parameter	Removed Parameter	Reaction Volume	Initial Concentration	UV Source	US Source	O_3 Source	Oxidant	Catalyst	References
For phenol UV, US, O_3, UV+US US + O_3, UV+O_3, US + UV + O_3	OMI ww	COD, phenol	phenol	100 ml	235.275 mg/l	254 nm, ULTRAMAX STL 257, 15W	300 kHz, Undatim ultrasonics, 25W	Ozonelab OL-100 model, 36W at 0.75 l/min	O_3 4.40 mg/l	-	Kidak & Ince (2007)
Fenton and US + Fenton	OMI ww	COD, phenol	phenol	350 ml	63.05 mg/l	-	35 kHz SODEVA 50W	-	H_2O_2 200 mg/l	$CuSO_4$ 250 mg/l	Entezari et al. (2003)
US	OMI ww	**(a)**	**(a)**	500 ml	4090 mg/l		35 kHz, 640 W		**(d)**	**(e)**	In this study
For reactive azo dye UV, US, O_3, UV+US US + O_3, UV+O_3, US + UV + O_3	TI ww	COD, color	color	1200 ml	19.95 mg/l	254 nm, Philips, PL-L 18WTUV two lamps	520 kHz, Undatim Ultrasonics, 600W	Ozonelab OL-100 model, 36W at 0.25 l/min	O_3 40.00 mg/l	-	Tezcanli-Güyer & Ince (2004)
US	TI ww	**(b)**	**(b)**	500 ml	962.99 mg/l	-	35 kHz, 640 W	-	**(d)**	**(e)**	In this study
US	PCI ww	**(c)**	**(c)**	500 ml	1378.77 ng/ml 1027.43 mg/l	-	35 kHz, 640 W	-	**(d)**	**(e)**	In this study

(a): COD_{dis}, TOC, color, total phenol, TAAs and TFAs; (b): COD_{dis}, TOC, color and TAAs; (c): Total PAHs, COD_{dis} and TOC; (d): H_2O_2, $O_2(g)$, $N_2(g)$; (e): air, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH.

Table 5.199 Rate constants of various AOPs throughout sono-degradation.

Wastewater	**Item**	**Removed Parameter**	**k (1/min)**	**References**
OMI ww	UV (254 nm)	phenol	$2.10x10^{-3}$	Kidak & Ince (2007)
OMI ww	O_3 (2.00 mg/l)	phenol	$2.79x10^{-2}$	Kidak & Ince (2007)
OMI ww	Fenton	phenol	$1.06x10^{-2}$	Entezari et al. (2003)
OMI ww	US	COD_{dis}	$1.00x10^{-4}$	In this study
OMI ww	US	TOC	$1.00x10^{-4}$	In this study
OMI ww	US	color	$8.33x10^{-5}$	In this study
OMI ww	US	phenol	$1.00x10^{-4}$	In this study
OMI ww	US	TAAs	$1.00x10^{-4}$	In this study
OMI ww	US	TFAs	$5.00x10^{-5}$	In this study
TI ww	UV (254 nm)	color	No degradation observed	Tezcanli-Güyer & Ince (2004)
TI ww	O_3 (12.40 mg/l)	color	$11.08x10^{-3}$	Tezcanli-Güyer & Ince (2004)
TI ww	US	COD_{dis}	$1.50x10^{-4}$	In this study
TI ww	US	TOC	$1.33x10^{-4}$	In this study
TI ww	US	color	$1.00x10^{-4}$	In this study
TI ww	US	TAAs	$3.33x10^{-5}$	In this study
PCI ww	US	COD_{dis}	$5.33x10^{-4}$	In this study
PCI ww	US	TOC	$3.00x10^{-4}$	In this study
PCI ww	US	PAHs	$7.83x10^{-4}$	In this study

5.19.2 The Calculation of Energy Requirement in Sonication Reactor

From the referred publications or calculations from the data in the publications (energy density, ε), the total energy requirement in the AOP reactor is given by X ε watt (Fogler, 2004).

From the manufacturer quotations, the energy supplied by single unit of AOP = E watt. The number of such standard commercial units required is given in Eq. (5.112);

$$N = X\,(W)\,/\,E(W) \qquad (5.112)$$

where;

N: The number of such standard commercial units

X: The total energy requirement in the AOP reactor (W),

E: The energy supplied by single unit of AOP

$$\text{Total cost of N units} = \text{Cost of AOP reactor} = P = N\,/\,C(\$) \qquad (5.113)$$

where;

C: Cost of each unit from the manufacturer=1500 TL=1000 $=789.47 €

P: Cost of AOP reactor ($)=1500 TL=1000 $=789.47 €

5.19.2.1 The Calculation of Energy Requirement in Sonication Reactor for PCI ww

In this study, for PCI ww;

X=640 W=0.64 kW

E=640 W=0.64 kW

N=(640 W) / (640 W)=1 units

P=Total cost of 1 units=Cost of AOP reactor=1500 TL=1000 $=789.47 €

Note: Rate of electricity=0.165454 TL/kWh=0.17 TL/kWh=0.11 $/kWh=0.09 €/kWh

In the present study for PCI ww;

The total hourly electrical cost=0.165454 TL/kWh * 0.64 kWh
=0.11 TL/hour
=0.07 $/hour.
=0.06 €/hour

5.19.2.2 The Calculation of Energy Requirement in Sonication Reactor for OMI ww

In this study, for OMI ww;

X=640 W=0.64 kW
E=640 W=0.64 kW
N=(640 W) / (640 W)=1 units
P=Total cost of 1 units=Cost of AOP reactor=1500 TL=1000 $=789.47 €

In the present study, for OMI ww;

The total hourly electrical cost=0.165454 TL/kWh * 0.64 kWh
=0.11 TL/hour
=0.07 $/hour.
=0.06 €/hour

5.19.2.3 The Calculation of Energy Requirement in Sonication Reactor Capacity for TI ww

In this study, for TI ww;

X=640 W=0.64 kW
E=640 W=0.64 kW
N=(640 W) / (640 W)=1 units
P=Total cost of 1 units=Cost of AOP reactor=1500 TL=1000 $=789.47 €

In the present study, for TI ww;

The total hourly electrical cost=0.165454 TL/kWh * 0.64 kWh
=0.11 TL/hour

=0.07 \$/hour.
=0.06 €/hour

5.19.3 General Calculation of Capital Cost in Sonication Reactor

The general calculation of capital cost for PCI ww, OMI ww and TI ww during sonication process ARE presented in Table 5.200. The capital cost is amortized over a span of years at given amortization rate. Amortized capital cost (A) is given by following formula (Zhou & Tol, 2004) in Eq. (5.114):

$$A = \frac{1.2S * r}{1 - \left(\frac{1}{1 + r} \right)^{n}} \tag{5.114}$$

where;

A: Amortized annual capital cost
r: Annual discount rate (assumption = 7.00%)
1.2S: Total capital cost
n: Life of project (assumption = 30 years) EE/O is kWh/m^3/order

In this study;

The total capital cost of US system=Cost of US System=1500 TL/year
=1000 \$/year
=789.47 €/year

In this study;

Using Eq. (5.114),
Amortized capital cost (A)=[(1500 Tl * 0.07) / {1-(1/(1+0.07))^{30}}]=120 TL/year
=80.00 \$/year
=63.16 €/year

In this study;

Total amortized capital cost=A + Cost of US system=120 TL + 1500 TL
=1620 TL/year
=1080 \$/year
=852.63 €/year

5.19.3.1 General Calculation of Capital Cost in Sonication Reactor for PCI ww

In this study, for PCI ww;

r=7.00%=0.07
1.2S=5 N/ C=2.2 P
n=30 year
A=[(2.2 P * 0.07) / {1-(1/(1+0.07))^{30}}]=0.18 P=270 TL=180 \$=142.11 €

5.19.3.2 General Calculation of Capital Cost in Sonication Reactor for OMI ww

In this study, for OMI ww;

r=7.00%=0.07
1.2S=5 N/ C=2.2 P
n=30 year
A=[(2.2 P * 0.07) / {1-(1/(1+0.07))^{30}}]=0.18 P=270 TL=180 \$=142.11 €

5.19.3.3 General Calculation of Capital Cost in Sonication Reactor for TI ww

In this study, for TI ww;

r=7.00%=0.07
1.2S=5 N/ C=2.2 P
n=30 year
A=[(2.2 P * 0.07) / {1-(1/(1+0.07))^{30}}]=0.18 P=270 TL=180 \$=142.11 €

Table 5.200 General calculation of capital cost in this study.

Item	**PCI ww Capital Cost**				**OMI ww Capital Cost**				**TI ww Capital Cost**			
	PCI ww	**Cost (TL)**	**Cost ($)**	**Cost (€)**	**OMI ww**	**Cost (TL)**	**Cost ($)**	**Cost (€)**	**TI ww**	**Cost (TL)**	**Cost ($)**	**Cost (€)**
AOP reactor	P	1500	1000	789.47	P	1500	1000	789.47	P	1500	1000	789.47
Piping, valves, electrical (30.00%)	0.30 P	450	300	236.84	0.30 P	450	300	236.84	0.30 P	450	300	236.84
Site work (10.00%)	0.10 P	150	100	78.95	0.10 P	150	100	78.95	0.10 P	150	100	78.95
Subtotal	1.40 P = Q	2100	1400	1105.26	1.40 P = Q	2100	1400	1105.26	1.40 P = Q	2100	1400	1105.26
Contractor O&P (15.00%)	0.15 Q	315	210	165.79	0.15 Q	315	210	165.79	0.15 Q	315	210	165.79
Subtotal	1.15 Q = R	2415	1610	1271.05	1.15 Q = R	2415	1610	1271.05	1.15 Q = R	2415	1610	1271.05
Engineering (15.00%)	0.15 R	362.25	241.50	190.66	0.15 R	362.25	241.50	190.66	0.15 R	362.25	241.50	190.66
Subtotal	1.15 R = S	2777.25	1851.50	1461.71	1.15 R = S	2777.25	1851.50	1461.71	1.15 R = S	2777.25	1851.50	1461.71
Contingency (20.00%)	0.20 S	555.45	370.30	292.34	0.20 S	555.45	370.30	292.34	0.20 S	555.45	370.30	292.34
Total capital	1.20 S=2.2 P	3332.70	2221.80	1754.05	1.20 S=2.2 P	3332.70	2221.80	1754.05	1.20 S=2.2P	3332.70	2221.80	1754.05

P: Total cost of one unit or cost of AOP reactor; Q: Subtotal of labor cost; R: Subtotal of contractor cost; S: Subtotal of part replacement cost.

5.19.4 The Comparison of Cost for AOPs in Different Litearature Studies

Table 5.201 summarizes the cost estimation of some literature data performed with AOP and sonication including the cost results for PCI, OMI and TI wws.

Table 5.201 Summary of cost estimation of various AOPs for degradation of some parameters

Wastewater	**Item**	**Removed Parameter**	**k (1/min)**	**P_{elec} (kW)**	**t (min)**	**V (liter)**	**C_0 (COD_{dis})**	**C (COD_{dis})**	**Energy Density (W/ml)**	**Specific Energy (kWh / kg COD_0**	**EE/O or EE/M**	**Cost $/ 3790 liters**	**References**
OMI ww	UV (254 nm)	phenol	0.0021	0.015	1096.47	0.10	235.28	23.528	0.15	-	2741.20	1520.86	Kidak & Ince (2007)
OMI ww	O_3 (2.00 mg/l)	phenol	0.0279	0.036	82.53	0.10	235.28	23.528	0.36	-	495.18	1.2023	Kidak & Ince (2007)
OMI ww	Fenton	phenol	0.0106	-	218	0.35	63.00	6.30	-	-	-	14.2829	Entezari et al. (2003)
OMI ww	US	**(a)**	0.0007	0.64	150	0.50	109444	42779	1.28	0.03	7804.88	1000	In this study
TI ww	UV (254 nm)	color	No	0.036	60.00	1.20	20.00	20.00	0.03	-	$1.38x10^9$	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3 (12.40 mg/l)	color	0.01108	0.036	207.814	1.20	20.00	2.00	0.03	-	103.91	4.0839	Tezcanli-Güyer & Ince (2004)
TI ww	US	**(b)**	0.00015	0.64	150	0.50	962.99	247.75	1.28	3.32	5423.73	1000	In this study
PCI ww		**(c)**	0.00012	0.64	150	0.50	1027.43	203.835	1.28	3.12	4481.80	1000	In this study

(a): COD_{dis}, TOC, color, total phenol, TAAs and TFAs; (b): COD_{dis}, TOC, color and TAAs; (c): Total PAHs, COD_{dis} and TOC. 1 US galon=3.79 liter and 1000 US galon=3790 liter. Total capital cost of 0.50 l=1000 $.

5.19.5 Capital Cost Calculations for US System

Capital cost estimation ($) of various AOPs for degradation given in Table 5.202.

Note: In this study; 1.50 TL=1.00 $ (was assumed).
1.90 TL=1.00 € (was assumed).

In this study;

The total capital cost of US system=Cost of US System=1500 TL/year
=1000 $/year
=789.47 €/year

In this study;

Using Eq. (5.114), Amortized capital cost (A)=120 TL/year
=80.00 $/year
=63.16 €/year

In this study;

Total amortized capital cost=A + Cost of US system=120 TL + 1500 TL
=1620 TL/year
=1080 $/year
=852.63 €/year

Table 5.202 summarizes the capital cost estimation in different AOPs and in PCI, OMI and TI ww throughout sonication.

Table 5.202 Capital cost estimation ($) for various AOPs for degradation of some parameters.

Item	Removed Parameter	AOP Reactor ($)	Piping, Valves, Electrical (30.00%)($)	Site Work (10.00%)	Subtotal ($)	Contractor O&P (15.00%)	Subtotal ($)	Engineering (15.00%)	Subtotal ($)	Contingency (20.00%)	Total Capital ($)	Amortized Annual Capital Cost ($)	References
UV	phenol	2.47x10^{8}	7.40x10^{7}	2.47x10^{7}	3.46x10^{8}	5.18x10^{7}	3.97x10^{8}	5.96x10^{7}	4.57x10^{8}	9.14x10^{7}	5.48x10^{8}	4.42x10^{7}	Kidak & Ince (2007)
US	phenol	9.00x10^{9}	2.70x10^{9}	9.00x10^{8}	1.26x10^{10}	1.89x10^{9}	1.45x10^{10}	2.17x10^{9}	1.67x10^{10}	3.33x10^{9}	2.00x10^{10}	1.61x10^{9}	Kidak & Ince (2007)
O_3	phenol	3.40x10^{4}	1.02x10^{4}	3.40x10^{3}	4.76x10^{4}	7.14x10^{3}	5.47x10^{4}	8.21x10^{3}	6.30x10^{4}	1.26x10^{4}	7.55x10^{4}	7.55x10^{4} [a]	Entezari et al. (2003)
US+ Fenton	phenol	7.14x10^{7}	2.14x10^{7}	7.14x10^{6}	1.00x10^{8}	1.50x10^{7}	1.15x10^{8}	1.72x10^{7}	1.32x10^{8}	2.64x10^{7}	1.59x10^{8}	1.28x10^{7}	Entezari et al. (2003)
US, OMI ww	**(b)**	1.00x10^{3}	-	-	-	-	-	-	8.00x10^{1}	-	1.00x10^{3}	1.08x10^{3}	In this study
UV	color	-	-	-	-	-	-	-	-	-	-	-	T.-Guyer & Ince (2004)
O_3	color	2.04x10^{5}	6.12x10^{4}	2.04x10^{4}	2.86x10^{5}	4.28x10^{4}	3.28x10^{5}	4.93x10^{4}	3.78x10^{5}	7.55x10^{4}	4.53x10^{5}	4.53x10^{5} [a]	T.-Guyer & Ince (2004)
US, TI ww	**(c)**	1.00x10^{3}	-	-	-	-	-	-	8.00x10^{1}	-	1.00x10^{3}	1.08x10^{3}	In this study
US, PCI ww	**(d)**	1.00x10^{3}	-	-	-	-	-	-	8.00x10^{1}	-	1.00x10^{3}	1.08x10^{3}	In this study

a: Since O_3 generator is assumed to be replaced every year, amortized cost is taken as the same as that of the capital cost. (b): COD_{dis}, TOC, color, total phenol, TAAs and TFAs; (c): COD_{dis}, TOC, color and TAAs; (d): Total PAHs, COD_{dis} and TOC.

5.19.6 Operating and Maintenance (O & M) Cost Calculations for Sonication Process

The O & M (operating and maintenance cost) consists of labor costs, analytical costs, chemical costs, energy (electrical) costs and part replacement costs.

Total O&M cost=labor cost + analytical cost + chemical cost + energy (electrical) cost + part replacement cost

5.19.6.1 Labor Cost for Sonication Process

The labor costs consisted of water sampling cost, general and specific system O&M costs. System specific operation and maintenance consisted of inspection, replacement and repair based on hours of service life. General O&M annual labor consists of general system oversight and maintenance such as pressure gauges, control panels, leakages etc.

For ultrasonic systems, it was assumed that sampling frequency (Sf)=2 samples/week; sampling time (St)=2 min/sample=0.033 hours/sample or 1.00 hours/week and time required for O&M=17.16 hours/year. Breakdown of labor costs ($) of various AOPs for degradation determined in Table 5.203.

In this study;

US systems, the sampling frequency was taking 2 samples/day. It was assumed to be 52 weeks in a year. The sampling period was 2 min/sample=(2 min/sample) * (2 samples/day)=4 min/day=(4 min/day) * (1 hour/60 min)=0.067 hours/day=(0.067 hours/day) * (5 days/week) =0.335 hours/week

In this study;

Annual sampling labor=1.00 hours/week * 52 weeks/year=52.00 hours/year

In this study;

Sampling labor hours=1.00 hours/week

US system O & M=1.0 hours/week * 52 weeks/year
=52.00 hours/year.

Total annual labor hours=52.00 hours/year + 52.00 hours/year
=104 hours/year

In this study;

The sample analysis labor cost is 30.00 TL/hour.

Total annual labor cost=104.00 hours/year * 30.00 TL/hour
=3120 TL/year
=2080 $/year
=1642.11 €/year

Table 5.203 summarizes the labor cost estimation in different AOPs and in PCI, OMI and TI ww throughout sonication.

Table 5.203 Labor costs ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Sampling Frequency (Samples/Week)**	**Sampling Annual Labor (h)** [a]	**AOP System O&M (h/year)**	**General O&M whole Treatment Plant (h/year)**	**Total Annual Labor (h)**	**Total Annual Labor Cost ($)**	**References**
OMI ww	UV	phenol	3.00	156	18.00	312	486	38880	Kidak & Ince (2007)
OMI ww	O_3	phenol	4.00	208	48.00	312	568	45440	Kidak & Ince (2007)
OMI ww	Fenton	phenol	3.00	156	128	312	596	47680	Entezari et al. (2003)
OMI ww	US	**(b)**	2.00	52.00	52.00	-	104.00	2080	In this study
TI ww	UV	color	-	-	-	-	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3	color	4.00	208	48.00	312	568	45440	Tezcanli-Güyer & Ince (2004)
TI ww	US	**(c)**	2.00	52.00	52.00	-	104.00	2080	In this study
PCI ww	US	**(d)**	2.00	52.00	52.00	-	104.00	2080	In this study

a: It is assumed that the plant is working the whole year. Also there are 52 weeks in a year; (b): COD_{dis}, TOC, color, total phenol, TAAs and TFAs; (c): COD_{dis}, TOC, color and TAAs; (d): Total PAHs, COD_{dis} and TOC.

5.19.6.2 Analytical Costs for Sonication Process

Analytical costs were based upon sampling frequency, the labor required to do the analysis of the samples and the cost of chemicals required for analysis. These costs were considered at a rate of 200 $/h (Melin, 1999). Analytical costs ($) of various AOPs for degradation shown in Table 5.204.

In this study;

The sample analysis labor cost is 30.00 TL/hour.

Annual analysis labor=1 hours/week * 52 week/year=52.00 hours/year

Total annual labor hours=52.00 hours/year.

In this study;

Total annual analysis labor hours=Annual analysis labor + Total annual labor hours=52.00 hours/year + 52.00 hours/year=104.00 hours/year

In this study;

Total annual analysis labor cost=104.00 hours/year * 30.00 TL/hour
=3120 TL/year
=2080 $/year
=1642.11 €/year

Table 5.204 summarizes the analitical cost estimation in different AOPs and in PCI, OMI and TI ww throughout sonication.

Table 5.204 Analytical costs ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Sampling Frequency (samples/week)**	**Analysis Annual Labor (hours/year)**	**Total Annual Analytical Cost ($)** [a]	**References**
OMI ww	UV	phenol	3.00	156	31200 [a]	Kidak & Ince (2007)
OMI ww	O_3	phenol	4.00	208	41600 [a]	Kidak & Ince (2007)
OMI ww	Fenton	phenol	3.00	156	31200 [a]	Entezari et al. (2003)
OMI ww	US	**(b)**	2.00	104.00	20800 [a]	In this study
TI ww	UV	Color	-	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3	Color	4.00	208	41600 [a]	Tezcanli-Güyer & Ince (2004)
TI ww	US	**(c)**	2.00	104.00	20800 [a]	In this study
PCI ww	US	**(d)**	2.00	104.00	20800 [a]	In this study

a: Analytical labor rate was assumed to be $200 per hour; (b): COD_{dis}, TOC, color, total phenol, TAAs and TFAs; (c): COD_{dis}, TOC, color and TAAs; (d): Total PAHs, COD_{dis} and TOC.

5.19.6.3 Chemical Costs for Sonication Process

The chemical costs include the costs of consumables such as O_2(g), N_2(g), pH adjustment chemicals (H_2SO_4 and NaOH), H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH etc (Table 5.205) These prices were obtained from standard industrial suppliers such as International Construction Information Society (ICIS) Pricing and Inframat Advanced Materials (2011). Chemical costs ($) of various AOPs for degradation indicated in Table 5.206.

5.19.6.3.1 The Annual Chemical Cost for O_2(g) during Sonication Process.

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(2.50 TL/100 ml at 1 h) * 5=12.50 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for O_2(g) during US system=12.50 TL/hour * 52.00 hours/year=650 TL/500 ml wastewater in bottle for 1 year
=433.33 $/500 ml wastewater in bottle for 1 year
=342.11 €/500 ml wastewater in bottle for 1 year

5.19.6.3.2 The Annual Chemical Cost for N_2(g) during Sonication Process.

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5.00 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for N_2(g) during US system=5.00 TL/hour * 52.00 hours/year=260 TL/500 ml bottle for 1 year
=173.33 $/500 ml wastewater in bottle for 1 year
=136.84 €/500 ml wastewater in bottle for 1 year

5.19.6.3.3 The Annual Chemical Cost for H_2O_2 during Sonication Process.

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.50 TL/100 ml at 1 h) * 5=7.50 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for H_2O_2 during US system=7.50 TL/hour * 52.00 hours/year=390 TL/500 ml wastewater in bottle for 1 year
=260 $/500 ml wastewater in bottle for 1 year
=205.26 €/500 ml wastewater in bottle for 1 year

5.19.6.3.4 The Annual Chemical Cost for TiO_2 during Sonication Process.

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5.00 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for TiO_2 during US system=5.00 TL/hour * 52.00 hours/year=260 TL/500 ml wastewater in bottle for 1 year
=173.33 $/500 ml wastewater in bottle for 1 year
=136.84 €/500 ml wastewater in bottle for 1 year

5.19.6.3.5 The Annual Chemical Cost for NaCl during Sonication Process.

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5.00 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for NaCl during US system=5.00 TL/hour * 52.00 hours/year=260 TL/500 ml wastewater in bottle for 1 year
=173.33 $/500 ml wastewater in bottle for 1 year
=136.84 €/500 ml wastewater in bottle for 1 year

5.19.6.3.6 The Annual Chemical Cost for Fe^{+2} during Sonication Process.

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5.00 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for Fe^{+2} during US system=5.00 TL/hour * 52.00 hours/year=260 TL/500 ml wastewater in bottle for 1 year
=173.33 $/500 ml wastewater in bottle for 1 year
=136.84 €/500 ml wastewater in bottle for 1 year

5.19.6.3.7 The Annual Chemical Cost for Fe^{+3} during Sonication Process.

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5.00 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for Fe^{+3} during US system=5.00 TL/hour * 52.00 hours/year=260 TL/500 ml wastewater in bottle for 1 year
=173.33 $/500 ml wastewater in bottle for 1 year
=136.84 €/500 ml wastewater in bottle for 1 year

5.19.6.3.8 The Annual Chemical Cost for HCO_3^{-1} during Sonication Process.

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5.00 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for HCO_3^{-1} during US system=5.00 TL/hour * 52.00 hours/year=260 TL/500 ml wastewater in bottle for 1 year
=173.33 $/500 ml wastewater in bottle for 1 year
=136.84 €/500 ml wastewater in bottle for 1 year

5.19.6.3.9 The Annual Chemical Cost for C_4H_9OH during Sonication Process.

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5.00 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for C_4H_9OH during US system=5.00 TL/hour * 52.00 hours/year=260 TL/500 ml wastewater in bottle for 1 year
=173.33 $/500 ml wastewater in bottle for 1 year
=136.84 €/500 ml wastewater in bottle for 1 year

5.19.6.3.10 The Annual Chemical Cost for H_2SO_4 *during Sonication Process.*

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5.00 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for H_2SO_4 during US system=5.00 TL/hour * 52.00 hours/year=260 TL/500 ml wastewater in bottle for 1 year
=173.33 $/500 ml wastewater in bottle for 1 year
=136.84 €/500 ml wastewater in bottle for 1 year

5.19.6.3.11 The Annual Chemical Cost for NaOH *during Sonication Process.*

In the present study, 500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5.00 TL/500 ml at 1 h
For annual labor cost =52.00 hours/year

The annual chemical cost for NaOH during US system=5.00 TL/hour * 52.00 hours/year=260 TL/500 ml wastewater in bottle for 1 year
=173.33 $/500 ml wastewater in bottle for 1 year
=136.84 €/500 ml wastewater in bottle for 1 year

Table 5.205 summarizes the annual chemical cost estimation in different AOPs and in PCI, OMI and TI wws throughout sonication.

Table 5.205 The annual chemical cost of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Chemicals**	**Amount of Chemicals Consumed (g)**	**Cost of Chemicals ($)**	**Total Annual Chemical Cost ($/year)**	**Total Annual Cost ($/year)**
PCI ww	US	PAHs, COD, TOC	-	-	-	-	-
PCI ww	US	PAHs, COD, TOC	O_2(g)	$5.00x10^2$	$4.33x10^2$	$4.33x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	N_2(g)	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	H_2O_2	$5.00x10^2$	$2.60x10^2$	$2.60x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	TiO_2	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	NaCl	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	Fe^{+2}	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	Fe^{+3}	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	HCO_3^{-1}	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	C_4H_9OH	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	H_2SO_4	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	$1.35x10^5$
PCI ww	US	PAHs, COD, TOC	NaOH	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	$1.35x10^5$

Table 5.206 summarizes the chemical cost estimation in different AOPs and in PCI, OMI and TI wws throughout sonication.

Table 5.206 Chemical costs ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Chemicals**	**Amount of Chemicals Consumed (g)**	**Cost of Chemicals ($)**	**Total Cost of Chemicals ($)**	**References**
OMI ww	UV	phenol	-	-	-	-	Kidak & Ince (2007)
OMI ww	O_3	phenol	-	-	-	-	Kidak & Ince (2007)
OMI ww	Fenton	phenol	$CuSO_4$	$1.31x10^5$	$2.88x10^2$	$1.91x10^6$	Entezari et al. (2003)
OMI ww		phenol	H_2O_2	$2.16x10^9$	$1.91x10^6$	-	Entezari et al. (2003)
OMI ww	US	phenol	-	-	-	-	In this study
TI ww	UV	color	-	-	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3	color	-	-	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	US	color	$O_2(g)$	$5.00x10^2$	$4.33x10^2$	$4.33x10^2$	In this study
TI ww	US	color	$N_2(g)$	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	In this study
TI ww	US	color	H_2O_2	$5.00x10^2$	$2.60x10^2$	$2.60x10^2$	In this study
TI ww	US	color	TiO_2	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	In this study
TI ww	US	color	NaCl	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	In this study
TI ww	US	color	Fe^{+2}	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	In this study
TI ww	US	color	Fe^{+3}	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	In this study
TI ww	US	color	HCO_3^{-1}	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	In this study
TI ww	US	color	C_4H_9OH	$5.00x10^2$	$1.73x10^2$	$1.73x10^2$	In this study

5.19.6.4 Electrical Cost for US System

Electrical costs were based on the power consumption by a given AOP. The electricity cost was calculated at a rate of 0.165454 TL/kWh (=0.11 $/kWh=0.09 €/kWh). Power consumption was calculated for each AOP based upon the power consumed in a year multiplied by the electricity rate. Electrical costs ($) of various AOPs is demonstrated in Table 5.207.

In this study;

Power consumption in the US system=The sum of power consumed by US system in an hour=640 W/hour=0.64 kW/hour

Power consumption in the US system=The sum of power consumed by US system in a day=640 W/hour * 5 hours/day=3200 W/day= 3.20 kW/day

Power consumption in the US system=The sum of power consumed by US system in a week=640 W/hour * 5 hours/day * 5 days/week=16000 W/week=16.00 kW/week

Power consumption in the US system=The sum of power consumed by US system in a month=640 W/hour * 5 hours/day * 5 days/week * 4 weeks/month=64000 W/month=64.00 kW/month

Power consumption in the US system=The sum of power consumed by US system in a year=640 W/hour * 5 hours/day * 5 days/week * 52 weeks/year=832000 W/year =832.00 kW/year.

Note: 1 kWh=3.60×10^6 j=3.60×10^3 kj.

Note: Electrical energy consumed index constant per hour is 1.083 kW/hour.

In this study;

Total energy consumed in an hour=(1.083 kW/h) * 0.64 kW/h

=0.69 kW/h

Total energy consumed in a day=(1.083 kWh) * 3.20 kW/day * (24 hours/day)

=83.17 kWh/day

Total energy consumed in a week=(1.083 kWh) * 16.00 kW/week * (5 days/week) * 5 hours/day=433.20 kWh/week

Total energy consumed in a month=(1.083 kWh) * 64.00 kW/month * (4 weeks/month) * (5 days/week) * (5 hours/day)=6931.20 kWh/month

Total energy consumed in a year=(1.083 kWh) * (832 kW/year) * (52 weeks/year) * (5 day/week) * (5 hours/day)=1171372.80 kWh/year

Note: Rate of electricity=0.165454 TL/kWh=0.17 TL/kWh=0.11 $/kWh=0.09 €/kWh

In the present study;

The total hourly electrical cost=0.165454 TL/kWh * 0.69 kWh

=0.114 TL/hour

=0.076 $/hour.

=0.060 €/hour

The total daily electrical cost=0.165454 TL/kWh * 83.17 kWh

=13.761 TL/day

=9.174 $/day

=7.243 €/day

The total weekly electrical cost=0.165454 TL/kWh * 433.20 kWh
=71.675 TL/week
=47.78 $/week
=37.72 €/week

The total monthly electrical cost=0.165454 TL/kWh * 6931.20 kWh
=1146.80 TL/month
=764.53 $/month
=603.58 €/month

The total annual electrical cost=0.165454 TL/kWh * 1171372.80 kWh
=193808.32 TL/year
=129205.55 $/year
=102004.38 €/year

Table 5.207 summarizes the electrical cost estimation in different AOPs and in PCI, OMI and TI wws throughout sonication.

Table 5.207 Electrical costs ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Removal Efficiencies (%) (at 60°C)**	**Power Consumed (kW/year)**	**Total Annual Power Consumed (kWh/year)**	**Power Cost ($) [a]**	**References**
OMI ww	UV	phenol	-	$1.65x10^{5}$	$1.08x10^{10}$	$8.63x10^{8}$	Kidak & Ince (2007)
OMI ww	US	phenol	-	$1.92x10^{4}$	$1.68x10^{8}$	$1.35x10^{7}$	Fung et al. (2000a)
OMI ww	Fenton	phenol	-	-	-	-	Entezari et al. (2003)
OMI ww	US	**(b)**	66.83% COD_{dis}	832.00	$1.17x10^{6}$	$1.29x10^{5}$	In this study
TI ww	US	color	-	$1.88x10^{4}$	$1.65x10^{8}$	$1.35x10^{7}$	Drijvers et al. (1999)
TI ww	O_3	color	-	34.98	$3.06x10^{7}$	$2.45x10^{6}$	Tezcanli-Guyer & Ince (2004)
TI ww	US	**(c)**	84.92% COD_{dis}	832.00	$1.17x10^{6}$	$1.29x10^{5}$	In this study
PCI ww	US	**(d)**	96.90% PAHs	832.00	$1.17x10^{6}$	$1.29x10^{5}$	In this study

a: Electricity rate was assumed to be 0.17 TL/kWh=0.11 $/kWh; (b): COD_{dis}, TOC, color, total phenol, TAAs and TFAs; (c): COD_{dis}, TOC, color and TAAs; (d): Total PAHs, COD_{dis} and TOC.

5.19.6.5 Part Replacement Cost for Sonication Process

Part replacement cost may include bulb replacements for UV systems, O_3 generator parts for O_3 system, catalyst holder replacements for catalytic systems, tip replacements or electronic circuit replacements or transducer element replacements for ultrasound systems. The part replacement costs were assumed to be 0.50% of the capital cost (Melin, 1999; Mahamuni & Adewuyi, 2010). For UV systems, the part replacement costs were assumed to be 45.00% of the annual electrical power consumption costs (Hyman & Dupont, 2001; U.S. EPA, 2006). For O_3 systems, the annual part replacement cost was assumed to be 1.50% of the capital cost (Melin, 1999). Part replacement cost ($) of various AOPs is shown in Table 5.208.

In this study;

Part replacement cost=0.50% of capital cost of US system
=0.005 * 1500 TL/year
=7.50 TL/year
=5.00 $/year
=3.95 €/year

Table 5.208 summarizes the part replacement cost estimation in different AOPs and in PCI, OMI and TI wws throughout sonication.

Table 5.208 Part replacement cost ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Removal Efficiencies (%) (at 60^{o}C)**	**Part Replacement Cost ($/year)**	**References**
OMI ww	UV (45.00% of electrical cost)	phenol	-	5.19x10^{7}	Kidak & Ince (2007)
OMI ww	O_3 (1.50% of capital cost)	phenol	-	5.10x10^{2}	Kidak & Ince (2007)
OMI ww	Fenton	phenol	-	-	Entezari et al. (2003)
OMI ww	US	**(a)**	66.83% COd$_{dis}$	5.00	In this study
TI ww	UV (45.00% of electrical cost)	color	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3 (1.50% of capital cost)	color	-	3.06x10^{3}	Tezcanli -Güyer & Ince (2004)
TI ww	US	**(b)**	84.92% COd$_{dis}$	5.00	In this study
PCI ww	US	**(c)**	96.90% PAHs	5.00	In this study

(a): COD$_{dis}$, TOC, color, total phenol, TAAs and TFAs; (b): COD$_{dis}$, TOC, color and TAAs; (c): Total PAHs, COD$_{dis}$ and TOC.

In the present study;

Total O&M cost= total annual labor cost + total annual analytical cost + total annual chemical cost + total annual electrical cost + total annual part replacement cost

Total O&M cost=3120 TL + 3120 TL + 3380 TL + 193808.32 TL + 7.50 TL
=203435.82 TL/year
=135623.88 $/year
=107071.50 €/year

In this study;

Total annual operating cost for US system=Total amortized annual capital cost + annual O&M cost=1620 TL + 203435.82 TL/year=205055.82 TL/year
=136703.88 $/year
=107924.12 €/year

Annual operating and maintenance (O & M) cost estimation ($) of various AOPs for degradation of some parameters are shown in Table 5.209.

In this study;

The total annual cost = total annual labor cost + total annual analytical cost + total annual chemical cost + total annual electrical cost + total annual capital cost + total annual part replacement cost

Total annual cost=3120 TL + 3120 TL + 3380 TL + 193808.32 TL + 1500 TL + 7.50 TL=204935.82 TL/year
=136623.88 $/year
=107860.96 €/year

Table 5.209 Annual O & M cost estimation ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	Item	Removed Parameter	Removal Efficiencies (%) (at $60^{o}C$)	Part Replacement Cost ($/y)	Labor Cost ($/y)	Analytical Cost ($/y)	Chemical Cost ($/y)	Electrical Cost ($/y)	Total Annual O&M Cost ($/y)	References
OMI ww	UV	phenol	-	$5.19x10^{7}$	$3.89x10^{4}$	$3.12x10^{4}$	-	$1.15x10^{8}$	$1.67x10^{8}$	Kidak & Ince (2007)
OMI ww	O_3	phenol	-	$5.10x10^{3}$	$4.54x10^{4}$	$4.16x10^{4}$	-	$5.09x10^{4}$	$1.43x10^{5}$	Kidak & Ince (2007)
OMI ww	Fenton	phenol	-	-	$4.77x10^{4}$	$3.12x10^{4}$	$1.91x10^{6}$	-	$1.99x10^{6}$	Entezari et al. (2003)
OMI ww	US	**(a)**	66.83% COD_{dis}	5.00	$2.08x10^{3}$	$2.08x10^{3}$	$2.25x10^{3}$	$1.29x10^{5}$	$1.35x10^{5}$	In this study
TI ww	UV	color	-	-	-	-	-	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3	color	-	$3.06x10^{4}$	$4.54x10^{5}$	$4.16x10^{5}$	-	$2.45x10^{5}$	$1.15x10^{6}$	T.-Güyer & Ince (2004)
TI ww	US	**(b)**	84.92% COD_{dis}	5.00	$2.08x10^{3}$	$2.08x10^{3}$	$2.25x10^{3}$	$1.29x10^{5}$	$1.35x10^{5}$	In this study
PCI ww	US	**(c)**	96.90% PAHs	5.00	$2.08x10^{3}$	$2.08x10^{3}$	$2.25x10^{3}$	$1.29x10^{5}$	$1.35x10^{5}$	In this study

(a): COD_{dis}, TOC, color, total phenol, TAAs and TFAs; (b): COD_{dis}, TOC, color and TAAs; (c): Total PAHs, COD_{dis} and TOC.

5.19.7 General Procedure for Calculation of Electric Energy per Order (EE / O) or Electrical Energy per Unit Mass (EE / M)

5.19.7.1 EE/O Calculation for US System

Electric energy per order (EE/O) is the electric energy in kilowatt hours [kWh] required to degrade a contaminant by one order of magnitude in a unit volume (e.g., 1 m^3 = 1000 l) of contaminated water or air Bolton et al., 2001). This figure-of-merit is best used for situations where final concentration, (C_A, mg/l) is low (i.e., cases that are overall first-order in concentration of pollutant) because the amount of electric energy required to bring about a reduction by one order of magnitude in concentration is independent of (C_A). Thus, it would take the same amount of electric energy to reduce the contaminant concentration from 10.00 mg/l to 1.00 mg/l in a given volume as it would to reduce it from 10.00 µg/l to 1.00 µg/l. EE/O is, in general, a measure of operating cost. It allows for easy and accurate scale up to a full scale design and costs. EE/O is defined by Bolton et al. (2001) as Eq. (5.115).

$$EE/O = \frac{P_{elec} * t * 1000}{V * 60 * \log\left(\frac{C_{AO}}{C_A}\right)} \tag{5.115}$$

where;

EE/O: Electric energy per order , (kWh/m^3/order)
P_{elec}: The input power (kW) to the AOP system
t: The irradiation time (min)
V: The volume in liter of water in the reactor (l)
C_{AO}: Initial concentration in ppm (mg/l)
C_A: Final concentration in ppm (mg/l)

5.19.7.1.1 EE/O Calculation for US System in PCI ww.

In this study, for PCI ww at 25^{o}C;

Sonication power=640 W

Sonication time=150 min

Sonication volume=V=500 ml=0.50 l

$COD_0=COD_{influent}$=1027.43 mg/l

$COD_{effluent}$=203.835 mg/l

EE/O=[0.64 kW * 150 min * 1000] / [0.50 l * 60 * log (1027.43/203.835)]

=4481.80 kWh/m^3/order COD_{dis}

The electrical cost=0.165454 TL/kWh * 4481.80 kWh/m^3/order COD_{dis}

=741.53 TL/m^3/order COD_{dis}

=494.35 $/ m^3/order COD_{dis}

=390.28 €/m^3/order COD_{dis}

5.19.7.1.2 EE/O Calculation for US System in OMI ww.

In this study, for OMI ww at 25^{o}C;

Sonication power=640 W

Sonication time=150 min

Sonication volume=V=500 ml=0.50 l

$COD_0=COD_{influent}$=109444 mg/l

$COD_{effluent}$=42779 mg/l

EE/O=[0.64 kW * 150 min * 1000] / [0.50 l * 60 * log (109444/42779)]

=7804.88 kWh/m^3/order COD_{dis}

The electrical cost=0.165454 TL/kWh * 7804.88 kWh/m^3/order COD_{dis}

=1291.35 TL/m^3/order COD_{dis}

=860.90 $/ m^3/order COD_{dis}

=679.66 €/m^3/order COD_{dis}

5.19.7.1.3 EE/O Calculation for US System in TI ww.

In this study, for TI ww at 25°C;

Sonication power=640 W

Sonication time=150 min

Sonication volume=V=500 ml=0.50 l

COD_0=$COD_{influent}$=962.99 mg/l

$COD_{effluent}$=247.75 mg/l

EE/O=[0.64 kW * 150 min * 1000] / [0.50 l * 60 * log (962.99/247.75)]
=5427.33 kWh/m^3/order COD_{dis}

The electrical cost=0.165454 TL/kWh * 5427.33 kWh/m^3/order COD_{dis}
=897.97 TL/m^3/order COD_{dis}
=598.65 \$/ m^3/order COD_{dis}
=472.62 €/m^3/order COD_{dis}

5.19.7.2 EE/M Calculation for US System

For zero order degradations, EE/M (electrical energy per unit mass) is used instead of EE/O. EE/M is defined as Eq. (5.116):

$$EE/M = \frac{P_{elec} * t * 1000}{V * M * 60 * \left(C_{AO} - C_A\right)} \tag{5.116}$$

where;

EE/M: Electrical energy per unit mass (kWh/kg/order)

M: Mass (kg)

P_{elec}: The input power (kW) to the AOP system

t: The irradiation time (min)

V: The volume in liter of water in the reactor

C_{AO}: Initial concentration in ppm (mg/l)

C_A: Final concentration in ppm (mg/l)

5.19.7.2.1 EE/M Calculation for US System in PCI ww.

In this study, for PCI ww at 25°C;

Sonication power=640 W

Sonication time=150 min

Sonication volume=V=500 ml=0.50 l

$COD_0=COD_{influent}=1027.43$ mg/l

$COD_{effluent}=203.835$ mg/l

EE/M=[0.64 kW * 150 min * 1000] / [0.50 l * 0.001 kg/g * 60 * (1027.43-203.835)]
=3995.41 kWh/kg/order COD_{dis}

The electrical cost=0.165454 TL/kWh * 3995.41 kWh/kg/order COD_{dis}
=661.06 TL/kg/order COD_{dis}
=440.70 $/ kg/order COD_{dis}
=347.93 €/kg/order COD_{dis}

5.19.7.2.2 EE/M Calculation for US System in OMI ww.

In this study, for OMI ww at 25°C;

Sonication power=640 W

Sonication time=150 min

Sonication volume=V=500 ml=0.50 l

$COD_0=COD_{influent}=109444$ mg/l

$COD_{effluent}=42779$ mg/l

EE/M=[0.64 kW * 150 min * 1000] / [0.50 l * 0.001 kg/g * 60 * (109444-42779)]
=48.00 kWh/kg/order COD_{dis}

The electrical cost=0.165454 TL/kWh * 48.00 kWh/kg/order COD_{dis}
=7.94 TL/kg/order COD_{dis}
=5.30 $/ kg/order COD_{dis}
=4.18 €/kg/order COD_{dis}

5.19.7.2.3 EE/M Calculation for US System in TI ww.

In this study, for TI ww at 25^{o}C;

Sonication power=640 W

Sonication time=150 min

Sonication volume=V=500 ml=0.50 l

COD_0=$COD_{influent}$=962.99 mg/l

$COD_{effluent}$=247.75 mg/l

EE/M=[0.64 kW * 150 min * 1000] / [0.50 l * 0.001 kg/g * 60 * (962.99-247.75)]

=4474.02 kWh/kg/order COD_{dis}

The electrical cost=0.165454 TL/kWh * 4474.02 kWh/kg/order COD_{dis}

=740.25 TL/kg/order COD_{dis}

=493.50 $/ kg/order COD_{dis}

=389.60 €/kg/order COD_{dis}

5.19.8 Specific Energy Calculations for US System

The specific energy was calculated according to the Eq. (4.3) given in 4.2.1.8 Section at Chapter 4:

$$E_s \ (kWh/kg\ COD_0) = \frac{Sonicator\ \ power(W)*Time(h)*(1\,kj/1000\,j)}{V(l)*COD_0\,(g/l)*(1\,kg/1000g)} \tag{4.3}$$

where;

E_s: The specific energy for the maximum COD_{dis} removal after sonication process (kWh/kg COD_0),

Sonicator power: The input power of sonicator during sonication experiments (W),

Time: The sonication time during sonication process (h),

(1 kj/1000 j): The equation of transformation from 1 kilojoule to 1 joule,

V: The sample volume during sonication process (l),

COD_0: Initial COD_{dis} concentration before sonication process (g/l),

(1 kg/1000 g): the equation of transformation from 1 kilogram to 1 gram.

5.19.8.1 The Specific Energy (E_s) Calculation for US System in PCI ww

In this study, for PCI ww at 25°C;

Sonication power=640 W

Sonication time=150 min=2.50 h

Sonication volume=V=500 ml=0.50 l

COD_0=1027.43 mg/l=1.02743 g/l

E_s = {[(640 W * 2.50 h * 1 kj/1000 j)] / [(0.50 l * 1.02743 g/l * 1 kg/1000g)]}

=3114.57 Wh / kg COD_0

=3.12 kWh / kg COD_0

The electrical cost=0.165454 TL/kWh * 3.12 kWh/ kg COD_0

=0.52 TL/kg COD_0

=0.34 $/ kg COD_0

=0.27 €/ kg COD_0

5.19.8.2 The Specific Energy (E_s) Calculation for US System in OMI ww

In this study, for OMI ww at 25°C;

Sonication power=640 W

Sonication time=150 min=2.50 h

Sonication volume=V=500 ml=0.50 l

COD_0=109444 mg/l=109.444 g/l

E_s = {[(640 W * 2.50 h * 1 kj/1000 j)] / [(0.50 l * 109.444 g/l * 1 kg/1000g)]}

=29.24 Wh / kg COD_0

=0.03 kWh / kg COD_0

The electrical cost=0.165454 TL/kWh * 0.03 kWh/ kg COD_0

=0.0050 TL/kg COD_0

=0.0033 $/ kg COD_0

=0.0026 €/ kg COD_0

5.19.8.3 The Specific Energy (E_s) Calculation for US System in TI ww

In this study, for TI ww at 25°C;

Sonication power=640 W

Sonication time=150 min=2.50 h

Sonication volume=V=500 ml=0.50 l

COD_0=962.99 mg/l=0.96299 g/l

E_s = {[(640 W * 2.50 h * 1 kj/1000 j)] / [(0.50 l * 0.96299 g/l * 1 kg/1000g)]}

=3322.98 Wh / kg COD_0

=3.32 kWh / kg COD_0

The electrical cost=0.165454 TL/kWh * 3.32 kWh/ kg COD_0

=0.55 TL/kg COD_0

=0.37 $/ kg COD_0

=0.29 €/ kg COD_0

5.19.9 The Cost Comparison of Anaerobic, Aerobic, UV, O_3 and Sonication Treatment

In this study, total enery consumed in a day was calculated to 83.17 kWh/day. The total energy consumed is equal to 83.40 kW/day to obtain 80.00% PAHs yields at a sonication time of 120 min with a flow rate of 1 l/min at a power of 640 W without additives (Melin, 1999; Mahamuni & Adewuyi, 2010). In this study, the total enery consumed in a day is lower than total enery consumed in a day obtained by Melin (1999) and Mahamuni & Adewuyi (2010) as mentioned above.

In this study, the annual chemical cost of TiO_2, H_2O_2 and N_2(g) sparged were calculated as 260, 390 and 260 TL/year (136.84, 205.26 and 136.84 €/year), respectively. For TiO_2, H_2O_2 and N_2(g) sparged systems the annual chemical cost was calculated as 67.00-60.00 and 40.00 Euro/year (127.30, 114.00 and 76.00 TL/year), respectively (Melin, 1999; Mahamuni & Adewuyi, 2010). In this study, the total annual chemical cost of TiO_2, H_2O_2 and N_2(g) sparged is higher than the total annual chemical cost obtained by Melin (1999) and Mahamuni & Adewuyi (2010) as mentioned above.

In this study, the total annual cost was calculated as 202205.82 TL/year (=134803.88 \$/year=106424.12 €/year) with O_2(g) sparging condition including the labor costs, analytical costs, chemical costs, energy (electrical) costs, capital costs and part replacement costs. The removal of PAHs with UV, O_3 and photocatalytic processes the annual total cost increased to $7.35x10^9$, $1.00x10^7$ and $1.276x10^{10}$ €/year ($1.39x10^{10}$, $1.90x10^7$ and $2.42x10^{10}$ TL/year), respectively (Melin, 1999; Mahamuni & Adewuyi, 2010). In this study, the total annual cost of O_2(g) sparged is lower than the total annual cost obtained by Melin (1999) and Mahamuni & Adewuyi (2010) as mentioned above.

Table 5.210 summarizes the cost comparison of anaerobic, aerobic, UV, O_3 and sonication treatment. The electrical energy requirements of conventional activated sludge process reported by Eckenfelder et al. (2008) between 250 and 1000 kWh/m^3 water (75.00–300.00 TL m^3/h=655200–2620800 TL m^3/year=436800–1747200 \$/year=344842.11–1379368.42 €/year) with mechanic mixing and recycle pump equipments (1 kWh/m^3 electric energy was assumed 0.30 TL m^3/h). In this study, 193808.32 TL/year (=129205.55 \$/year=102004.38 €/year) total annual electrical cost was observed for sonication process in PCI ww, OMI ww and TI ww. In this study, the total annual electrical cost is lower than the total annual electrical cost obtained by Eckenfelder et al. (2008) as mentioned above.

Table 5.210 The cost comparison of Anaerobic, Aerobic, UV, O_3 and Sonication treatment processes (Eckenfelder et al., 2008).

Parameters	**Anaerobic Treatment**	**Aerobic Treatment**	**UV Treatment**	**O_3 Treatment**	**Sonication Treatment**
Energy requirements	Low	High	High	Medium	Low
Nutrient requirements	Low	High (for certain industrial wastes)	No	No	No
Alkalinity requirements	High (for certain industrial wastes)	Low	No	No	Low
Chemicals costs	High	Medium	No	No	Low
Reactor requirement	High	Medium	High	High	Low
Part replacement cost (generator, piping, pumps, valves, etc).	High	High	High	High	Low
Analytical cost	High	Medium	Medium	High	Low
CH_4 production cost	High	No	No	No	No
Natural gas (biogas) production cost (electric energy requirement in anaerobic digester)	Yes (net benefit is contingent on the need for reactor heating)	No	No	No	No

Table 5.210 The cost comparison of Anaerobic, Aerobic, UV, O_3 and Sonication treatment processes (Eckenfelder et al., 2008) (cont.).

Parameters	**Anaerobic Treatment**	**Aerobic Treatment**	**UV Treatment**	**O_3 Treatment**	**Sonication Treatment**
Sludge production (mechanic mixing, recycle pump, etc.)	Low	High	No	No	No
Site work	Low	High	Medium	Medium	Very low
Site / area requirement	Low	High	Medium	Medium	Very low
Labor costs	High	High	High	High	Very low
Engineering costs	High	High	High	High	Very low
Contractor costs	High	High	High	High	Very low
Contingency costs	High	High	High	High	Low
Cleaning costs	High	High	Low	Low	Very low
Capital cost	High	High	High	Medium	Low

Tchobanoglous & Burton (1991) determined the electrical energy requirements of $CH_4(g)$ gas production from 60.00 to 100.00 kWh/m^3 water (18.00–30.00 TL m^3/h=157248–262080 TL m^3/year=104832–174720 \$/year=82762.11–137936.84 €/year) in an anaerobic digester. In this study, 193808.32 TL/year (=129205.55 \$/year=102004.38 €/year) total annual electrical cost was measured for sonication process in PCI ww, OMI ww and TI ww. In this study, the total annual electrical cost is lower than the total annual electrical cost found by Tchobanoglous & Burton (1991) as mentioned above.

Although, Zhang, G. et al. (2008) found the electrical energy requirement of sonication process only 1.00–10.00 kWh/m^3 water (0.30–3.00 TL m^3/h=2620.80-26208 TL m^3/year=1747.20–17472 \$/year=1379.37–13793.70 €/year) in a sonicator. In this study, 193808.32 TL/year (=129205.55 \$/year=102004.38 €/year) total annual electrical cost was measured for sonication process in PCI ww, OMI ww and TI ww. In this study, the total annual electrical cost is higher than the total annual electrical cost obtained by Zhang, G. et al. (2008) as mentioned above.

Also, the electrical energy consumption of natural gas (biogas, etc) production was higher than 110.00 kWh/m^3 water (33.00 TL m^3/h=288288 TL m^3/year=192192 \$/year=151730.53 €/year) in an anaerobic digester reported by Tchobanoglous & Burton (1991). In this study, 193808.32 TL/year (=129205.55 \$/year=102004.38 €/year) total annual electrical cost was calculated for sonication process in PCI ww, OMI ww and TI ww. In this study, the total annual electrical cost is lower than the total annual electrical cost observed by Tchobanoglous & Burton (1991) as mentioned above.

5.19.10 Conclusions

The sonication process does not require the use of extra chemicals (e.g. oxidants and catalysts) commonly employed in several AOPs (for instance, ozonation, Fenton's reagent), thus avoiding the respective costs as well as the need to remove the excess of toxic compounds prior to discharge (Psillakis et al., 2004). The operating and maintenance (O&M) cost in sonication systems consists of labor costs, analytical costs, chemical costs, electrical costs and part replacement costs.

For ultrasonic systems, the annual analysis labor time is 52 hours/year (sampling frequency is 2 samples/week), sampling time (1.00 hours/week) while the total annual labor cost is 3120 TL/year (=2080 \$/year=1642.11 €/year).

In the present study, the total annual analytical cost was calculated as 3120 TL/year (=2080 \$/year=1642.11 €/year) with sonication process in PCI ww, OMI ww and TI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time.

The capital cost and the part replacement costs in this study were 1500 TL/year (=1000 \$/year=789 €/year) and 7.50 TL/year (=5.00 \$/year=3.95 €/year), respectively.

In this study, the total energy consumed in this study was measured as 3.20 kW/day to obtain 79.65% total PAHs removal without additives at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25^{o}C. The annual total energy utilization was 832 kWh/year while the annual total energy cost was 193808.32 TL/year =129205.55 \$/year=102004.38 €/year). The electricity cost was calculated at a rate of electricity of 0.17 TL/kWh (=0.11 \$/kWh=0.09 €/kWh).

4481.80, 5427.33 and 7804.88 kW/m^3/order COD electric energy per order (EE/O) values calculated in PCI ww, TI ww and OMI ww, respectively, at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, without additives, after 150 min sonication time at 25°C. 741.53, 897.97 and 1291.35 TL/m^3/order COD electrical costs were obtained in PCI ww, TI ww and OMI ww, respectively, for EE/O values during sonication process.

48.00, 3995.41 and 4474.02 kWh/kg/order COD electrical energy per unit mass (EE/M) values were measured in OMI ww, PCI ww and TI ww, respectively, at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, without additives, after 150 min sonication time at 25°C. 7.94, 661.06 and 740.25 TL/kg/order COD electrical costs were calculated in OMI ww, PCI ww and TI ww, respectively, for EE/M values during sonication process.

0.03, 3.12 and 3.32 kWh / kg COD_0 specific energy (E_s) values were calculated in OMI ww, PCI ww and TI ww, respectively, at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, without additives, after 150 min sonication time at 25°C. 0.005, 0.52 and 0.55 TL/kg COD_0 electrical costs were observed in OMI ww, PCI ww and TI ww, respectively, for E_s values during sonication process (Appendix 7.47).

In this study, the total annual cost for only sonication (without additives) was calculated as follows:

Total annual cost= total annual labor cost + total annual analytical cost + total annual electrical cost + total annual capital cost + total annual part replacement cost. 201555.82 TL/year (=134370.55 \$/year=106082.01 €/year) total annual cost was calculated for only sonication process without additives in PCI ww (Appendix 7.48).

In this study, the total annual cost for sonication with O_2(g) sparging was calculated as follows:

Total annual cost with O_2(g) sparging=total annual labor cost + total annual analytical cost + total annual O_2(g) chemical cost + total annual electrical cost + total annual capital cost + total annual part replacement cost. 202205.82 TL/year

(=134803.88 \$/year=106424.12 €/year) total annual cost was calculated for sonication with O_2(g) sparging conditions in PCI ww (Appendix 7.49).

In this study, the total annual cost of sonication with H_2O_2 addition was calculated as follows:

Total annual cost with H_2O_2 addition=total annual labor cost + total annual analytical cost + total annual H_2O_2 chemical cost + total annual electrical cost + total annual capital cost + total annual part replacement cost. 201945.82 TL/year (=134630.55 \$/year=106287.27 €/year) total annual cost was calculated for sonication with H_2O_2 addition conditions in PCI ww.

In this study, the total annual cost of sonication with TiO_2 addition was calculated as follows:

Total annual cost with TiO_2 addition=total annual labor cost + total annual analytical cost + total annual TiO_2 chemical cost + total annual electrical cost + total annual capital cost + total annual part replacement cost. 201815.82 TL/year (=134543.88 \$/year=106218.85 €/year) total annual cost was calculated for sonication with TiO_2 addition conditions in PCI ww.

Finally, sonication process is cheaper than that the anaerobic, aerobic treatment processes and than the other AOPs processses. Sonication process is a cost-effective AOP for the treatment of toxic and recalcitrant compounds in PCI ww, OMI ww and TI ww, compared to the anaerobic, aerobic, UV and O_3 treatment processes (Table 5.210).

CHAPTER SIX
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The results of this study showed that sonodegradation is a very useful process in the removal of toxic and refractory compounds in PCI, OMI and TI wws. Low frequency (35 kHz) sonication proved to be a viable tool for the effective degradation of refractory compounds in PCI, OMI and TI wws. The removals increased after 120 and 150 min sonication times at 30°C and at 60°C. The sonication process could prove to be less land-intensive, less expensive and require less maintenance than traditional biological treatment processes and other AOPs processes. Sonication technology can provide a cost-effective alternative for destroying and detoxifying refractory compounds in PCI, OMI and TI wws.

6.1.1 The Removal of Toxic and Refractory Compounds in PCI ww, OMI ww and TI ww during Sonication Process with only Sonication

In this section, COD_{dis}, TOC and total PAHs removal efficiencies in PCI ww; COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals in OMI ww and COD_{dis}, TOC, color and TAAs yields in TI ww were measured during sonication process with only sonication. The effects of only sonication to the yields of the parameters given above were isvestigated. Toxic and refractory compounds removal efficiencies were determined in PCI ww, OMI ww and TI ww after 120 and 150 min sonication times at 30°C and at 60°C with only sonication.

6.1.1.1 The Removal of Toxic and Refractory Compounds in PCI ww during Sonication Process with only Sonication

The maximum COD_{dis} (E=92.48%), TOC (E=94.23%) and total PAHs (E=96.90%) yields in PCI ww were obtained at 60°C after 150 min sonication time only with sonication.

6.1.1.2 The Removal of Toxic and Refractory Compounds in OMI ww during Sonication Process with only Sonication

The maximum color (E=83.77%), total phenol (E=61.24%), TAAs (E=70.52%) removals in OMI ww were observed at 60°C after 150 min sonication time only with sonication.

6.1.1.3 The Removal of Toxic and Refractory Compounds in TI ww during Sonication Process with only Sonication

The maximum COD_{dis} (E=84.92%), TOC (E=83.22%), color (E=87.66%) yields in TI ww were measured at 60°C after 150 min sonication time only with sonication.

6.1.2 The Removal of Toxic and Refractory Compounds in PCI ww, OMI ww and TI ww during Sonication Process with the Addition of Some Chemicals

In this section, COD_{dis}, TOC and total PAHs removal efficiencies in PCI ww; COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals in OMI ww; COD_{dis}, TOC, Color and TAAs yields in TI ww were measured during sonication process with the addition of some chemicals (for example, air, N_2(g), acids or alkaline chemicals, DO, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1}, C_4H_9OH, etc. The removal yields in the parameters given above were investigated in PCI ww, OMI ww and TI ww after 120 and 150 min sonication times at 30°C and at 60°C with the addition of some chemicals.

6.1.2.1 COD_{dis}, TOC and Total PAHs removal efficıencıes in PCI ww during Sonication Process with the Addition of Some Chemicals

The maximum COD_{dis} (E=99.68%), total PAHs (E=97.62%) yields in PCI ww were obtained with 1 h aeration at 60°C after 150 min sonication time. The maximum TOC (E=95.27%) yield in PCI ww were found with 1 h aeration at 30°C after 150 min sonication time.

The maximum COD_{dis} (E=96.27%), TOC (E=96.69%), total PAHs (E=96.27%) removals in PCI ww were observed with 30 min N_2(g) (6.00 mg/l N_2) sparging at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=96.90%), total PAHs (E=96.09%) yields in PCI ww were obtained at pH=7.0 and at 60°C after 150 min sonication time. The maximum TOC (E=95.27%) removal in PCI ww were measured at pH=7.0 and at 30°C after 150 min sonication time.

The maximum COD_{dis} (E=97.23%), TOC (E=98.35%), total PAHs (E=97.23%) yields in PCI ww were observed with DO=10.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=98.04%), TOC (E=95.88%), total PAHs (E=98.04%) removals in PCI ww were found with H_2O_2=2000 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=93.88%), TOC (E=93.20%), total PAHs (E=93.88%) yields in PCI ww were observed with TiO_2=20.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=99.68%), TOC (E=98.30%), total PAHs (E=99.68%) removals in PCI ww were measured with NaCl=15.00 g/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=98.56%), TOC (E=95.73%), total PAHs (E=98.56%) yields in PCI ww were obtained with Fe^{+2}=20.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=96.76%), TOC (E=92.45%), total PAHs (E=96.76%) removals in PCI ww were observed with Fe^{+3}=50.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=82.62%), TOC (E=83.09%) yields in PCI ww were measured with HCO_3^{-1}=5.00 g/l at 60^{o}C after 150 min sonication time. The maximum total PAHs (E=81.69%) removal in PCI ww were observed with HCO_3^{-1}=1.00 g/l at 30^{o}C after 150 min sonication time.

The maximum COD_{dis} (E=82.62%), TOC (E=82.75%), total PAHs (E=82.62%) removals in PCI ww were found with C_4H_9OH=2.00 g/l at 60^{o}C after 150 min sonication time..

6.1.2.2 The Removal Efficiencies of COD_{dis}, TOC, Color, Total Phenol, TAAs and TFAs in OMI ww during Sonication Process with the Addition of Some Chemicals

The maximum COD_{dis} (E=86.32%), TOC (E=85.26%), color (E=81.86%), total phenol (E=72.69%), TAAs (E=72.83%), TFAs (E=78.33%) removals in OMI ww were obtained with 1 h aeration at 60^{o}C after 150 min sonication time.

The maximum COD_{dis} (E=85.51%), TOC (E=83.76%), color (E=91.88%), total phenol (E=78.98%), TAAs (E=74.56%), TFAs (E=80.18%) yields in OMI ww were observed with 30 min N_2(g) (6.00 mg/l N_2) sparging at 60^{o}C after 150 min sonication time.

The maximum COD_{dis} (E=89.31%), TOC (E=88.16%), color (E=92.38%), total phenol (E=85.51%), TAAs (E=86.25%) removals in OMI ww were measured at pH=10.0 and at 60^{o}C after 150 min sonication time. The maximum TFAs (E=78.87%) yield in OMI ww were found at pH=7.0 and at 60^{o}C after 150 min sonication time.

The maximum COD_{dis} (E=88.73%), TOC (E=87.19%), color (E=93.79%), total phenol (E=91.38%), TAAs (E=91.58%), TFAs (E=74.44%) removals in OMI ww were obtained with DO=10.00 mg/l at 60^{o}C after 150 min sonication time.

The maximum COD_{dis} (E=93.19%), TOC (E=92.14%), color (E=93.59%), total phenol (E=93.65%), TAAs (E=83.68%), TFAs (E=90.30%) removals in OMI ww were measured with H_2O_2=2000 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=93.93%), TOC (E=93.35%), color (E=95.39%), total phenol (E=94.77%), TAAs (E=88.54%), TFAs (E=84.52%) yields in OMI ww were observed with TiO_2=20.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=93.15%), TOC (E=92.31%), color (E=96.09%), total phenol (E=93.72%), TAAs (E=91.44%), TFAs (E=71.23%) removals in OMI ww were found with NaCl=15.00 g/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=90.36%), TOC (E=89.62%), color (E=93.89%), total phenol (E=89.64%), TAAs (E=85.88%), TFAs (E=68.40%) yields in OMI ww were obtained with Fe^{+2}=20.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=90.75%), TOC (E=89.60%), color (E=91.08%), total phenol (E=92.58%), TAAs (E=89.56%), TFAs (E=65.93%) yields in OMI ww were found with Fe^{+3}=50.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=85.21%), TOC (E=84.92%), color (E=91.78%), total phenol (E=93.72%), TAAs (E=84.78%), TFAs (E=61.91%) removals in OMI ww were observed with HCO_3^{-1}=5.00 g/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=90.70%), TOC (E=89.17%), color (E=89.78%), total phenol (E=90.47%), TAAs (E=87.01%), TFAs (E=70.16%) yields in OMI ww were measured with C_4H_9OH=2.00 g/l at 60°C after 150 min sonication time.

6.1.2.3 The Removal Efficiencies of COD_{dis}, TOC, Color and TAAs in TI ww during Sonication Process with the Addition of Some Chemicals

The maximum COD_{dis} (E=84.28%), TOC (E=83.27%), color (E=90.25%) yields in TI ww were obtained with 1 h aeration at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=98.23%), TOC (E=98.26%), color (E=95.30%), TAAs (E=68.08%) removals in TI ww were observed with 30 min N_2(g) (6.00 mg/l N_2) sparging at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=94.70%), TOC (E=93.01%), color (E=95.06%), TAAs (E=64.89%) removals in TI ww were measured at pH=10.0 and at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=94.07%), TOC (E=92.77%), color (E=97.65%), TAAs (E=71.56%) yields in TI ww were found with DO=10.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=97.92%), TOC (E=95.98%), color (E=95.06%), TAAs (E=80.16%) removals in TI ww were observed with H_2O_2=2000 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=98.13%), TOC (E=98.18%), color (E=96.24%), TAAs (E=77.02%) removals in TI ww were obtained with TiO_2=20.00 mg/l and at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=97.32%), TOC (E=96.83%), color (E=97.53%), TAAs (E=65.33%) yields in TI ww were found with NaCl=15.00 g/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=99.26%), TOC (E=99.23%), color (E=96.59%), TAAs (E=76.91%) removals in TI ww were observed with Fe^{+2}=20.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=99.37%), TOC (E=99.35%), TAAs (E=70.24%) yields in TI ww were measured with Fe^{+3}=50.00 mg/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=82.50%), TOC (E=83.84%), color (E=96.12%), TAAs (E=65.49%) yields in TI ww were obtained with HCO_3^{-1}= 5.00 g/l at 60°C after 150 min sonication time.

The maximum COD_{dis} (E=82.40%), TOC (E=84.50%), color (E=94.48%), TAAs (E=65.52%) removals in TI ww were found with C_4H_9OH= 2.00 g/l at 60°C after 150 min sonication time.

6.1.3 Microtox and Daphnia magna Acute Toxicity Removal Efficiencies in PCI ww, OMI ww and TI ww with only Sonication Process

In this section, Microtox and *Daphnia magna* acute toxicity assays were applied to the sonicated and non-sonicated samples taken from PCI, OMI and TI wws during sonication process when some chemical additives were not used.

6.1.3.1 Acute Toxicity Removal Efficiencies in Microtox and Daphnia magna Tests for PCI ww during Sonication Process when Some Chemical Additives were not Used

The maximum acute toxicity removal (E=66.67%) in Microtox toxicity test for PCI ww were measured after 150 min sonication time at 30°C and at 60°C temperature only with sonication.

6.1.3.2 Microtox and Daphnia magna Acute Toxicicty Removal Efficiencies in OMI ww during Sonication Process with only Sonication

The maximum *Daphnia magna* acute toxicity (E=60.00%) removal in OMI ww were observed after 150 min sonication time at 30°C and at 60°C only with sonication.

6.1.3.3 Microtox and Daphnia magna Acute Toxicicty Removal Efficiencies in OMI ww during Sonication Process with only Sonication

The maximum Microtox acute toxicity (E=66.67%) in TI ww were measured after 150 min sonication time at 30°C and at 60°C only with sonication.

6.1.4 Microtox and Daphnia magna Acute Toxicity Removal Efficiencies in PCI ww, OMI ww and TI ww during Sonication Process with the Addition of Some Chemicals

In this section, the Microtox and *Daphnia magna* acute toxicity tests were performed in the samples containing some additives such as air, N_2(g), acids or alkaline chemicals, DO, H_2O_2, TiO_2, NaCl, Fe^{+2}, Fe^{+3}, HCO_3^{-1} and C_4H_9OH in PCI ww, OMI ww and TI ww after 150 min sonication time.

6.1.4.1 Microtox and Daphnia magna Acute Toxicity Removal Efficiencies in PCI ww during Sonication Process with the Addition of Some Chemicals

The maximum Microtox acute toxicity (E=83.33%), *Daphnia magna* acute toxicity (E=90.00%) yields in PCI ww were obtained with 1 h aeration at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=83.33%), *Daphnia magna* acute toxicity (E=90.00%) removals in PCI ww were measured with 30 min N_2(g) (6.00 mg/l N_2) sparging at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=66.67%) removal in PCI ww were observed at pH=7.0 and at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=77.78%), *Daphnia magna* acute toxicity (E=90.00%) yields in PCI ww were found with DO=10.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) removals in PCI ww were obtained with H_2O_2=500 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) yields in PCI ww were found with TiO_2=10.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) removals in PCI ww were obtained with NaCl=2.50 g/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=88.89%), *Daphnia magna* acute toxicity (E=80.00%) yields in PCI ww were observed Fe^{+2}=8.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=88.89%), *Daphnia magna* acute toxicity (E=80.00%) yields in PCI ww were obtained with Fe^{+3}=20.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=83.33%), *Daphnia magna* acute toxicity (E=80.00%) removals in PCI ww were measured with HCO_3^{-1}=1.00 g/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=88.89%), *Daphnia magna* acute toxicity (E=80.00%) removals in PCI ww were found with C_4H_9OH=0.50 g/l at 60°C after 150 min sonication time.

6.1.4.2 Microtox and Daphnia magna Acute Toxicity Removal Efficiencies in OMI ww during Sonication Process with the Addition of Some Chemicals

The maximum Microtox acute toxicity (E=83.33%), *Daphnia magna* acute toxicity (E=90.00%) yields in OMI ww were obtained with 1 h Aeration at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=83.33%), *Daphnia magna* acute toxicity (E=90.00%) removals in OMI ww were observed with 30 min N_2(g) (6.00 mg/l N_2) sparging at 60°C after 150 min sonication time.

The maximum *Daphnia magna* acute toxicity (E=70.00%) yield in OMI ww were measured at pH=10.0 and at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=77.78%), *Daphnia magna* acute toxicity (E=90.00%) removals in OMI ww were found with DO=10.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) yields in OMI ww were found with H_2O_2=500 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) removals in OMI ww were observed with TiO_2=10.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) yields in OMI ww were measured with NaCl=2.50 g/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) yields in OMI ww were found with Fe^{+2}=8.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=88.89%), *Daphnia magna* acute toxicity (E=80.00%) removals in OMI ww were measured with Fe^{+3}=20.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=83.33%), *Daphnia magna* acute toxicity (E=80.00%) yields in OMI ww were obtained with HCO_3^{-1}=1.00 g/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=83.33%), *Daphnia magna* acute toxicity (E=80.00%) removals in OMI ww were observed with C_4H_9OH=0.50 g/l at 60°C after 150 min sonication time.

6.1.4.3 Microtox and Daphnia magna Acute Toxicity Removal Efficiencies in TI ww during Sonication Process with the Addition of Some Chemicals

The maximum Microtox acute toxicity (E=83.33%), *Daphnia magna* acute toxicity (E=90.00%) yields in TI ww were found with 1 h aeration at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=83.33%), *Daphnia magna* acute toxicity (E=90.00%) removals in TI ww were measured with 30 min N_2(g) (6.00 mg/l N_2) sparging at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=72.22%), *Daphnia magna* acute toxicity (E=70.00%) yields in TI ww were observed at pH=10.0 and at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=77.78%), *Daphnia magna* acute toxicity (E=80.00%) yields in TI ww were obtained with DO=10.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) removals in TI ww were measured at H_2O_2=500 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) yields in TI ww were observed with TiO_2=10.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) removals in TI ww were observed with NaCl=2.50 g/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) yields in TI ww were found with Fe^{+2}=8.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=94.44%), *Daphnia magna* acute toxicity (E=90.00%) removals in TI ww were measured with Fe^{+3}=20.00 mg/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=88.89%), *Daphnia magna* acute toxicity (E=80.00%) yields in TI ww were obtained with HCO_3^{-1}= 1.00 g/l at 60°C after 150 min sonication time.

The maximum Microtox acute toxicity (E=88.89%), *Daphnia magna* acute toxicity (E=80.00%) removals in TI ww were observed with C_4H_9OH= 2.00 g/l at 60°C after 150 min sonication time.

6.1.5 Evaluation of Reaction Kinetics in PCI ww, OMI ww and TI ww during Sonication Process with only Sonication and with the Addition of Some Chemicals

6.1.5.1 Evaluation of Reaction Kinetics in PCI ww during Sonication Process with only Sonication and with the Addition of Some Chemicals

The reaction kinetic of PCI ww was found with only sonication process after 60 min, 120 and 150 min sonication times. The pseudo first order reaction kinetic was found to be suitable for total PAHs removals in PCI ww after 150 min sonication time when chemical was not added (only with sonication).

The kinetic mechanisms of PCI ww was defined with the addition of some chemicals after 60 min, 120 and 150 min sonication times. The pseudo first order reaction kinetic was suitable for total PAHs removals in PCI ww after 150 min sonication time with the addition of some chemicals.

6.1.5.2 The Evaluation of Reaction Kinetics in OMI ww during Sonication Process with only Sonication and with the Addition of Some Chemicals

The kinetic mechanisms of OMI ww was determined with only sonication process after 60 min, 120 and 150 min sonication times. The pseudo first order reaction kinetic was suitable for COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals in OMI ww after 150 min sonication time with only sonication.

The kinetic mechanisms of OMI ww was defined with the addition of some chemicals after 60 min, 120 and 150 min sonication times. The pseudo first order reaction kinetic was suitable for COD_{dis}, TOC, color, total phenol, TAAs and TFAs removals in OMI ww after 150 min sonication time with the addition of some chemicals.

6.1.5.3 The Evaluation of Reaction Kinetics in TI ww during Sonication Process with only Sonication and with the Addition of Some Chemicals

The reaction kinetic of TI ww was defined with only sonication process after 60 min, 120 and 150 min sonication times. The pseudo first order reaction kinetic was found to be suitable for COD_{dis}, TOC, color and TAAs removals in TI ww after 150 min sonication time with only sonication.

The kinetic mechanisms of TI ww was determined with the addition of some chemicals after 60 min, 120 and 150 min sonication times. The pseudo first order reaction kinetic was suitable for COD_{dis}, TOC, color and TAAs removals in TI ww after 150 min sonication time with the addition of some chemicals.

6.1.6 Mechanism of Sonication in PCI ww, OMI ww and TI ww during Sonication Process with only Sonication and with the Addition of Some Chemicals

6.1.6.1 Mechanism of Sonication in PCI ww during Sonication Process with only Sonication and with the Addition of Some Chemicals

No increase in $OH^\bullet$ ion concentrations was observed throughout sonication of more hydrophobic PAHs (BbF, BkF, BaP, DahA, BghiP and IcdP) in PCI ww. The contribution of $OH^\bullet$ ion concentration is minor for the ultimate sonodegradation of more hydrophobic PAHs (BbF, BkF, BaP, DahA, BghiP and IcdP) in PCI ww. The $OH^\bullet$ ion concentrations of more hydrophobic PAHs (BbF, BkF, BaP, DahA, BghiP and IcdP) are lower than the $OH^\bullet$ ion concentrations of less hydrophobic PAHs (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA and CHR) in PCI ww. This showed that hydroxylation process is not the main mechanism for the removal of more hydrophobic PAHs (BbF, BkF, BaP, DahA, BghiP and IcdP) in PCI ww. This indicates that the main process for the destruction of more hydrophobic PAHs (BbF, BkF, BaP, DahA, BghiP and IcdP) is pyrolysis process in PCI ww with sonication.

6.1.6.2 Mechanism of Sonication in OMI ww during Sonication Process with only Sonication and with the Addition of Some Chemicals

The initial rate of H_2O_2 formation associated to the toxic and refractory pollutant (COD_{dis}, TOC, color, total phenol, TAAs and TFAs) treatments by sonication in OMI ww decreases with increasing sonication time (30 min, 120 and 150 min) at 60^oC. The high H_2O_2 production through sonication of OMI ww verified the presence of high $OH^\bullet$ ion concentrations. The high $OH^\bullet$ ion concentration is the major process for complete degradation of toxic and refractory pollutants (COD_{dis}, TOC, color, total phenol, TAAs and TFAs) in OMI ww. This showed that hydroxylation is the main mechanism for the removal of the toxic and refractory pollutants (COD_{dis}, TOC, color, total phenol, TAAs and TFAs) in OMI ww with sonication process.

6.1.6.3 Mechanism of Sonication in TI ww during Sonication Process with only Sonication and with the Addition of Chemicals

The initial rate of H_2O_2 formation associated to the toxic and refractory pollutant (COD_{dis}, TOC, color and TAAs) treatments by sonication in TI ww decreases with increasing sonication time (30 min, 120 and 150 min) at 60^oC. The high H_2O_2 production through sonication of TI ww verified the presence of high $OH^\bullet$ ion concentrations. The high $OH^\bullet$ ion concentration is the major process for complete degradation of toxic and refractory pollutants (COD_{dis}, TOC, color and TAAs) in TI ww. This showed that hydroxylation is the main mechanism for the removal of the toxic and refractory pollutant (COD_{dis}, TOC, color and TAAs) in TI ww by sonication process.

6.1.7 The Evaluation of by-Products Removal Efficiencies in PCI ww and OMI ww during Sonication Process with only Sonication and with the Addition of Some Chemicals

6.1.7.1 The Evaluation of by-Products Removal Efficiencies in PCI ww during Sonication Process with only Sonication

The measurements of PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww were performed with GC-MS (Agilent), GC-FID (Agilent) and Shimadzu CLASS–VP V6.14 HPLC, Phenomenex Hyperclone 125 mm x 4.60 mm 5.00 μm PAHs HPLC column, respectively, in raw PCI ww after 120 and 150 min sonication times at pH=7.0 and at 25^{o}C. Higher than 61.33% and 76.77% PAHs removal efficiencies of PAHs intermediates were detected after 120 and 150 min sonication times, respectively, at pH=7.0 and at 25^{o}C.

6.1.7.2 The Evaluation of by-Products Removal Efficiencies in PCI ww during Sonication Process with the Addition of Some Chemicals

The measurements of PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww were performed with GC-MS, GC-FID and HPLC, respectviely, in DO=10.00 mg/l after 120 and 150 min sonication times at pH=7.0 and at 25^{o}C. Higher than 70.00% and 80.11% PAHs removal efficiencies of PAHs intermediates were detected with HPLC after 120 and 150 min sonication times, respectively, at pH=7.0 and at 25^{o}C.

The measurements of PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww were performed in H_2O_2=2000 mg/l after 120 and 150 min sonication times at pH=7.0 and at 25^{o}C. Over 80.00% and 83.56% PAHs removal efficiencies of PAHs intermediates were detected with HPLC after 120 and 150 min sonication times, respectively, at pH=7.0 and at 25^{o}C.

The measurements of PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid) in PCI ww were performed in TiO_2=20.00 mg/l after 120 and 150 min sonication times at pH=7.0 and at 25°C. Higher than 84.00% and 85.00% PAHs removal efficiencies of PAHs intermediates were detected with HPLC after 120 and 150 min sonication times, respectively, at pH=7.0 and at 25°C.

6.1.7.3 The Evaluation of by-Products Removal Efficiencies in OMI ww during Sonication Process with only Sonication

Some phenolic by-products (2–phenyl–phenol, 3–phenyl–phenol) were identified in raw OMI ww after 60 min, 120 and 150 min sonication times at pH=7.0 and at 25°C. Over 83.41% and 90.50% phenol by-products removal yields were detected after 120 and 150 min sonication times, respectively, at pH=7.0 and at 25°C.

6.1.8 The Evaluation of Specific Energies in COD_{dis} (E_s), Electric Energy per Unit Volume in COD_{dis} (EE/O) and Electrical Energy per Unit Mass in COD_{dis} (EE/M) Values in PCI ww, OMI ww and TI ww during Sonication Process with only Sonication

6.1.8.1 The Evaluation of Specific Energies in COD_{dis} (E_s), Electric Energy per Unit Volume in COD_{dis} (EE/O) and Electrical Energy per Unit Mass in COD_{dis} (EE/M) Values in PCI ww during Sonication Process with only Sonication

The specific energy in COD_{dis} (E_s) parameter was calculated as 3.12 kWh / kg COD_{dis} in PCI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C with only sonication process. The cost of this specific energy for COD_{dis} (E_s) parameter was found as 0.52 TL/kg COD_{dis} in PCI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C, with only sonication processs.

The electric energy per unit volume in COD_{dis} (EE/O) parameter was calculated as 4481.80 kW/m^3/COD_{dis} in PCI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C with only sonication process. The cost of this electric energy per unit volume for COD_{dis} (EE/O) parameter was found as 741.53 TL/m^3/COD_{dis} in PCI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C, with only sonication process.

The electric energy per unit mass in COD_{dis} (EE/M) parameter was calculated 3995.41 kWh/kg/COD_{dis} in PCI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C with only sonication process. The cost of this electric energy per unit mass for COD_{dis} (EE/M) parameter was found 661.06 TL/kg/COD_{dis} in PCI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C, with only sonication process.

6.1.8.2 The Evaluation of Specific Energies in COD_{dis} (E_s), Electric Energy per Unit Volume in COD_{dis} (EE/O) and Electrical Energy per Unit Mass in COD_{dis} (EE/M) Values in OMI ww during Sonication Process with only Sonication

The specific energy in COD_{dis} (E_s) parameter was calculated 0.03 kWh / kg COD_{dis} in OMI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C with only sonication process. The cost of this specific energy for COD_{dis} (E_s) parameter was found 0.005 TL/kg COD_{dis} in OMI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C, with only sonication process.

The electric energy per unit volume in COD_{dis} (EE/O) parameter was calculated 7804.88 kW/m^3/COD_{dis} in OMI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C with only sonication process. The cost of this electric energy per unit volume for COD_{dis} (EE/O) parameter was found 1291.35 TL/m^3/COD_{dis} in OMI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C, with only sonication process.

The electric energy per unit mass in COD_{dis} (EE/M) parameter was calculated 48.00 kWh/kg/COD_{dis} in OMI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C with only sonication process. The cost of this electric energy per unit mass for COD_{dis} (EE/M) parameter was found 7.94 TL/kg/COD_{dis} in OMI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C, with only sonication process.

6.1.8.3 The Evaluation of Specific Energies in COD_{dis} (E_s), Electric Energy per Unit Volume in COD_{dis} (EE/O) and Electrical Energy per Unit Mass in COD_{dis} (EE/M) Values in TI ww during Sonication Process with only Sonication

The specific energy in COD_{dis} (E_s) parameter was calculated 3.32 kWh / kg COD_{dis} in TI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C with only sonication process. The cost of this specific energy for COD_{dis} (E_s) parameter was found 0.55 TL/kg COD_{dis} in TI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C, with only sonication process.

The electric energy per unit volume in COD_{dis} (EE/O) parameter was calculated as 5427.33 kW/m^3/COD_{dis} in TI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C with only sonication process. The cost of this electric energy per unit volume for COD_{dis} (EE/O) parameter was measured 897.97 TL/m^3/COD_{dis} in TI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25°C, with only sonication process.

The electric energy per unit mass in COD_{dis} (EE/M) parameter was calculated 4474.02 kWh/kg/COD_{dis} in TI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25^oC with only sonication process. The cost of this electric energy per unit mass for COD_{dis} (EE/M) parameter was measured 740.25 TL/kg/COD_{dis} in TI ww at 35 kHz sonication frequency, at 640 W sonication power, at 500 ml sonication volume, after 150 min sonication time at 25^oC, with only sonication process.

6.1.9 The Evaluation of Costs in PCI ww, OMI ww, TI ww during Sonication Process with on ly Sonication and with the Addition of Some Chemicals

6.1.9.1 The Evaluation of Costs in PCI ww, OMI ww and TI ww during Sonication Process with only Sonication

The evaluation of costs in PCI ww, OMI ww, TI ww during sonication process with only sonication and with the addition of some chemicals were calculated for annual, monthly, weekly, daily and hourly time periods. 3120, 3120, 193808.32, 7.50, 200055.82, 120, 1500, 1620, 201675.82 and 201555.82 TL/year was calculated for total annual labor cost, total annual analysis cost, total annual electrical cost, total annual part replacement cost, total annual O&M cost, amortized capital cost, total annual capital cost, total annual amortized capital cost, total annual operating cost and total annual cost, respectively, for PCI ww, OMI ww and TI ww with only sonication process.

In this study, the total annual cost with only sonication was calculated as 201555.82 TL/year (=134370.55 $/year=106082.01 €/year) including the annual labor costs, the annual analytical costs, the annual chemical costs, the annual energy (electrical) costs, the annual capital costs and the annual part replacement costs.

6.1.9.2 The Evaluation of Costs in PCI ww, OMI ww and TI ww during Sonication Process with the Addition of Some Chemicals

The evaluation of costs in PCI ww, OMI ww and TI ww during sonication process with the addition of some chemicals (such as O_2(g) sparging, etc.) were calculated for annual, monthly, weekly, daily and hourly time periods. 3120, 3120, 650, 193808.32, 7.50, 200705.82, 120, 1500, 1620, 202325.82 and 202205.82 TL/year was calculated for total annual labor cost, total annual analysis cost, total annual O_2(g) chemical cost, total annual electrical cost, total annual part replacement cost, total annual O&M cost, amortized capital cost, total annual capital cost, total annual amortized capital cost, total annual operating cost and total annual cost, respectively, for PCI ww, OMI ww and TI ww with the addition of O_2(g) sparging during sonication process.

In this study, the total annual cost with O_2(g) sparging was calculated as 202205.82 TL/year (=134803.88 $/year=106424.12 €/year) including the annual labor costs, the annual analytical costs, the annual chemical costs, the annual energy (electrical) costs, the annual capital costs and the annual part replacement costs.

6.1.10 The Disscussions of Specific Energy and Cost in PCI ww, OMI ww and TI ww during Sonication Process with only Sonication and with the Addition of Some Chemicals

Less specific energy (3.12 kWh / kg COD_{dis}) is required to derive a better sonication treatment and cost savings for PCI ww treatment plants with only sonication and with the addition of some chemicals compared to the other AOP processes.

Less specific energy (0.03 kWh / kg COD_{dis}) is required to derive a better sonication treatment and cost savings for OMI ww treatment plants with only sonication and with the addition of some chemicals compared to the other AOP processes.

Less specific energy (3.32 kWh / kg COD_{dis}) is required to derive a better sonication treatment and cost savings for TI ww treatment plants with only sonication and with the addition of some chemicals compared to the other AOPs processes.

6.1.11 The Comparison of Anaerobic, Aerobic, Ultraviolet (UV), Ozone (O_3) and Sonication Treatment Processes

Anaerobic pretreatment is most effectively applied to wastewaters with high concentrations of readily degradable organic constituents. The cost-effectiveness of anaerobic pretreatment is specific to each wastewater and associated parameters (for example, ability to use biogas, power costs, sludge disposal costs) (Appendix 7.50).

For the operating and maintenance (O&M) cost components, off-site sludge disposal costs and macro-nutrients costs are linear functions of the wastewater strength for both treatment methods; however, absolute costs for the aerobic option are much higher. The energy requirement for aeobic treatment increases rapidly with wastewater strength, since aeration comprises most of the energy needs. For anaerobic systems, the electricity consumption is much lower and virtually constant for the influent strength range, since only pumping costs are incurred. Maintenance costs for both systems are considered aa function of capital costs in this analysis. Alkalinity requirements for anaerobic treatment are higher than for aerobic treatment and increase proportionately with influent strength. This is a consequence of the sensitivity of anaerobic processes to low pH upsets and the necessity to buffer volatile acids generated during the initial reaction step. Labor requirements for both treatment options are not a function of wastewater strength for the plant sizes considered. Heating is specific for anaerobic treatment only. Since heating is mostly a function of the wastewater flow (reactor volume), it does not increase with wastewater strength in the range considered. O&M costs of the anaerobic plant are credited with the biogas generated during the treatment, and the credits are proportional to the mass of organic matter removed (wastewater strength).

Although high energy requirement and high removal efficiencies observed with UV treatment methods in many industrial wastewater, hovever, high capital and high operating area are required for the UV treatment process. Energy requirement, start up time, operation time and capital cost of UV treatment are higher than Sonication treatment for many industrial wastewaters.

Although, high removal efficiencies provided with O_3 treatment process in many industrial wastewater, high capital cost and medium operating area are required for O_3 treatment process. Energy requirement, start up time, operation time and capital cost of O_3 treatment ara higher than Sonication treatment for many industrial wastewaters.

The PCI ww, OMI ww and TI ww have been treated using biological treatment, physical-chemical treatment and their combinations. These processes can not completely remove the COD_{dis}, TOC, total PAHs and toxicity in PCI ww. However, sonication process remove the COD_{dis}, TOC, total PAHs, and the acute toxicity with high yields. Similarly, the sonication process easily remove the COD_{dis}, TOC, color, total phenol, TAAs, TFAs and toxicity from the OMI ww. On the other hand, the TI ww was treated using aerobic biological processes, physico/chemical processes and their modifications. The most commonly employed biological processes are conventional and extended activated sludge system. Nevertheless, these processes can not be degraded the dyes, COD_{dis}, TOC and toxicity in TI ww ultimately. Therefore, sonication process easily remove the COD_{dis}, TOC, color, TAAs, and the acute toxicity from TI ww.

The extent of sonodegradation is a function of sonication time and operating conditions such as ultrasound intensity, ultrasonic frequency, sonication power, sonication temperature and initial concentration, and also depends on the presence of matrix species. These can produce more cavities and free radicals. They may have either a beneficial or detrimental impact on degradation depending on their type and function i.e. whether they act as radical promoters or scavengers. Furthermore, their presence may alter the physicochemical properties of the reaction mixture and consequently affect the cavitation process and associated reaction mechanisms and pathways.

The more hydrophobic PAHs with high benzene rings could be removed just as successfully as the less hydrophobic PAHs with lower benzene rings by sonication. The use of ultrasound in PAHs destruction presents unique advantages such as enhancement of mass transfer and removal yields, improvement of surface properties, and lowering of chemical consumption. Sonication is economical for effectively degrading and destroying way fort the all pollutant parameters and some intermediates in PCI ww, OMI ww and TI ww.

Ultrasonic degradation of all classes of OMI ww is feasible due to free radical reactions, mainly $OH^{\bullet}$. Hydroxilation was an important degradation mechanism of OMI ww with only sonication and the addition of some additives. Sonication treatment is economical for effectively degrading and destroying way COD_{dis}, TOC, color, total phenol, TAAs, TFAs and some intermediates in OMI ww with only sonication and the addition of some additives.

Sonication process works on the principle of generating free radicals and their subsequent attack on the contaminant molecules with the aim of either, completely mineralizing the contaminants or converting it into less harmful or lower chain compounds which can not be efficiently treated by biological processes.

The sonolysis process can be removed the toxicity and can be increased the biodegradability of pollutant compounds. The chemicals are mineralized or degraded to smaller molecules with improved biodegradability or lower toxicity. The intensification of the organic matter solubilization induced by the ultrasonic action, can lead to an increase of the bioavailability of some micropollutants to the degrader consortium.

The combination of ultrasonic treatment with some additives and biodegradation represents a promising new technique in the field of environmental engineering.

Toxic compounds inhibiting the microbial degradation processes can be removed by ultrasound.

The sonication process could prove to be less land-intensive, less expensive and require less maintenance and undergo lesser inhibition by the anions than other treatment processes in PCI ww, OMI ww and TI ww with only sonication and the addition of some additives (Appendix 7.50).

6.2 Recommendations

The recommendations of this study were summarized as follows.

1. Sonicationn process can be easily applied all kind of wastewater type with only sonication and with the addition of some additives. Sonication removal efficiencies can be increased with the addition of some chemicals (solids or gas bubbles to act as nuclei).

2. The optimization of sonication frequency can be required before the sonication process for effectively cavitation reaction. The frequency of irradiation should be selected depending on the desired effects for the specific application, the higher frequency or combination of lower frequencies can be recommended for application dominated by chemical effects and lower frequency can be recommended for applications where the physical effects are controlling.

3. The optimization of sonication power can be made before the sonication process for effectively reaction in acoustic cavitation. The optimization of sonication temperature can be done before the sonication process for effectively cavitation reaction.

4. The optimization of sonication time can be made before the sonication experiments for effectively acoustic cavitation reaction. The optimization of sonication volume can be fixed before the sonication process for effectively cavitation reaction.

5. The sonication process is recommended for the removal of toxic and refractory compounds from wastewater, compared to the other wastewater treatment processes.

As a result of this Ph.D. dissertation, sonication process is recommended for the treatment of PCI ww, OMI ww and TI ww containing toxic and refractory compounds. Sonication process can be applied as a pre-treatment or post-treatment in combination with other water purification processes.

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CHAPTER SEVEN

APPENDICES

7.1. List of Tables

7.2 List of Figures

7.3 List of Appendices

Appendix 7.1 Total PAHs removal efficiencies of PCI ww before and after sonication process

No	Parameters	**Total PAHs Removal Efficiencies (%)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
1	Raw ww, control	0.00		54.92		61.33		79.65	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
2	Raw ww, control	0.00	45.34	62.40	90.11	0.00	54.21	79.31	96.90
3	1 h aeration	0.00	48.95	75.39	94.48	0.00	54.21	80.16	97.62
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	51.42	81.11	92.46	0.00	47.21	80.04	88.33
	30 min N_2(g) (6.00 mg/l N_2)	0.00	58.52	80.91	94.16	0.00	59.92	81.00	96.27
5	pH=4.0	0.00	63.11	78.98	91.59	0.00	46.14	76.70	93.37
	pH=7.0	0.00	44.16	61.33	90.05	0.00	42.36	73.95	96.09
	pH=10.0	0.00	58.29	75.70	92.25	0.00	40.82	75.96	95.66
6	DO=2.00 mg/l	0.00	61.54	77.44	90.22	0.00	53.04	79.87	94.67
	DO=4.00 mg/l	0.00	58.95	75.86	92.27	0.00	51.80	81.02	95.00
	DO=6.00 mg/l	0.00	64.67	79.45	93.77	0.00	56.94	82.61	96.79
	DO=10.00 mg/l	0.00	64.66	80.34	94.32	0.00	58.23	83.22	97.23
7	H_2O_2=100 mg/l	0.00	60.54	77.92	89.63	0.00	52.61	81.28	91.33
	H_2O_2=500 mg/l	0.00	59.73	76.85	93.28	0.00	57.90	77.22	94.19
	H_2O_2=2000 mg/l	0.00	59.83	78.88	96.46	0.00	56.80	82.19	98.04
8	TiO_2=0.10 mg/l	0.00	55.40	74.58	79.69	0.00	48.32	70.30	82.06
	TiO_2=0.50 mg/l	0.00	57.71	75.41	81.58	0.00	47.34	79.27	87.34
	TiO_2=10.00 mg/l	0.00	64.67	79.44	87.61	0.00	56.94	82.61	91.74
	TiO_2=20.00 mg/l	0.00	65.99	81.67	91.66	0.00	58.90	83.43	93.88
9	NaCl=1.00 g/l	0.00	58.65	79.19	90.13	0.00	60.56	83.34	93.17
	NaCl=2.50 g/l	0.00	61.86	77.98	92.14	0.00	61.63	85.76	96.08
	NaCl=15.00 g/l	0.00	64.24	80.65	99.23	0.00	65.24	88.00	99.68
10	Fe^{+2}=2.00 mg/l	0.00	60.68	79.20	83.27	0.00	61.77	81.38	86.28
	Fe^{+2}=8.00 mg/l	0.00	63.66	82.49	92.62	0.00	64.94	83.62	95.27
	Fe^{+2}=20.00 mg/l	0.00	69.72	85.74	95.12	0.00	72.54	87.20	98.56
11	Fe^{+3}=10.00 mg/l	0.00	60.00	78.61	82.92	0.00	61.27	80.56	84.61
	Fe^{+3}=20.00 mg/l	0.00	62.65	80.55	91.72	0.00	61.82	82.64	93.00
	Fe^{+3}=50.00 mg/l	0.00	67.62	82.95	93.58	0.00	69.62	84.35	96.76
12	HCO_3^{-1}=0.50 g/l	0.00	14.41	58.12	80.43	0.00	15.24	59.72	78.09
	HCO_3^{-1}=1.00 g/l	0.00	14.64	59.45	92.14	0.00	16.30	58.98	81.69
	HCO_3^{-1}=5.00 g/l	0.00	16.76	60.14	81.66	0.00	17.05	60.56	82.62
13	C_4H_9OH=0.10 g/l	0.00	14.40	58.20	79.33	0.00	15.24	59.04	78.09
	C_4H_9OH=0.50 g/l	0.00	14.64	59.15	80.57	0.00	16.30	59.27	81.69
	C_4H_9OH=2.00 g/l	0.00	16.29	59.94	81.85	0.00	16.27	59.97	82.62

Appendix 7.2 COD$_{dis}$ removal efficiencies of PCI ww prior and after sonication experiments

No	Parameters	COD$_{dis}$ Removal Efficiencies (%)							
		$25^{o}C$							
		0. min		60. min		120. min		150. min	
1	Raw ww, control	0.00		56.05		62.30		80.16	
		$30^{o}C$				$60^{o}C$			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0.00	44.05	61.22	89.94	0.00	46.50	67.37	92.48
3	1 h aeration	0.00	48.84	75.28	94.37	0.00	54.21	79.31	96.90
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	51.31	81.00	92.35	0.00	47.21	80.04	88.33
	30 min N_2(g) (6.00 mg/l N_2)	0.00	58.41	80.80	94.05	0.00	59.92	81.00	96.27
5	pH=4.0	0.00	63.00	78.87	91.48	0.00	46.14	76.70	87.69
	pH=7.0	0.00	44.05	61.22	89.94	0.00	54.21	79.31	96.90
	pH=10.0	0.00	58.18	75.69	92.14	0.00	40.82	75.96	95.66
6	DO=2.00 mg/l	0.00	61.44	77.33	90.11	0.00	53.04	79.87	94.67
	DO=4.00 mg/l	0.00	58.84	75.75	92.16	0.00	51.80	81.02	95.00
	DO=6.00 mg/l	0.00	64.56	79.33	93.66	0.00	56.94	82.61	96.79
	DO=10.00 mg/l	0.00	64.55	80.23	94.21	0.00	58.23	83.22	97.23
7	H_2O_2=100 mg/l	0.00	60.43	77.81	89.52	0.00	52.61	81.28	91.33
	H_2O_2=500 mg/l	0.00	59.62	76.73	93.17	0.00	57.90	77.22	94.19
	H_2O_2=2000 mg/l	0.00	59.72	78.77	96.35	0.00	56.80	82.19	98.04
8	TiO_2=0.10 mg/l	0.00	55.39	74.47	79.58	0.00	48.32	70.30	82.06
	TiO_2=0.50 mg/l	0.00	57.60	75.39	81.47	0.00	47.34	79.27	87.34
	TiO_2=10.00 mg/l	0.00	64.56	79.33	87.59	0.00	56.94	82.61	91.74
	TiO_2=20.00 mg/l	0.00	65.88	81.56	91.55	0.00	58.90	83.43	93.88
9	NaCl=1.00 g/l	0.00	58.54	79.08	90.02	0.00	60.56	83.34	93.17
	NaCl=2.50 g/l	0.00	61.75	77.87	92.03	0.00	61.63	85.76	96.08
	NaCl=15.00 g/l	0.00	64.13	80.54	99.12	0.00	65.24	88.00	99.68
10	Fe^{+2}=2.00 mg/l	0.00	60.57	79.19	83.97	0.00	61.77	81.38	86.28
	Fe^{+2}=8.00 mg/l	0.00	63.33	82.38	92.51	0.00	64.94	83.62	95.27
	Fe^{+2}=20.00 mg/l	0.00	69.61	85.62	95.05	0.00	72.54	87.20	98.56
11	Fe^{+3}=10.00 mg/l	0.00	59.99	78.50	82.81	0.00	61.27	80.56	84.61
	Fe^{+3}=20.00 mg/l	0.00	62.54	80.44	91.61	0.00	61.82	82.64	93.00
	Fe^{+3}=50.00 mg/l	0.00	67.51	82.84	93.47	0.00	69.62	84.35	96.76
12	HCO_3^{-1}=0.50 g/l	0.00	14.30	58.09	80.32	0.00	15.24	59.72	78.09
	HCO_3^{-1}=1.00 g/l	0.00	14.53	59.34	81.24	0.00	16.30	58.98	81.69
	HCO_3^{-1}=5.00 g/l	0.00	16.96	60.03	81.55	0.00	17.05	60.56	82.62
13	C_4H_9OH=0.10 g/l	0.00	14.30	58.09	79.93	0.00	15.24	59.04	78.09
	C_4H_9OH=0.50 g/l	0.00	14.53	59.04	80.46	0.00	16.30	59.27	81.69
	C_4H_9OH=2.00 g/l	0.00	16.18	59.83	81.74	0.00	16.27	59.97	82.62

Appendix 7.3 TOC removal efficiencies of PCI ww before and after sonication process

No	Parameters	TOC Removal Efficiencies (%)							
		25^oC							
		0. min		60. min		120. min		150. min	
1	Raw ww, control	0.00		55.39		62.74		78.37	
		30^oC				60^oC			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0.00	47.70	63.38	90.89	0.00	49.50	70.00	94.23
3	1 h aeration	0.00	52.99	76.84	95.27	0.00	53.67	79.87	91.94
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	64.49	77.39	93.13	0.00	46.90	75.33	95.02
	30 min N_2(g) (6.00 mg/l N_2)	0.00	57.20	74.73	95.54	0.00	60.92	81.20	96.69
5	pH=4.0	0.00	62.27	80.32	88.57	0.00	45.30	74.96	93.39
	pH=7.0	0.00	52.99	76.84	95.27	0.00	53.67	79.87	91.94
	pH=10.0	0.00	57.67	63.25	86.90	0.00	42.75	72.99	91.78
6	DO=2.00 mg/l	0.00	63.35	74.35	86.47	0.00	52.17	77.61	91.13
	DO=4.00 mg/l	0.00	60.01	76.62	87.64	0.00	49.45	83.38	91.86
	DO=6.00 mg/l	0.00	65.27	79.55	89.26	0.00	54.84	77.70	91.22
	DO=10.00 mg/l	0.00	66.93	80.74	93.07	0.00	66.15	86.40	98.35
7	H_2O_2=100 mg/l	0.00	61.65	74.46	85.74	0.00	51.82	79.71	92.74
	H_2O_2=500 mg/l	0.00	61.33	74.33	91.45	0.00	57.18	78.59	91.53
	H_2O_2=2000 mg/l	0.00	57.01	74.48	91.13	0.00	55.40	83.57	95.88
8	TiO_2=0.10 mg/l	0.00	53.61	68.47	77.87	0.00	50.75	71.98	77.89
	TiO_2=0.50 mg/l	0.00	56.72	74.67	79.38	0.00	48.31	77.60	88.11
	TiO_2=10.00 mg/l	0.00	65.29	80.78	86.50	0.00	55.49	81.01	93.20
	TiO_2=20.00 mg/l	0.00	62.19	75.36	88.37	0.00	60.26	85.16	92.67
9	NaCl=1.00 g/l	0.00	55.25	77.43	88.38	0.00	56.65	80.19	90.17
	NaCl=2.50 g/l	0.00	59.33	76.23	88.74	0.00	60.18	87.20	91.72
	NaCl=15.00 g/l	0.00	59.31	77.31	96.71	0.00	62.39	85.15	98.30
10	Fe^{+2}=2.00 mg/l	0.00	54.97	75.74	80.61	0.00	58.12	78.18	81.70
	Fe^{+2}=8.00 mg/l	0.00	60.01	79.15	87.69	0.00	63.40	71.26	87.55
	Fe^{+2}=20.00 mg/l	0.00	65.34	83.85	90.78	0.00	69.71	84.22	95.73
11	Fe^{+3}=10.00 mg/l	0.00	56.54	71.97	81.19	0.00	58.14	78.08	82.99
	Fe^{+3}=20.00 mg/l	0.00	60.97	78.87	87.68	0.00	63.37	79.23	88.20
	Fe^{+3}=50.00 mg/l	0.00	65.34	81.61	90.58	0.00	71.13	82.20	92.45
12	HCO_3^{-1}=0.50 g/l	0.00	18.69	61.29	82.35	0.00	19.77	61.60	79.73
	HCO_3^{-1}=1.00 g/l	0.00	19.22	62.20	81.04	0.00	19.20	61.81	83.71
	HCO_3^{-1}=5.00 g/l	0.00	20.96	62.31	82.97	0.00	18.50	62.42	83.09
13	C_4H_9OH=0.10 g/l	0.00	13.48	73.76	80.09	0.00	14.43	58.65	78.09
	C_4H_9OH=0.50 g/l	0.00	13.71	58.65	80.27	0.00	15.50	58.89	81.51
	C_4H_9OH=2.00 g/l	0.00	15.38	59.45	81.57	0.00	16.86	60.25	82.75

Appendix 7.4 Microtox acute toxicity values of PCI ww before and after sonication process

<table>
<tr><th rowspan="4">No</th><th rowspan="4">Parameters</th><th colspan="8">Microtox Acute Toxicity Values, * EC (mg/l)</th></tr>
<tr><th colspan="8">25°C</th></tr>
<tr><th colspan="2">0. min</th><th colspan="2">60. min</th><th colspan="2">120. min</th><th colspan="2">150. min</th></tr>
<tr><th colspan="2">*EC_{90}</th><th colspan="2">*EC</th><th colspan="2">*EC</th><th colspan="2">*EC</th></tr>
<tr><td>1</td><td>Raw ww, control</td><td colspan="2">600</td><td colspan="2">EC_{80}=610</td><td colspan="2">EC_{60}=510</td><td colspan="2">EC_{50}=525</td></tr>
<tr><td rowspan="3"></td><td rowspan="3"></td><th colspan="4">30°C</th><th colspan="4">60°C</th></tr>
<tr><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th><th>0. min</th><th>60. min</th><th>120. min</th><th>150. min</th></tr>
<tr><th>*EC_{90}</th><th>*EC</th><th>*EC</th><th>*EC</th><th>*EC_{90}</th><th>*EC</th><th>*EC</th><th>*EC</th></tr>
<tr><td>2</td><td>Raw ww, control</td><td>600</td><td>EC_{70}=610</td><td>EC_{50}=590</td><td>EC_{40}=680</td><td>600</td><td>EC_{60}=680</td><td>EC_{40}=610</td><td>EC_{30}=410</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>3</td><td>1 h aeration</td><td>600</td><td>EC_{55}=688</td><td>EC_{35}=501</td><td>EC_{20}=563</td><td>600</td><td>EC_{50}=676</td><td>EC_{20}=777</td><td>EC_{15}=358</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>4</td><td>15 min $N_2(g)$ (3.00 mg/l N_2)</td><td>600</td><td>EC_{70}=611</td><td>EC_{35}=523</td><td>EC_{25}=456</td><td>600</td><td>EC_{65}=608</td><td>EC_{30}=762</td><td>EC_{20}=456</td></tr>
<tr><td></td><td>30 min $N_2(g)$ (6.00 mg/l N_2)</td><td>600</td><td>EC_{70}=607</td><td>EC_{30}=521</td><td>EC_{25}=445</td><td>600</td><td>EC_{60}=605</td><td>EC_{25}=760</td><td>EC_{15}=442</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>5</td><td>pH=4.0</td><td>600</td><td>EC_{70}=713</td><td>EC_{50}=602</td><td>EC_{40}=755</td><td>600</td><td>EC_{60}=709</td><td>EC_{40}=800</td><td>EC_{30}=466</td></tr>
<tr><td></td><td>pH=7.0</td><td>600</td><td>EC_{70}=710</td><td>EC_{50}=590</td><td>EC_{40}=680</td><td>600</td><td>EC_{60}=680</td><td>EC_{40}=810</td><td>EC_{30}=410</td></tr>
<tr><td></td><td>pH=10.0</td><td>600</td><td>EC_{70}=711</td><td>EC_{45}=591</td><td>EC_{40}=653</td><td>600</td><td>EC_{65}=706</td><td>EC_{45}=767</td><td>EC_{30}=465</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>6</td><td>DO=2.00 mg/l</td><td>600</td><td>EC_{70}=714</td><td>EC_{50}=501</td><td>EC_{35}=653</td><td>600</td><td>EC_{60}=609</td><td>EC_{35}=789</td><td>EC_{25}=365</td></tr>
<tr><td></td><td>DO=4.00 mg/l</td><td>600</td><td>EC_{70}=711</td><td>EC_{45}=431</td><td>EC_{30}=652</td><td>600</td><td>EC_{60}=608</td><td>EC_{35}=726</td><td>EC_{25}=365</td></tr>
<tr><td></td><td>DO=6.00 mg/l</td><td>600</td><td>EC_{65}=711</td><td>EC_{40}=430</td><td>EC_{25}=652</td><td>600</td><td>EC_{60}=596</td><td>EC_{30}=787</td><td>EC_{25}=364</td></tr>
<tr><td></td><td>DO=10.00 mg/l</td><td>600</td><td>EC_{60}=708</td><td>EC_{35}=431</td><td>EC_{20}=663</td><td>600</td><td>EC_{55}=596</td><td>EC_{30}=783</td><td>EC_{20}=358</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>7</td><td>H_2O_2=100 mg/l</td><td>600</td><td>EC_{70}=815</td><td>EC_{35}=630</td><td>EC_{20}=653</td><td>600</td><td>EC_{60}=807</td><td>EC_{30}=596</td><td>EC_{15}=664</td></tr>
<tr><td></td><td>H_2O_2=500 mg/l</td><td>600</td><td>EC_{65}=810</td><td>EC_{30}=651</td><td>EC_{10}=629</td><td>600</td><td>EC_{50}=790</td><td>EC_{20}=580</td><td>EC_{5}=680</td></tr>
<tr><td></td><td>H_2O_2=2000 mg/l</td><td>600</td><td>EC_{70}=806</td><td>EC_{35}=627</td><td>EC_{25}=650</td><td>600</td><td>EC_{65}=804</td><td>EC_{30}=587</td><td>EC_{20}=664</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>8</td><td>TiO_2=0.10 mg/l</td><td>600</td><td>EC_{70}=832</td><td>EC_{35}=796</td><td>EC_{20}=655</td><td>600</td><td>EC_{60}=824</td><td>EC_{30}=765</td><td>EC_{20}=738</td></tr>
<tr><td></td><td>TiO_2=0.50 mg/l</td><td>600</td><td>EC_{70}=824</td><td>EC_{30}=781</td><td>EC_{15}=652</td><td>600</td><td>EC_{60}=817</td><td>EC_{25}=796</td><td>EC_{15}=665</td></tr>
<tr><td></td><td>TiO_2=10.00 mg/l</td><td>600</td><td>EC_{60}=819</td><td>EC_{25}=771</td><td>EC_{10}=652</td><td>600</td><td>EC_{50}=640</td><td>EC_{20}=600</td><td>EC_{5}=520</td></tr>
<tr><td></td><td>TiO_2=20.00 mg/l</td><td>600</td><td>EC_{65}=813</td><td>EC_{35}=777</td><td>EC_{25}=649</td><td>600</td><td>EC_{60}=811</td><td>EC_{30}=796</td><td>EC_{20}=663</td></tr>
</table>

* EC values were calculated based on COD_{dis} (mg/l).

Appendix 7.4 Microtox acute toxicity values of PCI ww before and after sonication process (cont.).

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC$_{90}$**		***EC**		***EC**		***EC**	
1	Raw ww, control	600		EC$_{80}$=610		EC$_{60}$=510		EC$_{50}$=525	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC$_{90}$**	***EC**	***EC**	***EC**	***EC$_{90}$**	***EC**	***EC**	***EC**
2	Raw ww, control	600	EC$_{70}$= 610	EC$_{50}$= 590	EC$_{40}$= 680	600	EC$_{60}$= 680	EC$_{40}$= 610	EC$_{30}$= 410
9	NaCl=1.00 g/l	600	EC$_{60}$= 614	EC$_{35}$= 498	EC$_{15}$= 354	600	EC$_{60}$= 605	EC$_{30}$= 494	EC$_{10}$= 454
	NaCl=2.50 g/l	600	EC$_{60}$= 612	EC$_{30}$= 429	EC$_{10}$= 350	600	EC$_{50}$= 607	EC$_{20}$= 482	EC$_{5}$= 357
	NaCl=15.00 g/l	600	EC$_{65}$= 603	EC$_{40}$= 448	EC$_{25}$= 327	600	EC$_{60}$= 696	EC$_{35}$= 579	EC$_{20}$= 452
10	Fe^{+2}=2.00 mg/l	600	EC$_{65}$= 622	EC$_{30}$= 479	EC$_{20}$= 353	600	EC$_{60}$= 620	EC$_{30}$= 477	EC$_{15}$= 354
	Fe^{+2}=8.00 mg/l	600	EC$_{60}$= 611	EC$_{30}$= 485	EC$_{15}$= 350	600	EC$_{55}$= 608	EC$_{20}$= 463	EC$_{10}$= 349
	Fe^{+2}=20.00 mg/l	600	EC$_{70}$= 609	EC$_{35}$= 472	EC$_{20}$= 346	600	EC$_{60}$= 604	EC$_{30}$= 480	EC$_{20}$= 342
11	Fe^{+3}=10.00 mg/l	600	EC$_{65}$= 624	EC$_{35}$= 469	EC$_{20}$= 353	600	EC$_{55}$= 623	EC$_{30}$= 478	EC$_{15}$= 354
	Fe^{+3}=20.00 mg/l	600	EC$_{60}$= 613	EC$_{30}$= 477	EC$_{15}$= 351	600	EC$_{55}$= 611	EC$_{20}$= 475	EC$_{10}$= 353
	Fe^{+3}=50.00 mg/l	600	EC$_{70}$= 611	EC$_{40}$= 486	EC$_{25}$= 348	600	EC$_{60}$= 606	EC$_{35}$= 464	EC$_{20}$= 346
12	HCO_3^{-1}=0.50 g/l	600	EC$_{70}$= 627	EC$_{40}$= 455	EC$_{25}$= 312	600	EC$_{65}$= 625	EC$_{30}$= 410	EC$_{20}$= 353
	HCO_3^{-1}=1.00 g/l	600	EC$_{65}$= 626	EC$_{30}$= 454	EC$_{20}$= 311	600	EC$_{60}$= 625	EC$_{20}$= 354	EC$_{15}$= 309
	HCO_3^{-1}=5.00 g/l	600	EC$_{70}$= 625	EC$_{45}$= 453	EC$_{30}$= 308	600	EC$_{65}$= 624	EC$_{35}$= 452	EC$_{25}$= 308
13	C_4H_9OH=0.10 g/l	600	EC$_{70}$= 627	EC$_{35}$= 455	EC$_{25}$= 311	600	EC$_{60}$= 625	EC$_{30}$= 454	EC$_{15}$= 310
	C_4H_9OH=0.50 g/l	600	EC$_{65}$= 626	EC$_{30}$= 454	EC$_{20}$= 211	600	EC$_{55}$= 625	EC$_{20}$= 409	EC$_{10}$= 254
	C_4H_9OH=2.00 g/l	600	EC$_{70}$= 625	EC$_{40}$= 509	EC$_{30}$= 353	600	EC$_{65}$= 624	EC$_{35}$= 493	EC$_{20}$= 409

* EC values were calculated based on COD$_{dis}$ (mg/l).

Appendix 7.5 *Daphnia magna* acute toxicity values of PCI ww before and after sonication process

No	Parameters	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$*EC_{50}$		**$*EC$**		**$*EC$**		**$*EC$**	
1	Raw ww, control	618		EC_{45}=425		EC_{40}=325		EC_{35}=182	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$*EC_{50}$	**$*EC$**	**$*EC$**	**$*EC$**	**$*EC_{50}$**	**$*EC$**	**$*EC$**	**$*EC$**
2	Raw ww, control	618	EC_{40}= 510	EC_{35}= 340	EC_{30}= 85	618	EC_{40}= 425	EC_{30}= 190	EC_{25}= 32
3	1 h aeration	618	EC_{30}= 465	EC_{20}= 437	EC_{10}= 197	618	EC_{20}= 19	EC_{15}= 370	EC_{5}= 119
4	15 min $N_2(g)$ (3.00 mg/l N_2)	618	EC_{35}= 400	EC_{30}= 58	EC_{20}= 64	618	EC_{30}= 350	EC_{20}= 47	EC_{10}= 148
	30 min $N_2(g)$ (6.00 mg/l N_2)	618	EC_{30}= 300	EC_{20}= 140	EC_{15}= 42	618	EC_{25}= 29	EC_{15}= 300	EC_{5}= 120
5	pH=4.0	618	EC_{45}= 220	EC_{40}= 150	EC_{35}= 67	618	EC_{45}= 420	EC_{35}= 180	EC_{30}= 51
	pH=7.0	618	EC_{40}= 430	EC_{35}= 340	EC_{30}= 49	618	EC_{40}= 400	EC_{30}= 175	EC_{25}= 24
	pH=10.0	618	EC_{45}= 340	EC_{40}= 65	EC_{35}= 210	618	EC_{45}= 330	EC_{35}= 150	EC_{30}= 32
6	DO=2.00 mg/l	618	EC_{45}= 330	EC_{30}= 200	EC_{20}= 75	618	EC_{35}= 460	EC_{25}= 200	EC_{15}= 47
	DO=4.00 mg/l	618	EC_{40}= 67	EC_{25}= 375	EC_{20}= 225	618	EC_{30}= 51	EC_{20}= 440	EC_{15}= 160
	DO=6.00 mg/l	618	EC_{40}= 350	EC_{25}= 63	EC_{15}= 190	618	EC_{30}= 325	EC_{20}= 150	EC_{10}= 32
	DO=10.00 mg/l	618	EC_{35}= 465	EC_{20}= 437	EC_{15}= 197	618	EC_{25}= 19	EC_{15}= 370	EC_{5}= 119
7	H_2O_2=100 mg/l	618	EC_{40}= 87	EC_{30}= 35	EC_{15}= 170	618	EC_{35}= 38	EC_{25}= 375	EC_{10}= 135
	H_2O_2=500 mg/l	618	EC_{35}= 325	EC_{20}= 57	EC_{10}= 180	618	EC_{30}= 425	EC_{15}= 200	EC_{5}= 35
	H_2O_2=2000 mg/l	618	EC_{40}= 200	EC_{30}= 100	EC_{20}= 23	618	EC_{35}= 250	EC_{20}= 110	EC_{10}= 15
8	TiO_2=0.10 mg/l	618	EC_{40}= 350	EC_{25}= 160	EC_{15}= 200	618	EC_{35}= 165	EC_{15}= 425	EC_{10}= 260
	TiO_2=0.50 mg/l	618	EC_{40}= 340	EC_{20}= 137	EC_{10}= 115	618	EC_{35}= 450	EC_{15}= 120	EC_{5}= 105
	TiO_2=10.00 mg/l	618	EC_{35}= 290	EC_{20}= 200	EC_{10}= 122	618	EC_{30}= 400	EC_{10}= 105	EC_{5}= 55
	TiO_2=20.00 mg/l	618	EC_{45}= 250	EC_{30}= 150	EC_{20}= 87	618	EC_{40}= 325	EC_{20}= 135	EC_{15}= 50

* EC values were calculated based on COD_{dis} (mg/l).

Appendix 7.5 *Daphnia magna* acute toxicity values of PCI ww before and after sonication process (cont.).

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC$_{50}$**		***EC**		***EC**		***EC**	
1	Raw ww, control	618		EC$_{45}$=425		EC$_{40}$=325		EC$_{35}$=182	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC$_{50}$**	***EC**	***EC**	***EC**	***EC$_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	618	EC$_{40}$= 510	EC$_{35}$= 340	EC$_{30}$= 85	618	EC$_{40}$= 425	EC$_{30}$= 190	EC$_{25}$= 32
9	NaCl=1.00 g/l	618	EC$_{40}$= 485	EC$_{25}$= 370	EC$_{15}$= 190	618	EC$_{35}$= 375	EC$_{20}$= 23	EC$_{10}$= 135
	NaCl=2.50 g/l	618	EC$_{35}$= 325	EC$_{20}$= 170	EC$_{10}$= 70	618	EC$_{30}$= 360	EC$_{15}$= 140	EC$_{5}$= 39
	NaCl=15.00 g/l	618	EC$_{45}$= 330	EC$_{30}$= 170	EC$_{20}$= 6.5	618	EC$_{40}$= 400	EC$_{25}$= 125	EC$_{15}$= 33
10	Fe^{+2}=2.00 mg/l	618	EC$_{40}$= 360	EC$_{30}$= 180	EC$_{20}$= 125	618	EC$_{35}$= 350	EC$_{25}$= 170	EC$_{15}$= 110
	Fe^{+2}=8.00 mg/l	618	EC$_{35}$= 340	EC$_{25}$= 160	EC$_{15}$= 65	618	EC$_{30}$= 310	EC$_{20}$= 150	EC$_{10}$= 47
	Fe^{+2}=20.00 mg/l	618	EC$_{45}$= 300	EC$_{35}$= 150	EC$_{25}$= 50	618	EC$_{35}$= 275	EC$_{30}$= 130	EC$_{20}$= 15
11	Fe^{+3}=10.00 mg/l	618	EC$_{40}$= 350	EC$_{30}$= 210	EC$_{20}$= 160	618	EC$_{35}$= 390	EC$_{25}$= 170	EC$_{15}$= 130
	Fe^{+3}=20.00 mg/l	618	EC$_{35}$= 360	EC$_{25}$= 175	EC$_{15}$= 70	618	EC$_{30}$= 355	EC$_{20}$= 180	EC$_{10}$= 60
	Fe^{+3}=50.00 mg/l	618	EC$_{45}$= 460	EC$_{40}$= 180	EC$_{25}$= 65	618	EC$_{40}$= 300	EC$_{30}$= 160	EC$_{20}$= 32
12	HCO$_3^{-1}$=0.50 g/l	618	EC$_{40}$= 180	EC$_{35}$= 700	EC$_{25}$= 375	618	EC$_{35}$= 800	EC$_{25}$= 160	EC$_{15}$= 350
	HCO$_3^{-1}$=1.00 g/l	618	EC$_{40}$= 750	EC$_{30}$= 325	EC$_{20}$= 140	618	EC$_{35}$= 700	EC$_{25}$= 350	EC$_{10}$= 160
	HCO$_3^{-1}$=5.00 g/l	618	EC$_{45}$= 700	EC$_{35}$= 340	EC$_{30}$= 170	618	EC$_{40}$= 750	EC$_{30}$= 360	EC$_{20}$= 162
13	C$_4$H$_9$OH=0.10 g/l	618	EC$_{40}$= 160	EC$_{30}$= 750	EC$_{25}$= 400	618	EC$_{35}$= 175	EC$_{25}$= 800	EC$_{15}$= 375
	C$_4$H$_9$OH=0.50 g/l	618	EC$_{40}$= 700	EC$_{30}$= 170	EC$_{20}$= 350	618	EC$_{35}$= 170	EC$_{25}$= 700	EC$_{10}$= 370
	C$_4$H$_9$OH=2.00 g/l	618	EC$_{45}$= 430	EC$_{35}$= 200	EC$_{25}$= 108	618	EC$_{40}$= 400	EC$_{30}$= 230	EC$_{20}$= 118

* EC values were calculated based on COD$_{dis}$ (mg/l).

Appendix 7.6 COD_{dis} removal efficiencies of OMI ww before and after sonication process

No	Parameters	**COD_{dis} Removal Efficiencies (%)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
1	Raw ww, control	0.00		12.58		22.70		31.40	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
2	Raw ww, control	0.00	12.76	25.58	32.43	0.00	17.77	39.51	47.67
3	1 h aeration	0.00	35.49	47.11	77.82	0.00	37.96	67.71	86.32
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	28.21	42.29	70.56	0.00	37.81	60.09	79.89
	30 min N_2(g) (6.00 mg/l N_2)	0.00	30.39	53.46	77.36	0.00	40.44	61.62	84.51
5	pH=4.0	0.00	33.41	48.59	62.59	0.00	35.26	50.99	78.23
	pH=7.0	0.00	48.46	66.52	73.99	0.00	53.32	70.08	81.11
	pH=10.0	0.00	49.96	67.64	80.04	0.00	56.46	72.61	89.31
6	DO=2.00 mg/l	0.00	36.05	43.90	62.71	0.00	41.16	50.99	73.12
	DO=4.00 mg/l	0.00	38.88	47.60	71.22	0.00	47.54	59.21	79.41
	DO=6.00 mg/l	0.00	40.18	50.01	74.83	0.00	53.32	61.70	84.32
	DO=10.00 mg/l	0.00	42.17	59.23	79.86	0.00	55.56	68.68	88.73
7	H_2O_2=100 mg/l	0.00	49.16	64.34	73.87	0.00	56.11	75.39	89.09
	H_2O_2=500 mg/l	0.00	53.98	70.65	80.80	0.00	57.91	76.83	91.13
	H_2O_2=2000 mg/l	0.00	55.14	73.15	85.61	0.00	61.77	79.58	93.19
8	TiO_2=0.10 mg/l	0.00	41.85	61.17	73.08	0.00	43.18	64.45	79.38
	TiO_2=0.50 mg/l	0.00	42.74	68.11	78.51	0.00	46.78	68.36	87.90
	TiO_2=10.00 mg/l	0.00	44.51	69.31	84.42	0.00	52.72	75.22	92.44
	TiO_2=20.00 mg/l	0.00	45.94	70.44	87.76	0.00	56.57	78.19	93.93
9	NaCl=1.00 g/l	0.00	51.58	71.43	78.43	0.00	63.14	73.58	84.85
	NaCl=2.50 g/l	0.00	54.76	76.17	81.85	0.00	68.63	76.28	90.58
	NaCl=15.00 g/l	0.00	57.63	81.03	86.43	0.00	70.36	79.37	93.15
10	Fe^{+2}=2.00 mg/l	0.00	50.01	67.20	72.48	0.00	50.95	65.25	84.95
	Fe^{+2}=8.00 mg/l	0.00	52.77	67.74	74.38	0.00	53.10	69.82	87.33
	Fe^{+2}=20.00 mg/l	0.00	54.99	72.87	82.24	0.00	61.77	81.81	90.36
11	Fe^{+3}=10.00 mg/l	0.00	46.89	69.21	75.24	0.00	60.15	76.16	85.70
	Fe^{+3}=20.00 mg/l	0.00	49.25	71.69	81.08	0.00	61.70	80.71	88.61
	Fe^{+3}=50.00 mg/l	0.00	56.89	74.57	83.42	0.00	64.15	83.43	90.75
12	HCO_3^{-1}=0.50 g/l	0.00	46.19	58.49	66.92	0.00	50.77	56.66	74.23
	HCO_3^{-1}=1.00 g/l	0.00	49.86	61.24	69.66	0.00	51.70	62.15	79.72
	HCO_3^{-1}=5.00 g/l	0.00	52.61	63.07	76.06	0.00	56.27	68.55	85.21
13	C_4H_9OH=0.10 g/l	0.00	46.20	58.49	69.66	0.00	48.04	61.24	83.38
	C_4H_9OH=0.50 g/l	0.00	48.03	61.24	72.41	0.00	51.70	63.07	87.95
	C_4H_9OH=2.00 g/l	0.00	51.70	63.07	76.07	0.00	59.92	72.21	90.70

Appendix 7.7 TOC removal efficiencies of OMI ww before and after sonication process

No	Parameters	TOC Removal Efficiencies (%)							
		25^{o}C							
		0. min		60. min		120. min		150. min	
1	Raw ww, control	0.00		10.30		18.33		28.20	
		30^{o}C				60^{o}C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0.00	11.30	24.37	32.09	0.00	17.83	38.76	46.57
3	1 h aeration	0.00	35.28	46.08	76.91	0.00	37.16	67.03	85.26
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	27.77	42.34	70.29	0.00	37.23	59.86	78.28
	30 min N_2(g) (6.00 mg/l N_2)	0.00	29.54	52.69	76.18	0.00	39.88	69.20	83.76
5	pH=4.0	0.00	32.75	47.75	61.73	0.00	35.21	50.78	77.50
	pH=7.0	0.00	47.60	65.37	72.95	0.00	52.45	70.51	80.54
	pH=10.0	0.00	49.15	66.90	79.32	0.00	55.86	71.58	88.16
6	DO=2.00 mg/l	0.00	35.62	42.82	61.45	0.00	40.95	49.38	72.80
	DO=4.00 mg/l	0.00	37.78	46.34	70.67	0.00	47.36	58.79	78.81
	DO=6.00 mg/l	0.00	40.20	49.37	73.67	0.00	52.57	60.31	83.98
	DO=10.00 mg/l	0.00	41.73	58.08	78.75	0.00	54.65	68.43	87.19
7	H_2O_2=100 mg/l	0.00	48.94	63.24	72.34	0.00	55.02	75.14	88.03
	H_2O_2=500 mg/l	0.00	52.17	69.31	79.58	0.00	56.41	75.53	90.27
	H_2O_2=2000 mg/l	0.00	54.48	72.35	84.51	0.00	60.30	78.64	92.14
8	TiO_2=0.10 mg/l	0.00	39.30	57.43	70.22	0.00	42.38	63.76	78.48
	TiO_2=0.50 mg/l	0.00	41.28	64.19	74.33	0.00	46.34	67.75	87.23
	TiO_2=10.00 mg/l	0.00	43.77	64.73	83.72	0.00	51.82	75.12	91.62
	TiO_2=20.00 mg/l	0.00	45.19	69.00	86.70	0.00	56.13	77.55	93.35
9	NaCl=1.00 g/l	0.00	50.79	70.97	77.83	0.00	62.82	72.47	83.34
	NaCl=2.50 g/l	0.00	53.68	75.53	80.94	0.00	67.07	75.46	89.29
	NaCl=15.00 g/l	0.00	56.67	80.20	85.74	0.00	69.05	78.57	92.31
10	Fe^{+2}=2.00 mg/l	0.00	49.63	66.75	71.66	0.00	49.42	64.74	83.52
	Fe^{+2}=8.00 mg/l	0.00	51.33	69.39	73.10	0.00	52.91	71.85	87.11
	Fe^{+2}=20.00 mg/l	0.00	53.87	71.90	81.30	0.00	60.43	80.49	89.62
11	Fe^{+3}=10.00 mg/l	0.00	45.32	68.30	74.72	0.00	59.79	75.59	84.56
	Fe^{+3}=20.00 mg/l	0.00	48.69	72.60	80.01	0.00	60.37	79.32	87.59
	Fe^{+3}=50.00 mg/l	0.00	55.37	74.57	82.12	0.00	63.10	80.26	89.60
12	HCO_3^{-1}=0.50 g/l	0.00	45.91	57.91	65.29	0.00	50.40	61.13	73.19
	HCO_3^{-1}=1.00 g/l	0.00	49.21	60.61	68.82	0.00	51.18	61.59	78.52
	HCO_3^{-1}=5.00 g/l	0.00	51.70	62.47	75.45	0.00	55.55	67.58	84.92
13	C_4H_9OH=0.10 g/l	0.00	45.06	57.91	68.78	0.00	47.85	60.31	82.55
	C_4H_9OH=0.50 g/l	0.00	47.51	60.61	71.38	0.00	50.33	62.44	86.18
	C_4H_9OH=2.00 g/l	0.00	50.85	63.40	77.80	0.00	58.11	71.84	89.17

Appendix 7.8 Color removal efficiencies of OMI ww before and after sonication process

No	**Parameters**	**Color Removal Efficiencies (%)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
1	Raw ww, control	0.00		36.37		47.90		49.70	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
2	Raw ww, control	0.00	38.68	52.61	74.45	0.00	44.59	69.74	83.77
3	1 h aeration	0.00	65.73	68.64	77.45	0.00	67.54	78.16	81.86
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	76.15	77.66	82.36	0.00	78.06	80.36	85.87
	30 min N_2(g) (6.00 mg/l N_2)	0.00	77.56	83.17	89.28	0.00	79.26	85.77	91.88
5	pH=4.0	0.00	61.32	74.15	83.77	0.00	64.03	74.95	89.28
	pH=7.0	0.00	62.42	77.76	85.87	0.00	65.53	76.75	90.18
	pH=10.0	0.00	74.95	79.66	87.07	0.00	69.94	78.46	92.38
6	DO=2.00 mg/l	0.00	42.59	54.81	80.16	0.00	70.84	75.85	86.87
	DO=4.00 mg/l	0.00	52.00	77.66	84.07	0.00	73.75	79.86	89.58
	DO=6.00 mg/l	0.00	62.42	78.96	86.27	0.00	74.75	79.96	91.38
	DO=10.00 mg/l	0.00	68.84	78.06	87.47	0.00	80.86	84.17	93.79
7	H_2O_2=100 mg/l	0.00	50.50	72.34	81.96	0.00	63.93	77.25	90.58
	H_2O_2=500 mg/l	0.00	65.43	77.05	86.07	0.00	69.74	80.26	92.48
	H_2O_2=2000 mg/l	0.00	72.24	82.67	89.88	0.00	73.35	86.67	93.59
8	TiO_2=0.10 mg/l	0.00	57.21	74.25	85.07	0.00	61.92	75.55	87.88
	TiO_2=0.50 mg/l	0.00	62.12	77.15	88.08	0.00	71.04	82.06	91.38
	TiO_2=10.00 mg/l	0.00	67.74	79.06	90.08	0.00	72.14	84.47	93.19
	TiO_2=20.00 mg/l	0.00	72.34	83.77	91.88	0.00	74.55	87.07	95.39
9	NaCl=1.00 g/l	0.00	57.31	74.85	87.37	0.00	62.02	78.76	93.39
	NaCl=2.50 g/l	0.00	68.34	77.35	89.08	0.00	65.63	80.86	94.29
	NaCl=15.00 g/l	0.00	72.04	80.86	92.18	0.00	74.65	83.57	96.09
10	Fe^{+2}=2.00 mg/l	0.00	60.42	74.45	82.77	0.00	64.63	75.25	87.58
	Fe^{+2}=8.00 mg/l	0.00	63.43	77.66	85.57	0.00	71.34	78.86	89.18
	Fe^{+2}=20.00 mg/l	0.00	65.13	81.26	87.07	0.00	73.85	82.97	93.89
11	Fe^{+3}=10.00 mg/l	0.00	40.28	73.65	84.27	0.00	63.34	76.55	85.17
	Fe^{+3}=20.00 mg/l	0.00	42.08	75.15	86.67	0.00	70.44	80.76	88.28
	Fe^{+3}=50.00 mg/l	0.00	50.30	77.56	88.08	0.00	75.05	82.46	91.08
12	HCO_3^{-1}=0.50 g/l	0.00	61.52	73.75	80.96	0.00	73.85	79.96	87.47
	HCO_3^{-1}=1.00 g/l	0.00	64.43	75.85	82.97	0.00	77.45	82.57	89.18
	HCO_3^{-1}=5.00 g/l	0.00	67.64	77.76	85.17	0.00	81.06	83.87	91.78
13	C_4H_9OH=0.10 g/l	0.00	49.30	70.34	82.26	0.00	62.49	74.25	85.17
	C_4H_9OH=0.50 g/l	0.00	52.61	78.06	84.47	0.00	63.98	80.96	87.07
	C_4H_9OH=2.00 g/l	0.00	68.14	79.96	87.98	0.00	69.74	82.06	89.78

Appendix 7.9 Total phenol removal efficiencies of OMI ww before and after sonication process

No	**Parameters**	**Total Phenol Removal Efficiencies (%)**							
		25^{o}C							
		0. min		**60. min**		**120. min**		**150. min**	
1	Raw ww, control	0.00		26.89		54.74		58.25	
		30^{o}C				**60^{o}C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
2	Raw ww, control	0.00	28.26	56.00	59.40	0.00	30.20	57.94	61.24
3	1 h aeration	0.00	44.52	69.82	70.91	0.00	45.13	70.39	72.69
4	15 min $N_2(g)$ (3.00 mg/l N_2)	0.00	39.63	67.27	71.16	0.00	40.93	67.45	74.91
	30 min $N_2(g)$ (6.00 mg/l N_2)	0.00	40.63	67.78	73.99	0.00	41.37	68.21	78.98
5	pH=4.0	0.00	43.74	70.76	76.18	0.00	44.89	74.75	80.02
	pH=7.0	0.00	44.41	71.37	79.28	0.00	45.41	75.31	83.60
	pH=10.0	0.00	44.83	71.43	82.07	0.00	46.15	76.01	85.51
6	DO=2.00 mg/l	0.00	43.46	74.58	77.20	0.00	44.06	79.25	85.53
	DO=4.00 mg/l	0.00	43.50	76.89	80.04	0.00	44.24	79.51	88.02
	DO=6.00 mg/l	0.00	43.59	76.98	82.92	0.00	49.35	79.69	89.46
	DO=10.00 mg/l	0.00	43.98	81.83	88.02	0.00	73.80	84.66	91.38
7	H_2O_2=100 mg/l	0.00	48.82	77.89	79.20	0.00	50.13	78.59	85.48
	H_2O_2=500 mg/l	0.00	49.17	78.07	82.30	0.00	52.49	81.38	90.42
	H_2O_2=2000 mg/l	0.00	49.43	80.73	84.74	0.00	75.32	86.32	93.65
8	TiO_2=0.10 mg/l	0.00	45.22	76.10	79.98	0.00	50.30	81.34	85.57
	TiO_2=0.50 mg/l	0.00	47.60	78.68	82.52	0.00	50.83	82.62	88.71
	TiO_2=10.00 mg/l	0.00	47.73	81.25	85.13	0.00	50.96	86.93	91.20
	TiO_2=20.00 mg/l	0.00	50.30	85.41	87.88	0.00	51.39	89.37	94.77
9	NaCl=1.00 g/l	0.00	42.89	73.44	80.33	0.00	49.43	79.03	88.49
	NaCl=2.50 g/l	0.00	43.19	75.57	82.82	0.00	50.26	79.94	91.77
	NaCl=15.00 g/l	0.00	48.17	76.15	85.66	0.00	51.04	82.34	93.72
10	Fe^{+2}=2.00 mg/l	0.00	41.32	74.76	78.42	0.00	42.54	75.41	82.35
	Fe^{+2}=8.00 mg/l	0.00	42.45	77.69	81.22	0.00	47.61	78.08	84.88
	Fe^{+2}=20.00 mg/l	0.00	47.21	80.37	84.75	0.00	47.78	82.88	89.64
11	Fe^{+3}=10.00 mg/l	0.00	44.02	77.33	82.83	0.00	45.28	82.57	86.10
	Fe^{+3}=20.00 mg/l	0.00	49.43	79.95	85.97	0.00	50.04	82.78	88.85
	Fe^{+3}=50.00 mg/l	0.00	51.67	82.44	88.59	0.00	52.75	85.49	92.58
12	HCO_3^{-1}=0.50 g/l	0.00	42.89	73.44	80.33	0.00	44.54	79.03	88.49
	HCO_3^{-1}=1.00 g/l	0.00	48.08	76.06	82.82	0.00	50.26	82.39	91.77
	HCO_3^{-1}=5.00 g/l	0.00	50.86	81.04	85.66	0.00	55.93	87.23	93.72
13	C_4H_9OH=0.10 g/l	0.00	43.93	75.45	81.65	0.00	47.68	81.04	85.48
	C_4H_9OH=0.50 g/l	0.00	49.17	78.07	84.74	0.00	50.05	85.30	87.97
	C_4H_9OH=2.00 g/l	0.00	51.88	80.73	87.19	0.00	53.33	86.32	90.47

Appendix 7.10 TAAs removal efficiencies of OMI ww before and after sonication process

No	Parameters	TAAs Removal Efficiencies (%)							
		25^{o}C							
		0. min		60. min		120. min		150. min	
1	Raw ww, control	0.00		33.67		48.27		63.17	
		30^{o}C				60^{o}C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0.00	37.19	55.34	64.98	0.00	38.14	59.39	70.52
3	1 h aeration	0.00	41.06	58.85	67.12	0.00	58.56	66.29	72.83
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	51.02	62.08	67.43	0.00	52.80	62.67	72.43
	30 min N_2(g) (6.00 mg/l N_2)	0.00	52.45	65.41	71.18	0.00	53.40	66.78	74.56
5	pH=4.0	0.00	56.60	60.10	67.53	0.00	58.38	62.24	76.09
	pH=7.0	0.00	57.55	60.99	71.75	0.00	58.91	63.01	80.97
	pH=10.0	0.00	58.08	61.05	75.56	0.00	59.92	63.93	86.25
6	DO=2.00 mg/l	0.00	56.24	58.68	68.91	0.00	57.07	65.05	80.28
	DO=4.00 mg/l	0.00	56.30	61.83	69.45	0.00	57.31	68.74	83.67
	DO=6.00 mg/l	0.00	56.42	62.95	73.37	0.00	64.28	72.31	87.30
	DO=10.00 mg/l	0.00	56.96	65.22	77.00	0.00	67.61	75.76	91.58
7	H_2O_2=100 mg/l	0.00	56.90	66.53	68.31	0.00	58.68	69.15	70.21
	H_2O_2=500 mg/l	0.00	57.37	67.10	72.53	0.00	59.22	73.29	76.93
	H_2O_2=2000 mg/l	0.00	57.73	67.73	75.87	0.00	63.02	74.68	83.68
8	TiO_2=0.10 mg/l	0.00	58.62	64.09	72.71	0.00	58.91	67.89	73.66
	TiO_2=0.50 mg/l	0.00	61.89	67.60	76.16	0.00	62.96	71.64	77.94
	TiO_2=10.00 mg/l	0.00	65.40	71.11	79.73	0.00	66.47	75.48	81.34
	TiO_2=20.00 mg/l	0.00	68.91	74.44	83.48	0.00	70.40	78.84	88.54
9	NaCl=1.00 g/l	0.00	55.47	60.40	69.85	0.00	57.73	68.07	77.65
	NaCl=2.50 g/l	0.00	55.89	64.03	73.25	0.00	58.85	72.65	85.44
	NaCl=15.00 g/l	0.00	56.01	67.48	77.11	0.00	63.26	75.93	91.44
10	Fe^{+2}=2.00 mg/l	0.00	53.34	65.59	67.25	0.00	65.00	69.81	72.60
	Fe^{+2}=8.00 mg/l	0.00	54.88	69.58	71.06	0.00	68.57	70.11	76.06
	Fe^{+2}=20.00 mg/l	0.00	61.37	72.91	75.88	0.00	72.14	76.66	85.88
11	Fe^{+3}=10.00 mg/l	0.00	57.16	65.76	69.92	0.00	58.74	66.23	74.38
	Fe^{+3}=20.00 mg/l	0.00	64.39	69.33	74.21	0.00	65.22	69.86	81.47
	Fe^{+3}=50.00 mg/l	0.00	68.44	72.72	77.78	0.00	69.58	73.55	89.56
12	HCO_3^{-1}=0.50 g/l	0.00	58.81	63.73	69.85	0.00	64.39	68.07	70.98
	HCO_3^{-1}=1.00 g/l	0.00	65.89	67.36	73.91	0.00	68.85	72.65	78.77
	HCO_3^{-1}=5.00 g/l	0.00	69.34	70.81	77.11	0.00	73.26	75.93	84.78
13	C_4H_9OH=0.10 g/l	0.00	60.23	66.53	68.31	0.00	62.01	67.48	70.21
	C_4H_9OH=0.50 g/l	0.00	64.04	67.77	72.53	0.00	65.22	71.29	80.27
	C_4H_9OH=2.00 g/l	0.00	67.73	70.40	79.20	0.00	69.69	74.68	87.01

Appendix 7.11 TFAs removal efficiencies of OMI ww before and after sonication process

No	Parameters	TFAs Removal Efficiencies (%)							
		25°C							
		0. min		60. min		120. min		150. min	
1	Raw ww, control	0.00		12.73		18.84		37.51	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0.00	15.62	22.37	45.66	0.00	17.33	24.77	48.84
3	1 h aeration	0.00	38.60	64.39	75.07	0.00	38.71	68.13	78.33
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	38.90	65.79	76.05	0.00	39.10	66.50	77.22
	30 min N_2(g) (6.00 mg/l N_2)	0.00	38.92	69.46	78.62	0.00	39.29	70.86	80.18
5	pH=4.0	0.00	39.33	72.70	80.89	0.00	39.79	74.11	82.39
	pH=7.0	0.00	39.58	66.77	76.74	0.00	40.23	68.92	78.87
	pH=10.0	0.00	39.71	64.43	75.10	0.00	40.25	67.74	78.06
6	DO=2.00 mg/l	0.00	37.10	52.82	66.98	0.00	37.63	53.23	68.19
	DO=4.00 mg/l	0.00	37.15	56.01	69.21	0.00	37.67	57.62	71.18
	DO=6.00 mg/l	0.00	37.29	58.61	71.03	0.00	38.33	59.91	72.74
	DO=10.00 mg/l	0.00	37.56	60.04	72.03	0.00	38.38	62.41	74.44
7	H_2O_2=100 mg/l	0.00	44.00	75.36	82.75	0.00	46.35	78.54	85.41
	H_2O_2=500 mg/l	0.00	45.54	78.22	84.75	0.00	47.40	82.64	88.20
	H_2O_2=2000 mg/l	0.00	45.79	81.03	86.72	0.00	49.04	85.73	90.30
8	TiO_2=0.10 mg/l	0.00	40.33	61.21	72.85	0.00	41.46	68.97	78.90
	TiO_2=0.50 mg/l	0.00	40.73	63.25	74.28	0.00	42.44	70.65	80.04
	TiO_2=10.00 mg/l	0.00	40.85	64.51	75.16	0.00	42.69	73.07	81.68
	TiO_2=20.00 mg/l	0.00	41.02	65.79	76.05	0.00	43.10	77.24	84.52
9	NaCl=1.00 g/l	0.00	35.96	50.05	65.04	0.00	36.67	52.50	67.70
	NaCl=2.50 g/l	0.00	36.15	52.12	66.48	0.00	36.81	55.13	69.49
	NaCl=15.00 g/l	0.00	36.27	55.39	68.77	0.00	36.85	57.69	71.23
10	Fe^{+2}=2.00 mg/l	0.00	33.46	46.77	62.74	0.00	34.15	47.98	64.63
	Fe^{+2}=8.00 mg/l	0.00	33.65	49.58	64.70	0.00	34.50	51.53	67.04
	Fe^{+2}=20.00 mg/l	0.00	34.10	52.55	66.78	0.00	34.54	53.52	68.40
11	Fe^{+3}=10.00 mg/l	0.00	30.00	43.30	60.31	0.00	31.90	45.52	62.96
	Fe^{+3}=20.00 mg/l	0.00	30.40	45.02	61.51	0.00	32.73	48.20	64.78
	Fe^{+3}=50.00 mg/l	0.00	31.58	47.31	63.12	0.00	33.19	49.89	65.93
12	HCO_3^{-1}=0.50 g/l	0.00	22.71	30.44	51.31	0.00	25.79	38.40	58.12
	HCO_3^{-1}=1.00 g/l	0.00	23.60	33.53	53.47	0.00	29.37	42.08	60.61
	HCO_3^{-1}=5.00 g/l	0.00	23.92	35.33	54.73	0.00	29.98	43.98	61.91
13	C_4H_9OH=0.10 g/l	0.00	34.54	47.63	63.34	0.00	35.17	49.44	65.62
	C_4H_9OH=0.50 g/l	0.00	34.87	51.15	65.80	0.00	35.35	52.16	67.47
	C_4H_9OH=2.00 g/l	0.00	35.06	53.89	67.72	0.00	35.46	56.11	70.16

Appendix 7.12 Microtox acute toxicity values of OMI ww before and after sonication process

No	Parameters	Microtox Acute Toxicity Values, * EC (mg/l)							
		25°C							
		0. min		60. min		120. min		150. min	
		*EC_{90}		*EC		*EC		*EC	
1	Raw ww, control	100000		EC_{80}=90000		EC_{75}=98000		EC_{70}=95000	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
		*EC_{90}	*EC	*EC	*EC	*EC_{90}	*EC	*EC	*EC
2	Raw ww, control	100000	EC_{75}= 90000	EC_{70}= 94000	EC_{60}= 95000	100000	EC_{70}= 65000	EC_{70}= 65000	EC_{50}= 60000
3	1 h aeration	100000	EC_{60}= 79206	EC_{40}= 62627	EC_{25}= 46858	100000	EC_{55}= 78516	EC_{25}= 55590	EC_{15}= 45239
4	15 min N_2(g) (3.00 mg/l N_2)	100000	EC_{75}= 80186	EC_{40}= 57002	EC_{30}= 51629	100000	EC_{70}= 70482	EC_{35}= 61295	EC_{20}= 44984
	30 min N_2(g) (6.00 mg/l N_2)	100000	EC_{70}= 78796	EC_{35}= 59097	EC_{25}= 45963	100000	EC_{65}= 73990	EC_{30}= 55452	EC_{15}= 42171
5	pH=4.0	100000	EC_{75}= 82602	EC_{65}= 60384	EC_{55}= 47298	100000	EC_{65}= 72548	EC_{60}= 54243	EC_{50}= 43871
	pH=7.0	100000	EC_{75}= 90000	EC_{70}= 94000	EC_{60}= 95000	100000	EC_{70}= 65000	EC_{70}= 65000	EC_{50}= 60000
	pH=10.0	100000	EC_{70}= 71343	EC_{65}= 50764	EC_{55}= 36065	100000	EC_{65}= 63248	EC_{55}= 35383	EC_{40}= 30635
6	DO=2.00 mg/l	100000	EC_{75}= 87480	EC_{55}= 67742	EC_{40}= 53298	100000	EC_{70}= 72150	EC_{50}= 64126	EC_{35}= 48600
	DO=4.00 mg/l	100000	EC_{75}= 73016	EC_{50}= 63766	EC_{35}= 52223	100000	EC_{70}= 67162	EC_{45}= 59609	EC_{30}= 35880
	DO=6.00 mg/l	100000	EC_{70}= 77282	EC_{45}= 67388	EC_{30}= 35575	100000	EC_{60}= 66142	EC_{40}= 51960	EC_{25}= 32789
	DO=10.00 mg/l	100000	EC_{65}= 79206	EC_{40}= 62627	EC_{25}= 46858	100000	EC_{55}= 78516	EC_{35}= 55590	EC_{20}= 45239
7	H_2O_2=100 mg/l	100000	EC_{45}= 72500	EC_{25}= 56175	EC_{15}= 30282	100000	EC_{40}= 66782	EC_{20}= 34183	EC_{10}= 23271
	H_2O_2=500 mg/l	100000	EC_{40}= 63374	EC_{20}= 45660	EC_{10}= 26124	100000	EC_{35}= 60000	EC_{15}= 60000	EC_{5}= 60000
	H_2O_2=2000 mg/l	100000	EC_{50}= 61884	EC_{30}= 34131	EC_{20}= 19822	100000	EC_{45}= 59024	EC_{25}= 33418	EC_{15}= 11289
8	TiO_2=0.10 mg/l	100000	EC_{50}= 60955	EC_{25}= 43126	EC_{20}= 31168	100000	EC_{45}= 67776	EC_{20}= 43439	EC_{15}= 29255
	TiO_2=0.50 mg/l	100000	EC_{45}= 63188	EC_{20}= 37713	EC_{15}= 23515	100000	EC_{40}= 55019	EC_{15}= 32326	EC_{10}= 49620
	TiO_2=10.00 mg/l	100000	EC_{40}= 60316	EC_{15}= 37802	EC_{10}= 23804	100000	EC_{35}= 75000	EC_{10}= 62000	EC_{5}= 58000
	TiO_2=20.00 mg/l	100000	EC_{55}= 54774	EC_{30}= 34630	EC_{20}= 15280	100000	EC_{50}= 45350	EC_{25}= 30267	EC_{15}= 14580

* EC values were calculated based on COD_{dis} (mg/l)

Appendix 7.12 Microtox acute toxicity values of OMI ww before and after sonication process (cont.).

No	Parameters	Microtox Acute Toxicity Values, * EC (mg/l)							
		25°C							
		0. min		60. min		120. min		150. min	
		*EC_{90}		*EC		*EC		*EC	
1	Raw ww, control	100000		EC_{80}=90000		EC_{75}=98000		EC_{70}=95000	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
		*EC_{90}	*EC	*EC	*EC	*EC_{90}	*EC	*EC	*EC
2	Raw ww, control	100000	EC_{75}= 90000	EC_{70}= 94000	EC_{60}= 95000	100000	EC_{70}= 65000	EC_{70}= 65000	EC_{50}= 60000
9	NaCl=1.00 g/l	100000	EC_{55}= 66693	EC_{25}= 42196	EC_{15}= 27633	100000	EC_{50}= 65100	EC_{20}= 39671	EC_{10}= 27330
	NaCl=2.50 g/l	100000	EC_{50}= 63400	EC_{20}= 37164	EC_{10}= 26393	100000	EC_{45}= 58836	EC_{15}= 31172	EC_{5}= 11817
	NaCl=15.00 g/l	100000	EC_{60}= 57560	EC_{30}= 29623	EC_{25}= 21807	100000	EC_{55}= 46795	EC_{25}= 20554	EC_{20}= 6744
10	Fe^{+2}=2.00 mg/l	100000	EC_{65}= 62098	EC_{30}= 54330	EC_{15}= 47882	100000	EC_{60}= 60530	EC_{25}= 42755	EC_{10}= 21156
	Fe^{+2}=8.00 mg/l	100000	EC_{60}= 67520	EC_{25}= 50325	EC_{10}= 35250	100000	EC_{55}= 63276	EC_{20}= 49126	EC_{5}= 50840
	Fe^{+2}=20.00 mg/l	100000	EC_{70}= 61136	EC_{35}= 45125	EC_{25}= 18558	100000	EC_{65}= 55390	EC_{30}= 32235	EC_{20}= 3107
11	Fe^{+3}=10.00 mg/l	100000	EC_{70}= 63090	EC_{35}= 61498	EC_{25}= 58524	100000	EC_{65}= 65412	EC_{30}= 55815	EC_{20}= 50217
	Fe^{+3}=20.00 mg/l	100000	EC_{65}= 61283	EC_{30}= 39534	EC_{15}= 26682	100000	EC_{60}= 49152	EC_{25}= 44460	EC_{10}= 36672
	Fe^{+3}=50.00 mg/l	100000	EC_{75}= 43320	EC_{40}= 31732	EC_{30}= 23456	100000	EC_{70}= 29335	EC_{35}= 26811	EC_{25}= 14716
12	HCO_3^{-1}=0.50 g/l	100000	EC_{70}= 63993	EC_{40}= 51765	EC_{25}= 41784	100000	EC_{65}= 70886	EC_{35}= 51818	EC_{20}= 38699
	HCO_3^{-1}=1.00 g/l	100000	EC_{65}= 61250	EC_{35}= 48280	EC_{20}= 39498	100000	EC_{60}= 67473	EC_{30}= 55581	EC_{15}= 48952
	HCO_3^{-1}=5.00 g/l	100000	EC_{75}= 64089	EC_{45}= 52531	EC_{30}= 42771	100000	EC_{70}= 59125	EC_{40}= 44899	EC_{25}= 40362
13	C_4H_9OH=0.10 g/l	100000	EC_{70}= 67292	EC_{35}= 51689	EC_{25}= 45373	100000	EC_{65}= 65468	EC_{30}= 52269	EC_{20}= 44823
	C_4H_9OH=0.50 g/l	100000	EC_{65}= 66019	EC_{30}= 51534	EC_{20}= 36876	100000	EC_{60}= 69342	EC_{25}= 52868	EC_{15}= 40206
	C_4H_9OH=2.00 g/l	100000	EC_{75}= 66573	EC_{40}= 48191	EC_{30}= 41411	100000	EC_{70}= 57590	EC_{35}= 44143	EC_{20}= 41660

* EC values were calculated based on COD_{dis} (mg/l).

Appendix 7.13 *Daphnia magna* acute toxicity values of OMI ww before and after sonication process

No	**Parameters**	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25^{o}C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC_{50}**		***EC**		***EC**		***EC**	
1	Raw ww, control	78000		EC_{40}=85000		EC_{30}=55000		EC_{25}=39000	
		30^{o}C				**60^{o}C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC_{50}**	***EC**	***EC**	***EC**	***EC_{50}**	***EC**	***EC**	***EC**
2	Raw ww, control	78000	EC_{35}= 70000	EC_{30}= 65000	EC_{25}= 40000	78000	EC_{30}= 60000	EC_{25}= 37000	EC_{20}= 29000
3	1 h aeration	78000	EC_{20}= 60000	EC_{15}= 58000	EC_{10}= 70000	78000	EC_{15}= 68000	EC_{10}= 59000	EC_{5}= 47500
4	15 min N_2(g) (3.00 mg/l N_2)	78000	EC_{35}= 60000	EC_{30}= 50000	EC_{20}= 78000	78000	EC_{30}= 65000	EC_{20}= 67000	EC_{10}= 46000
	30 min N_2(g) (6.00 mg/l N_2)	78000	EC_{30}= 70000	EC_{20}= 65000	EC_{15}= 50000	78000	EC_{25}= 65000	EC_{15}= 44000	EC_{5}= 58000
5	pH=4.0	78000	EC_{35}= 50000	EC_{30}= 42000	EC_{25}= 40000	78000	EC_{30}= 68000	EC_{30}= 60000	EC_{20}= 42500
	pH=7.0	78000	EC_{35}= 70000	EC_{30}= 65000	EC_{25}= 40000	78000	EC_{30}= 60000	EC_{25}= 37000	EC_{20}= 29000
	pH=10.0	78000	EC_{30}= 64000	EC_{25}= 35000	EC_{20}= 50000	78000	EC_{25}= 47000	EC_{20}= 37000	EC_{15}= 28000
6	DO=2.00 mg/l	78000	EC_{35}= 75000	EC_{30}= 69000	EC_{20}= 46000	78000	EC_{30}= 70000	EC_{25}= 49000	EC_{20}= 48000
	DO=4.00 mg/l	78000	EC_{30}= 52000	EC_{25}= 81000	EC_{20}= 70000	78000	EC_{25}= 70000	EC_{20}= 36000	EC_{15}= 54000
	DO=6.00 mg/l	78000	EC_{30}= 74000	EC_{20}= 42000	EC_{15}= 65000	78000	EC_{25}= 45000	EC_{15}= 44000	EC_{10}= 32000
	DO=10.00 mg/l	78000	EC_{25}= 80000	EC_{20}= 58000	EC_{10}= 70000	78000	EC_{20}= 78000	EC_{15}= 59000	EC_{5}= 47500
7	H_2O_2=100 mg/l	78000	EC_{35}= 29000	EC_{25}= 60000	EC_{15}= 50000	78000	EC_{30}= 27500	EC_{20}= 60000	EC_{10}= 40000
	H_2O_2=500 mg/l	78000	EC_{30}= 54000	EC_{20}= 25000	EC_{10}= 40000	78000	EC_{30}= 42000	EC_{15}= 27000	EC_{5}= 15000
	H_2O_2=2000 mg/l	78000	EC_{35}= 35000	EC_{30}= 22500	EC_{20}= 12500	78000	EC_{35}= 30000	EC_{25}= 22500	EC_{15}= 8500
8	TiO_2=0.10 mg/l	78000	EC_{35}= 60000	EC_{25}= 32500	EC_{15}= 37500	78000	EC_{30}= 29000	EC_{20}= 60000	EC_{10}= 44000
	TiO_2=0.50 mg/l	78000	EC_{35}= 60000	EC_{25}= 27500	EC_{15}= 20000	78000	EC_{30}= 57500	EC_{20}= 27500	EC_{5}= 20000
	TiO_2=10.00 mg/l	78000	EC_{30}= 50000	EC_{20}= 40000	EC_{10}= 24000	78000	EC_{30}= 37000	EC_{15}= 21500	EC_{5}= 9750
	TiO_2=20.00 mg/l	78000	EC_{35}= 45000	EC_{25}= 32500	EC_{20}= 22000	78000	EC_{30}= 34000	EC_{20}= 24000	EC_{15}= 6000

* EC values were calculated based on COD_{dis} (mg/l).

Appendix 7.13 *Daphnia magna* acute toxicity values of OMI ww before and after sonication process (cont.).

No	Parameters	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		$^*EC_{50}$		***EC**		***EC**		***EC**	
1	Raw ww, control	78000		EC_{40}=85000		EC_{30}=55000		EC_{25}=39000	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		$^*EC_{50}$	***EC**	***EC**	***EC**	**$^*EC_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	78000	EC_{35}= 70000	EC_{30}= 65000	EC_{25}= 40000	78000	EC_{30}= 60000	EC_{25}= 37000	EC_{20}= 29000
9	NaCl=1.00 g/l	78000	EC_{35}= 32500	EC_{25}= 60000	EC_{15}= 45000	78000	EC_{30}= 65000	EC_{20}= 25000	EC_{10}= 42500
	NaCl=2.50 g/l	78000	EC_{30}= 54000	EC_{20}= 32500	EC_{10}= 27000	78000	EC_{30}= 54000	EC_{15}= 32500	EC_{5}= 14000
	NaCl=15.00 g/l	78000	EC_{35}= 60000	EC_{25}= 35000	EC_{20}= 17000	78000	EC_{30}= 54000	EC_{20}= 30000	EC_{10}= 7000
10	Fe^{+2}=2.00 mg/l	78000	EC_{35}= 65000	EC_{20}= 50000	EC_{10}= 37000	78000	EC_{30}= 60000	EC_{15}= 50000	EC_{10}= 35000
	Fe^{+2}=8.00 mg/l	78000	EC_{30}= 65000	EC_{20}= 45000	EC_{10}= 30000	78000	EC_{30}= 60000	EC_{15}= 44000	EC_{5}= 22500
	Fe^{+2}=20.00 mg/l	78000	EC_{35}= 60000	EC_{25}= 44000	EC_{15}= 25000	78000	EC_{30}= 52500	EC_{20}= 34000	EC_{10}= 12500
11	Fe^{+3}=10.00 mg/l	78000	EC_{30}= 65000	EC_{25}= 59000	EC_{20}= 35000	78000	EC_{30}= 70000	EC_{20}= 44000	EC_{15}= 27500
	Fe^{+3}=20.00 mg/l	78000	EC_{30}= 70000	EC_{20}= 45000	EC_{15}= 32500	78000	EC_{30}= 64000	EC_{15}= 45000	EC_{10}= 25000
	Fe^{+3}=50.00 mg/l	78000	EC_{35}= 50000	EC_{30}= 45000	EC_{20}= 25000	78000	EC_{30}= 58000	EC_{25}= 35000	EC_{15}= 14000
12	HCO_3^{-1}=0.50 g/l	78000	EC_{30}= 50000	EC_{25}= 65000	EC_{20}= 60000	78000	EC_{30}= 68000	EC_{20}= 50000	EC_{15}= 58000
	HCO_3^{-1}=1.00 g/l	78000	EC_{30}= 65000	EC_{20}= 47500	EC_{15}= 35000	78000	EC_{30}= 60000	EC_{15}= 54000	EC_{10}= 45000
	HCO_3^{-1}=5.00 g/l	78000	EC_{35}= 60000	EC_{30}= 50000	EC_{25}= 45000	78000	EC_{30}= 64000	EC_{25}= 50000	EC_{20}= 45000
13	C_4H_9OH=0.10 g/l	78000	EC_{30}= 40000	EC_{25}= 70000	EC_{20}= 60000	78000	EC_{30}= 47000	EC_{20}= 72000	EC_{15}= 57000
	C_4H_9OH=0.50 g/l	78000	EC_{30}= 65000	EC_{20}= 41000	EC_{15}= 57000	78000	EC_{30}= 47500	EC_{15}= 65000	EC_{10}= 55000
	C_4H_9OH=2.00 g/l	78000	EC_{35}= 37000	EC_{30}= 30000	EC_{25}= 28000	78000	EC_{30}= 37500	EC_{25}= 35000	EC_{15}= 34000

* EC values were calculated based on COD_{dis} (mg/l).

Appendix 7.14 COD_{dis} removal efficiencies of TI ww before and after sonication process

No	Parameters	COD_{dis} Removal Efficiencies (%)							
		25°C							
		0. min		60. min		120. min		150. min	
1	Raw ww, control	0.00		30.43		53.69		74.27	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0.00	42.39	67.34	81.53	0.00	48.08	64.48	84.92
3	1 h aeration	0.00	47.45	60.79	83.21	0.00	50.26	63.30	84.28
4	15 min $N_2(g)$ (3.00 mg/l N_2)	0.00	49.56	75.94	93.10	0.00	50.09	84.85	95.22
	30 min $N_2(g)$ (6.00 mg/l N_2)	0.00	52.04	78.26	96.21	0.00	63.47	88.70	98.23
5	pH=4.0	0.00	47.17	60.93	85.10	0.00	57.57	75.46	87.10
	pH=7.0	0.00	51.81	72.39	89.11	0.00	60.28	86.77	91.14
	pH=10.0	0.00	53.51	73.60	92.21	0.00	60.90	89.12	94.70
6	DO=2.00 mg/l	0.00	48.15	65.33	81.21	0.00	53.89	75.46	84.27
	DO=4.00 mg/l	0.00	51.30	71.61	82.44	0.00	50.76	74.41	86.59
	DO=6.00 mg/l	0.00	52.79	74.33	83.41	0.00	57.33	77.23	89.31
	DO=10.00 mg/l	0.00	55.05	74.44	87.30	0.00	59.88	80.25	94.07
7	H_2O_2=100 mg/l	0.00	42.22	59.47	85.22	0.00	48.04	72.03	87.42
	H_2O_2=500 mg/l	0.00	47.69	66.65	88.12	0.00	52.17	84.05	93.62
	H_2O_2=2000mg/l	0.00	49.02	79.87	95.10	0.00	56.55	87.17	97.92
8	TiO_2=0.10 mg/l	0.00	44.30	66.26	82.31	0.00	45.80	59.60	85.24
	TiO_2=0.50 mg/l	0.00	45.30	68.94	83.43	0.00	49.90	74.43	89.20
	TiO_2=10.00 mg/l	0.00	47.32	71.15	89.27	0.00	56.65	82.22	91.17
	TiO_2=20.00 mg/l	0.00	48.95	75.75	94.11	0.00	61.03	85.60	98.13
9	NaCl=1.00 g/l	0.00	44.97	67.53	84.10	0.00	55.61	69.98	88.13
	NaCl=2.50 g/l	0.00	48.59	72.91	89.15	0.00	64.34	81.86	94.35
	NaCl=15.00 g/l	0.00	51.85	78.44	92.10	0.00	65.24	83.03	97.32
10	Fe^{+2}=2.00 mg/l	0.00	43.19	66.35	86.27	0.00	54.63	70.90	90.29
	Fe^{+2}=8.00 mg/l	0.00	46.32	71.45	90.31	0.00	57.08	80.24	95.31
	Fe^{+2}=20.00 mg/l	0.00	48.85	73.84	96.53	0.00	66.94	88.73	99.26
11	Fe^{+3}=10.00 mg/l	0.00	39.64	65.00	88.41	0.00	54.71	72.90	91.18
	Fe^{+3}=20.00 mg/l	0.00	42.32	70.22	92.15	0.00	56.48	78.08	97.20
	Fe^{+3}=50.00 mg/l	0.00	51.00	79.51	97.39	0.00	59.25	89.24	99.37
12	HCO_3^{-1}=0.50 g/l	0.00	9.91	58.30	79.00	0.00	19.23	56.30	80.19
	HCO_3^{-1}=1.00 g/l	0.00	18.99	57.24	79.15	0.00	20.98	66.93	82.33
	HCO_3^{-1}=5.00 g/l	0.00	11.40	57.35	80.31	0.00	20.84	57.92	82.50
13	C_4H_9OH=0.10 g/l	0.00	18.95	65.67	79.22	0.00	19.96	66.68	81.23
	C_4H_9OH=0.50 g/l	0.00	19.19	66.69	80.29	0.00	21.08	66.93	81.50
	C_4H_9OH=2.00 g/l	0.00	20.95	67.53	80.63	0.00	21.05	67.68	82.40

Appendix 7.15 TOC removal efficiencies of TI ww before and after sonication process

No	Parameters	TOC Removal Efficiencies (%)							
		25°C							
		0. min		60. min		120. min		150. min	
1	Raw ww, control	0.00		31.64		51.42		72.95	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0.00	40.57	66.96	80.79	0.00	46.56	62.17	83.22
3	1 h aeration	0.00	47.11	58.99	82.22	0.00	48.98	61.46	83.27
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	47.79	73.88	92.29	0.00	49.24	83.41	93.57
	30 min N_2(g) (6.00 mg/l N_2)	0.00	50.40	76.93	95.36	0.00	62.39	88.88	98.26
5	pH=4.0	0.00	46.37	59.88	84.51	0.00	56.60	74.19	85.61
	pH=7.0	0.00	50.83	71.07	87.42	0.00	59.26	85.29	90.70
	pH=10.0	0.00	52.43	73.97	90.98	0.00	61.24	87.43	93.01
6	DO=2.00 mg/l	0.00	47.39	64.22	79.87	0.00	52.72	74.09	84.52
	DO=4.00 mg/l	0.00	50.35	69.96	80.95	0.00	50.65	73.23	85.01
	DO=6.00 mg/l	0.00	51.72	72.90	83.74	0.00	56.28	75.81	88.69
	DO=10.00 mg/l	0.00	54.03	72.99	85.58	0.00	58.78	79.65	92.77
7	H_2O_2=100 mg/l	0.00	41.43	58.60	85.48	0.00	47.49	72.42	86.75
	H_2O_2=500 mg/l	0.00	46.89	65.68	89.16	0.00	52.44	84.22	93.38
	H_2O_2=2000 mg/l	0.00	47.94	80.21	94.90	0.00	56.70	85.61	95.98
8	TiO_2=0.10 mg/l	0.00	43.38	65.13	81.15	0.00	45.03	58.59	84.93
	TiO_2=0.50 mg/l	0.00	44.53	67.60	82.95	0.00	50.59	73.33	89.66
	TiO_2=10.00 mg/l	0.00	46.69	70.09	88.58	0.00	55.68	80.91	89.87
	TiO_2=20.00 mg/l	0.00	49.14	75.06	95.02	0.00	61.78	85.84	98.18
9	NaCl=1.00 g/l	0.00	44.21	68.11	84.94	0.00	55.50	68.81	86.80
	NaCl=2.50 g/l	0.00	49.21	71.67	88.39	0.00	63.09	82.00	92.98
	NaCl=15.00 g/l	0.00	50.85	76.93	91.61	0.00	64.06	82.90	96.83
10	Fe^{+2}=2.00 mg/l	0.00	43.74	65.14	85.47	0.00	53.71	75.55	89.02
	Fe^{+2}=8.00 mg/l	0.00	45.54	70.24	88.85	0.00	56.37	78.63	95.38
	Fe^{+2}=20.00 mg/l	0.00	48.02	72.41	96.69	0.00	65.80	88.07	99.23
11	Fe^{+3}=10.00 mg/l	0.00	39.05	65.17	88.28	0.00	53.87	71.41	91.45
	Fe^{+3}=20.00 mg/l	0.00	43.11	69.71	92.30	0.00	57.13	77.49	97.26
	Fe^{+3}=50.00 mg/l	0.00	51.84	79.78	97.92	0.00	59.87	89.43	99.35
12	HCO_3^{-1}=0.50 g/l	0.00	14.13	59.12	80.85	0.00	15.27	58.77	82.83
	HCO_3^{-1}=1.00 g/l	0.00	14.86	60.08	81.16	0.00	16.37	57.97	82.80
	HCO_3^{-1}=5.00 g/l	0.00	17.04	60.19	81.16	0.00	15.63	58.61	83.84
13	C_4H_9OH=0.10 g/l	0.00	15.83	62.52	81.36	0.00	30.92	61.15	83.17
	C_4H_9OH=0.50 g/l	0.00	18.26	61.78	81.67	0.00	31.68	61.37	84.50
	C_4H_9OH=2.00 g/l	0.00	18.23	63.59	82.01	0.00	30.94	62.01	83.84

Appendix 7.16 Color removal efficiencies of TI ww before and after sonication process

No	Parameters	Color Removal Efficiencies (%)							
		25°C							
		0. min		60. min		120. min		150. min	
1	Raw ww, control	0.00		12.37		53.47		57.09	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0.00	52.29	76.38	78.26	0.00	79.32	83.20	87.66
3	1 h aeration	0.00	53.35	77.91	80.61	0.00	53.47	83.55	90.25
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	54.76	77.20	86.02	0.00	80.96	85.08	92.24
	30 min N_2(g) (6.00 mg/l N_2)	0.00	56.40	83.67	90.48	0.00	83.90	88.37	95.30
5	pH=4.0	0.00	76.15	84.14	87.43	0.00	87.54	91.07	94.01
	pH=7.0	0.00	78.61	86.25	88.84	0.00	89.54	91.54	93.77
	pH=10.0	0.00	81.20	86.96	89.07	0.00	89.89	91.77	95.06
6	DO=2.00 mg/l	0.00	87.78	88.84	90.25	0.00	91.07	93.77	95.65
	DO=4.00 mg/l	0.00	88.95	89.31	91.77	0.00	91.30	93.89	96.47
	DO=6.00 mg/l	0.00	89.19	91.07	92.83	0.00	91.42	94.24	97.06
	DO=10.00 mg/l	0.00	89.89	93.65	95.06	0.00	92.24	95.06	97.65
7	H_2O_2=100 mg/l	0.00	74.62	77.79	80.96	0.00	82.26	85.08	87.54
	H_2O_2=500 mg/l	0.00	75.44	78.61	82.14	0.00	83.78	86.37	89.19
	H_2O_2=2000 mg/l	0.00	77.67	80.73	83.78	0.00	87.31	91.07	95.06
8	TiO_2=0.10 mg/l	0.00	58.28	78.38	80.73	0.00	79.79	83.31	89.42
	TiO_2=0.50 mg/l	0.00	59.34	79.67	84.14	0.00	80.38	85.78	91.19
	TiO_2=10.00 mg/l	0.00	60.40	82.84	88.60	0.00	80.49	88.60	94.95
	TiO_2=20.00 mg/l	0.00	62.40	83.78	90.13	0.00	81.67	90.83	96.24
9	NaCl=1.00 g/l	0.00	78.03	80.14	83.43	0.00	83.31	94.95	96.71
	NaCl=2.50 g/l	0.00	78.50	80.61	84.96	0.00	91.66	96.36	97.06
	NaCl=15.00 g/l	0.00	78.61	83.20	87.19	0.00	92.95	96.94	97.53
10	Fe^{+2}=2.00 mg/l	0.00	79.91	84.96	88.13	0.00	87.19	90.72	95.30
	Fe^{+2}=8.00 mg/l	0.00	81.20	85.31	87.78	0.00	87.54	90.95	96.12
	Fe^{+2}=20.00 mg/l	0.00	83.20	86.96	88.13	0.00	88.72	91.89	96.59
11	Fe^{+3}=10.00 mg/l	0.00	84.14	87.31	89.31	0.00	87.31	88.95	91.42
	Fe^{+3}=20.00 mg/l	0.00	84.84	88.37	91.07	0.00	88.13	90.60	93.89
	Fe^{+3}=50.00 mg/l	0.00	84.96	89.31	93.42	0.00	88.72	91.30	93.07
12	HCO_3^{-1}=0.50 g/l	0.00	78.73	83.78	86.96	0.00	87.66	90.36	93.30
	HCO_3^{-1}=1.00 g/l	0.00	80.02	84.14	88.95	0.00	87.90	90.60	94.95
	HCO_3^{-1}=5.00 g/l	0.00	82.02	85.78	89.31	0.00	88.72	91.89	96.12
13	C_4H_9OH=0.10 g/l	0.00	83.90	87.19	88.13	0.00	87.19	88.95	91.07
	C_4H_9OH=0.50 g/l	0.00	84.72	88.25	91.30	0.00	88.25	90.72	94.01
	C_4H_9OH=2.00 g/l	0.00	84.96	89.42	93.54	0.00	88.84	91.66	94.48

Appendix 7.17 TAAs removal efficiencies of TI ww before and after sonication process

No	Parameters	TAAs Removal Efficiencies (%)							
		25°C							
		0. min		60. min		120. min		150.min	
1	Raw ww, control	0.00		16.73		20.15		26.98	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0.00	20.09	27.28	33.89	0.00	20.70	30.00	40.62
3	1 h aeration	0.00	20.48	39.87	52.82	0.00	20.86	46.10	59.38
4	15 min N_2(g) (3.00 mg/l N_2)	0.00	19.98	39.32	58.56	0.00	20.31	46.10	61.79
	30 min N_2(g) (6.00 mg/l N_2)	0.00	20.09	45.61	60.41	0.00	20.48	50.48	68.08
5	pH=4.0	0.00	19.38	32.33	45.39	0.00	19.43	32.60	48.57
	pH=7.0	0.00	19.43	35.47	52.05	0.00	19.54	39.10	58.61
	pH=10.0	0.00	19.56	38.72	58.39	0.00	19.54	45.39	64.89
6	DO=2.00 mg/l	0.00	19.93	33.15	46.27	0.00	20.31	33.59	49.57
	DO=4.00 mg/l	0.00	20.09	33.32	52.55	0.00	20.42	39.98	58.89
	DO=6.00 mg/l	0.00	20.15	39.60	55.26	0.00	20.59	46.16	65.17
	DO=10.00 mg/l	0.00	20.20	45.94	59.05	0.00	20.75	46.21	71.56
7	H_2O_2=100 mg/l	0.00	18.88	38.01	44.62	0.00	19.27	38.23	57.40
	H_2O_2=500 mg/l	0.00	18.94	44.23	51.07	0.00	19.32	44.45	62.09
	H_2O_2=2000 mg/l	0.00	19.16	47.48	68.40	0.00	19.43	50.74	80.16
8	TiO_2=0.10 mg/l	0.00	15.97	37.18	44.89	0.00	18.28	35.25	57.05
	TiO_2=0.50 mg/l	0.00	16.52	40.49	51.18	0.00	18.28	44.62	64.56
	TiO_2=10.00 mg/l	0.00	17.56	46.77	57.46	0.00	18.33	50.79	70.68
	TiO_2=20.00 mg/l	0.00	18.22	47.35	61.27	0.00	18.55	57.13	77.02
9	NaCl=1.00 g/l	0.00	18.50	32.49	45.55	0.00	19.60	38.83	52.44
	NaCl=2.50 g/l	0.00	18.66	35.69	52.11	0.00	19.76	39.27	59.00
	NaCl=15.00 g/l	0.00	19.27	32.66	58.28	0.00	19.98	45.55	65.33
10	Fe^{+2}=2.00 mg/l	0.00	16.85	37.57	44.95	0.00	17.89	38.66	52.11
	Fe^{+2}=8.00 mg/l	0.00	17.78	38.12	51.50	0.00	18.06	44.95	64.51
	Fe^{+2}=20.00 mg/l	0.00	17.78	39.28	58.01	0.00	18.72	51.46	76.91
11	Fe^{+3}=10.00 mg/l	0.00	18.11	37.79	44.78	0.00	18.99	41.31	51.56
	Fe^{+3}=20.00 mg/l	0.00	18.66	37.95	51.01	0.00	19.10	44.62	64.02
	Fe^{+3}=50.00 mg/l	0.00	18.66	41.20	57.24	0.00	19.21	50.96	70.24
12	HCO_3^{-1}=0.50 g/l	0.00	18.78	38.66	49.87	0.00	20.09	38.95	53.06
	HCO_3^{-1}=1.00 g/l	0.00	19.34	36.06	52.20	0.00	25.93	39.45	59.18
	HCO_3^{-1}=5.00 g/l	0.00	19.45	38.83	58.47	0.00	26.15	46.72	65.49
13	C_4H_9OH=0.10 g/l	0.00	24.67	38.66	45.71	0.00	25.77	39.45	53.06
	C_4H_9OH=0.50 g/l	0.00	19.27	32.66	58.28	0.00	25.93	39.89	59.61
	C_4H_9OH=2.00 g/l	0.00	24.84	38.90	52.39	0.00	26.43	45.95	65.52

Appendix 7.18 Microtox acute toxicity values of TI ww before and after sonication process

No	**Parameters**	**Microtox Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC$_{90}$**		***EC**		***EC**		***EC**	
1	Raw ww, control	825		EC$_{70}$=510		EC$_{60}$=650		EC$_{50}$=640	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC$_{90}$**	***EC**	***EC**	***EC**	***EC$_{90}$**	***EC**	***EC**	***EC**
2	Raw ww, control	825	EC$_{70}$= 580	EC$_{50}$= 580	EC$_{40}$= 550	825	EC$_{55}$= 550	EC$_{40}$= 590	EC$_{30}$= 690
3	1 h aeration	825	EC$_{60}$= 322	EC$_{30}$= 249	EC$_{20}$= 165	825	EC$_{50}$= 320	EC$_{25}$= 261	EC$_{15}$= 146
4	15 min N_2(g) (3.00 mg/l N_2)	825	EC$_{60}$= 410	EC$_{35}$= 230	EC$_{25}$= 162	825	EC$_{55}$= 407	EC$_{30}$= 220	EC$_{20}$= 162
	30 min N_2(g) (6.00 mg/l N_2)	825	EC$_{55}$= 406	EC$_{30}$= 228	EC$_{20}$= 159	825	EC$_{50}$= 403	EC$_{25}$= 215	EC$_{15}$= 145
5	pH=4.0	825	EC$_{65}$= 318	EC$_{55}$= 248	EC$_{40}$= 164	825	EC$_{60}$= 416	EC$_{50}$= 230	EC$_{35}$= 152
	pH=7.0	825	EC$_{70}$= 580	EC$_{50}$= 580	EC$_{40}$= 550	825	EC$_{55}$= 550	EC$_{40}$= 590	EC$_{30}$= 690
	pH=10.0	825	EC$_{65}$= 310	EC$_{55}$= 233	EC$_{30}$= 157	825	EC$_{50}$= 307	EC$_{45}$= 214	EC$_{25}$= 148
6	DO=2.00 mg/l	825	EC$_{65}$= 423	EC$_{45}$= 242	EC$_{35}$= 163	825	EC$_{60}$= 319	EC$_{40}$= 40	EC$_{30}$= 240
	DO=4.00 mg/l	825	EC$_{65}$= 422	EC$_{40}$= 235	EC$_{30}$= 159	825	EC$_{60}$= 317	EC$_{35}$= 231	EC$_{25}$= 160
	DO=6.00 mg/l	825	EC$_{60}$= 421	EC$_{35}$= 232	EC$_{25}$= 158	825	EC$_{55}$= 313	EC$_{30}$= 228	EC$_{20}$= 152
	DO=10.00 mg/l	825	EC$_{60}$= 322	EC$_{35}$= 249	EC$_{25}$= 165	825	EC$_{55}$= 320	EC$_{30}$= 261	EC$_{20}$= 146
7	H_2O_2=100 mg/l	825	EC$_{60}$= 419	EC$_{30}$= 350	EC$_{15}$= 271	825	EC$_{55}$= 417	EC$_{20}$= 235	EC$_{10}$= 264
	H_2O_2=500 mg/l	825	EC$_{55}$= 416	EC$_{25}$= 342	EC$_{10}$= 264	825	EC$_{45}$= 500	EC$_{15}$= 550	EC$_{5}$= 560
	H_2O_2=2000 mg/l	825	EC$_{60}$= 470	EC$_{30}$= 325	EC$_{20}$= 240	825	EC$_{55}$= 403	EC$_{25}$= 216	EC$_{15}$= 153
8	TiO_2=0.10 mg/l	825	EC$_{60}$= 422	EC$_{25}$= 241	EC$_{15}$= 168	825	EC$_{55}$= 419	EC$_{20}$= 266	EC$_{10}$= 150
	TiO_2=0.50 mg/l	825	EC$_{60}$= 421	EC$_{25}$= 239	EC$_{15}$= 167	825	EC$_{55}$= 414	EC$_{20}$= 232	EC$_{10}$= 161
	TiO_2=10.00 mg/l	825	EC$_{55}$= 414	EC$_{20}$= 236	EC$_{10}$= 165	825	EC$_{50}$= 550	EC$_{15}$= 540	EC$_{5}$= 500
	TiO_2=20.00 mg/l	825	EC$_{65}$= 408	EC$_{30}$= 230	EC$_{20}$= 162	825	EC$_{60}$= 403	EC$_{25}$= 218	EC$_{15}$= 148

* EC values were calculated based on COD_{dis} (mg/l).

Appendix 7.18 Microtox acute toxicity values of TI ww before and after sonication process (cont.).

No	Parameters	Microtox Acute Toxicity Values, * EC (mg/l)							
		25°C							
		0. min		60. min		120. min		150. min	
		*EC_{90}		*EC		*EC		*EC	
1	Raw ww, control	825		EC_{70}=510		EC_{60}=650		EC_{50}=640	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
		*EC_{90}	*EC	*EC	*EC	*EC_{90}	*EC	*EC	*EC
2	Raw ww, control	825	EC_{70}= 580	EC_{50}= 580	EC_{40}= 550	825	EC_{55}= 550	EC_{40}= 590	EC_{30}= 690
9	NaCl=1.00 g/l	825	EC_{60}= 320	EC_{30}= 140	EC_{15}= 67	825	EC_{55}= 315	EC_{25}= 137	EC_{10}= 54
	NaCl=2.50 g/l	825	EC_{55}= 314	EC_{25}= 133	EC_{10}= 62	825	EC_{50}= 307	EC_{20}= 143	EC_{5}= 22
	NaCl=15.00 g/l	825	EC_{65}= 310	EC_{35}= 127	EC_{20}= 59	825	EC_{60}= 304	EC_{30}= 121	EC_{15}= 42
10	Fe^{+2}=2.00 mg/l	825	EC_{60}= 317	EC_{30}= 141	EC_{15}= 69	825	EC_{55}= 313	EC_{25}= 136	EC_{10}= 55
	Fe^{+2}=8.00 mg/l	825	EC_{60}= 312	EC_{25}= 135	EC_{10}= 66	825	EC_{50}= 307	EC_{20}= 125	EC_{5}= 53
	Fe^{+2}=20.00 mg/l	825	EC_{65}= 305	EC_{35}= 132	EC_{20}= 62	825	EC_{60}= 301	EC_{30}= 115	EC_{15}= 41
11	Fe^{+3}=10.00 mg/l	825	EC_{60}= 415	EC_{30}= 243	EC_{15}= 174	825	EC_{55}= 412	EC_{25}= 234	EC_{10}= 156
	Fe^{+3}=20.00 mg/l	825	EC_{60}= 411	EC_{25}= 237	EC_{10}= 171	825	EC_{55}= 405	EC_{20}= 228	EC_{5}= 154
	Fe^{+3}=50.00 mg/l	825	EC_{65}= 405	EC_{35}= 226	EC_{20}= 160	825	EC_{60}= 401	EC_{30}= 214	EC_{15}= 151
12	HCO_3^{-1}=0.50 g/l	825	EC_{60}= 426	EC_{35}= 209	EC_{20}= 151	825	EC_{55}= 425	EC_{30}= 254	EC_{15}= 198
	HCO_3^{-1}=1.00 g/l	825	EC_{60}= 499	EC_{25}= 226	EC_{15}= 152	825	EC_{55}= 496	EC_{20}= 241	EC_{10}= 122
	HCO_3^{-1}=5.00 g/l	825	EC_{65}= 508	EC_{40}= 224	EC_{25}= 152	825	EC_{60}= 400	EC_{35}= 296	EC_{20}= 151
13	C_4H_9OH=0.10 g/l	825	EC_{60}= 526	EC_{35}= 242	EC_{20}= 99	825	EC_{55}= 423	EC_{30}= 297	EC_{15}= 141
	C_4H_9OH=0.50 g/l	825	EC_{60}= 525	EC_{25}= 241	EC_{15}= 98	825	EC_{55}= 423	EC_{20}= 296	EC_{10}= 141
	C_4H_9OH=2.00 g/l	825	EC_{65}= 524	EC_{40}= 240	EC_{25}= 96	825	EC_{60}= 422	EC_{35}= 239	EC_{20}= 96

* EC values were calculated based on COD_{dis} (mg/l).

Appendix 7.19 *Daphnia magna* acute toxicity values of TI ww before and after sonication process

No	Parameters	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC$_{50}$**		***EC**		***EC**		***EC**	
1	Raw ww, control	850		EC$_{45}$=625		EC$_{40}$=370		EC$_{30}$=155	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC$_{50}$**	***EC**	***EC**	***EC**	***EC$_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	850	EC$_{40}$= 470	EC$_{35}$= 230	EC$_{25}$= 115	850	EC$_{35}$= 375	EC$_{30}$= 212	EC$_{20}$= 75
3	1 h aeration	850	EC$_{20}$= 450	EC$_{15}$= 120	EC$_{10}$= 350	850	EC$_{15}$= 430	EC$_{10}$= 310	EC$_{5}$= 135
4	15 min N_2(g) (3.00 mg/l N_2)	850	EC$_{35}$= 440	EC$_{20}$= 60	EC$_{15}$= 210	850	EC$_{30}$= 430	EC$_{15}$= 130	EC$_{10}$= 40
	30 min N_2(g) (6.00 mg/l N_2)	850	EC$_{30}$= 425	EC$_{15}$= 180	EC$_{10}$= 35	850	EC$_{25}$= 325	EC$_{10}$= 15	EC$_{5}$= 100
5	pH=4.0	850	EC$_{40}$= 250	EC$_{30}$= 175	EC$_{25}$= 90	850	EC$_{35}$= 325	EC$_{25}$= 180	EC$_{20}$= 90
	pH=7.0	850	EC$_{40}$= 470	EC$_{35}$= 230	EC$_{25}$= 115	850	EC$_{35}$= 375	EC$_{30}$= 212	EC$_{20}$= 75
	pH=10.0	850	EC$_{35}$= 375	EC$_{30}$= 65	EC$_{20}$= 230	850	EC$_{30}$= 225	EC$_{25}$= 70	EC$_{15}$= 35
6	DO=2.00 mg/l	850	EC$_{40}$= 400	EC$_{30}$= 300	EC$_{25}$= 145	850	EC$_{35}$= 350	EC$_{25}$= 180	EC$_{20}$= 120
	DO=4.00 mg/l	850	EC$_{35}$= 140	EC$_{25}$= 425	EC$_{20}$= 250	850	EC$_{30}$= 105	EC$_{20}$= 390	EC$_{15}$= 200
	DO=6.00 mg/l	850	EC$_{30}$= 350	EC$_{20}$= 125	EC$_{15}$= 190	850	EC$_{25}$= 250	EC$_{15}$= 160	EC$_{10}$= 80
	DO=10.00 mg/l	850	EC$_{25}$= 450	EC$_{20}$= 120	EC$_{10}$= 350	850	EC$_{20}$= 430	EC$_{15}$= 310	EC$_{10}$= 135
7	H_2O_2=100 mg/l	850	EC$_{35}$= 130	EC$_{20}$= 450	EC$_{15}$= 340	850	EC$_{30}$= 105	EC$_{15}$= 440	EC$_{10}$= 230
	H_2O_2=500 mg/l	850	EC$_{30}$= 450	EC$_{15}$= 100	EC$_{10}$= 280	850	EC$_{25}$= 55	EC$_{10}$= 400	EC$_{5}$= 140
	H_2O_2=2000 mg/l	850	EC$_{40}$= 240	EC$_{25}$= 100	EC$_{20}$= 27	850	EC$_{35}$= 200	EC$_{20}$= 70	EC$_{15}$= 12
8	TiO_2=0.10 mg/l	850	EC$_{35}$= 450	EC$_{20}$= 145	EC$_{15}$= 260	850	EC$_{30}$= 130	EC$_{15}$= 425	EC$_{10}$= 340
	TiO_2=0.50 mg/l	850	EC$_{35}$= 450	EC$_{20}$= 175	EC$_{15}$= 100	850	EC$_{30}$= 425	EC$_{15}$= 140	EC$_{5}$= 90
	TiO_2=10.00 mg/l	850	EC$_{30}$= 350	EC$_{15}$= 240	EC$_{10}$= 90	850	EC$_{25}$= 150	EC$_{10}$= 60	EC$_{5}$= 375
	TiO_2=20.00 mg/l	850	EC$_{40}$= 300	EC$_{25}$= 170	EC$_{20}$= 52	850	EC$_{35}$= 250	EC$_{20}$= 110	EC$_{15}$= 11

* EC values were calculated based on COD$_{dis}$ (mg/l).

Appendix 7.19 *Daphnia magna* acute toxicity values of TI ww before and after sonication process (cont.).

No	Parameters	***Daphnia magna* Acute Toxicity Values, * EC (mg/l)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
		***EC$_{50}$**		***EC**		***EC**		***EC**	
1	Raw ww, control	850		EC$_{45}$=625		EC$_{40}$=370		EC$_{30}$=155	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
		***EC$_{50}$**	***EC**	***EC**	***EC**	***EC$_{50}$**	***EC**	***EC**	***EC**
2	Raw ww, control	850	EC$_{40}$= 470	EC$_{35}$= 230	EC$_{25}$= 115	850	EC$_{35}$=375	EC$_{30}$= 212	EC$_{20}$= 75
9	NaCl=1.00 g/l	850	EC$_{35}$= 140	EC$_{20}$= 450	EC$_{15}$= 280	850	EC$_{30}$= 375	EC$_{15}$= 95	EC$_{10}$= 250
	NaCl=2.50 g/l	850	EC$_{30}$= 350	EC$_{15}$= 190	EC$_{10}$= 85	850	EC$_{25}$= 275	EC$_{10}$= 160	EC$_{5}$= 45
	NaCl=15.00 g/l	850	EC$_{40}$= 400	EC$_{25}$= 170	EC$_{20}$= 63	850	EC$_{35}$= 275	EC$_{20}$= 145	EC$_{15}$= 22
10	Fe^{+2}=2.00 mg/l	850	EC$_{35}$= 475	EC$_{20}$= 270	EC$_{15}$= 105	850	EC$_{30}$= 350	EC$_{15}$= 240	EC$_{10}$= 80
	Fe^{+2}=8.00 mg/l	850	EC$_{30}$= 450	EC$_{15}$= 230	EC$_{10}$= 80	850	EC$_{25}$= 350	EC$_{10}$= 170	EC$_{5}$= 42
	Fe^{+2}=20.00 mg/l	850	EC$_{40}$= 425	EC$_{25}$= 210	EC$_{20}$= 29	850	EC$_{35}$= 260	EC$_{20}$= 95	EC$_{15}$= 6
11	Fe^{+3}=10.00 mg/l	850	EC$_{35}$= 480	EC$_{25}$= 320	EC$_{20}$= 95	850	EC$_{30}$= 390	EC$_{20}$= 230	EC$_{10}$= 75
	Fe^{+3}=20.00 mg/l	850	EC$_{35}$= 500	EC$_{20}$= 250	EC$_{15}$= 65	850	EC$_{30}$= 375	EC$_{10}$= 200	EC$_{5}$= 24
	Fe^{+3}=50.00 mg/l	850	EC$_{40}$= 325	EC$_{30}$= 180	EC$_{25}$= 22	850	EC$_{35}$= 350	EC$_{25}$= 90	EC$_{15}$= 5
12	HCO$_3^{-1}$=0.50 g/l	850	EC$_{40}$= 175	EC$_{25}$= 700	EC$_{20}$= 350	850	EC$_{30}$= 700	EC$_{20}$= 170	EC$_{15}$= 350
	HCO$_3^{-1}$=1.00 g/l	850	EC$_{35}$= 700	EC$_{25}$= 300	EC$_{15}$= 120	850	EC$_{30}$= 600	EC$_{20}$= 275	EC$_{10}$= 140
	HCO$_3^{-1}$=5.00 g/l	850	EC$_{40}$= 700	EC$_{30}$= 350	EC$_{25}$= 150	850	EC$_{35}$= 700	EC$_{25}$= 360	EC$_{20}$= 140
13	C$_4$H$_9$OH=0.10 g/l	850	EC$_{35}$= 175	EC$_{25}$= 700	EC$_{20}$= 275	850	EC$_{30}$= 150	EC$_{15}$= 700	EC$_{15}$= 275
	C$_4$H$_9$OH=0.50 g/l	850	EC$_{30}$= 650	EC$_{20}$= 160	EC$_{15}$= 300	850	EC$_{25}$= 160	EC$_{15}$= 650	EC$_{10}$= 280
	C$_4$H$_9$OH=2.00 g/l	850	EC$_{35}$= 350	EC$_{30}$= 150	EC$_{25}$= 100	850	EC$_{35}$= 370	EC$_{25}$= 170	EC$_{20}$= 100

* EC values were calculated based on COD$_{dis}$ (mg/l).

Appendix 7.20 Acute toxicity removal efficiencies in PCI ww, OMI ww and TI ww after 120 and 150 min sonication times at 30°C and at 60°C with only sonication for *Daphnia magna* and Microtox tests (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

Parameters	**Removal Efficiencies with only Sonication (%)**											
	PCI ww				**OMI ww**				**TI ww**			
	30°C		**60°C**		**30°C**		**60°C**		**30°C**		**60°C**	
	120 min	**150 min**	**120 min**	**150 min**	**120 min**	**150 min**	**120 min**	**150 min**	**120 Min**	**150 min**	**120 min**	**150 min**
Microtox acute toxicity assay	44.44	55.56	55.56	**66.67**	22.22	33.33	22.22	44.44	44.44	55.56	55.56	**66.67**
Daphnia magna acute toxicity assay	30.00	40.00	40.00	50.00	40.00	50.00	50.00	60.00	30.00	50.00	40.00	60.00

Appendix 7.21Acute toxicity removal efficiencies in PCI ww after 120 and 150 min sonication times at 30^{o}C and at 60^{o}C with the addition of some chemicals for *Daphnia magna* and Microtox tests (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

Removal Efficiencies in PCI ww with the Addition of Some Chemicals									
Microtox Acute Toxicity (%)					***Daphnia magna* Acute Toxicity (%)**				
Parameters	**30^{o}C**		**60^{o}C**		**Parameters**	**30^{o}C**		**60^{o}C**	
	120 min	**150 min**	**120 min**	**150 min**		**120 min**	**150 min**	**120 min**	**150 min**
1 h aeration	61.11	**77.78**	77.78	**83.33**	1 h aeration	60.00	**80.00**	70.00	**90.00**
30 min N_2(g) (6.00 mg/l N_2)	66.67	**72.22**	72.22	**83.33**	30 min N_2(g) (6.00 mg/l N_2)	60.00	**70.00**	70.00	**90.00**
pH=7.0	44.44	55.56	55.56	**66.67**	pH=7.0	30.00	40.00	40.00	50.00
DO=10.00 mg/l	61.11	**77.78**	66.67	**77.78**	DO=10.00 mg/l	60.00	**70.00**	70.00	**90.00**
H_2O_2=500 mg/l	66.67	**88.89**	77.78	**94.44**	H_2O_2=500 mg/l	60.00	**80.00**	70.00	**90.00**
TiO_2=10.00 mg/l	72.22	**88.89**	77.78	**94.44**	TiO_2=10.00 mg/l	60.00	**80.00**	80.00	**90.00**
NaCl=2.50 g/l	66.67	**88.89**	77.78	**94.44**	NaCl=2.50 g/l	60.00	**80.00**	70.00	**90.00**
Fe^{+2}=8.00 mg/l	66.67	**83.33**	77.78	**88.89**	Fe^{+2}=8.00 mg/l	50.00	**70.00**	60.00	**80.00**
Fe^{+3}=20.00 mg/l	66.67	**83.33**	77.78	**88.89**	Fe^{+3}=20.00 mg/l	50.00	**70.00**	60.00	**80.00**
HCO_3^{-1}=1.00 g/l	66.67	**77.78**	77.78	**83.33**	HCO_3^{-1}=1.00 g/l	40.00	60.00	50.00	**80.00**
C_4H_9OH=0.50 g/l	66.67	**77.78**	77.78	**88.89**	C_4H_9OH=0.50 g/l	40.00	60.00	50.00	**80.00**

Appendix 7.22 Acute toxicity removal efficiencies in OMI ww after 120 and 150 min sonication times at 30°C and at 60°C with the addition of some chemicals for *Daphnia magna* and Microtox tests (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

Removal Efficiencies in OMI ww with the Addition of Some Chemicals									
Microtox Acute Toxicity (%)					**Daphnia magna Acute Toxicity (%)**				
Parameters	**30°C**		**60°C**		**Parameters**	**30°C**		**60°C**	
	120 min	**150 min**	**120 min**	**150 min**		**120 min**	**150 min**	**120 min**	**150 min**
1 h aeration	55.56	**72.22**	72.22	**83.33**	1 h aeration	70.00	**80.00**	80.00	**90.00**
30 min $N_2(g)$ (6.00 mg/l N_2)	61.11	**72.22**	66.67	**83.33**	30 min $N_2(g)$ (6.00 mg/l N_2)	60.00	**70.00**	70.00	**90.00**
pH=10.0	27.78	38.89	38.89	55.56	pH=10.0	50.00	**60.00**	60.00	**70.00**
DO=10.00 mg/l	55.56	**72.22**	61.11	**77.78**	DO=10.00 mg/l	60.00	**80.00**	70.00	**90.00**
H_2O_2=500 mg/l	77.78	**88.89**	83.33	**94.44**	H_2O_2=500 mg/l	60.00	**80.00**	70.00	**90.00**
TiO_2=10.00 mg/l	83.33	**88.89**	88.89	**94.44**	TiO_2=10.00 mg/l	60.00	**80.00**	70.00	**90.00**
NaCl=2.50 g/l	77.78	**88.89**	83.33	**94.44**	NaCl=2.50 g/l	60.00	**80.00**	70.00	**90.00**
Fe^{+2}=8.00 mg/l	72.22	**88.89**	77.78	**94.44**	Fe^{+2}=8.00 mg/l	60.00	**80.00**	70.00	**90.00**
Fe^{+3}=20.00 mg/l	66.67	**83.33**	72.22	**88.89**	Fe^{+3}=20.00 mg/l	60.00	**70.00**	70.00	**80.00**
HCO_3^{-1}=1.00 g/l	61.11	**77.78**	66.61	**83.33**	HCO_3^{-1}=1.00 g/l	60.00	**70.00**	70.00	**80.00**
C_4H_9OH=0.50 g/l	66.61	**77.78**	72.22	**83.33**	C_4H_9OH=0.50 g/l	60.00	**70.00**	70.00	**80.00**

Appendix 7.23 Acute toxicity removal efficiencies in TI ww after 120 and 150 min sonication times at 30^{o}C and at 60^{o}C with the addition of some chemicals for *Daphnia magna* and Microtox tests (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

Removal Efficiencies in TI ww with the Addition of Some Chemicals									
Microtox Acute Toxicity (%)					**Daphnia magna Acute Toxicity (%)**				
Parameters	**30^{o}C**		**60^{o}C**		**Parameters**	**30^{o}C**		**60^{o}C**	
	120 min	**150 min**	**120 min**	**150 min**		**120 min**	**150 min**	**120 min**	**150 min**
1 h aeration	66.67	**77.78**	72.22	**83.33**	1 h aeration	70.00	**80.00**	80.00	**90.00**
30 min N_2(g) (6.00 mg/l N_2)	66.67	**77.78**	72.22	**83.33**	30 min N_2(g) (6.00 mg/l N_2)	70.00	**80.00**	80.00	**90.00**
pH=10.0	38.89	**66.67**	44.44	**72.22**	pH=10.0	40.00	**60.00**	50.00	**70.00**
DO=10.00 mg/l	61.11	**72.22**	66.67	**77.78**	DO=10.00 mg/l	60.00	**80.00**	70.00	**80.00**
H_2O_2=500 mg/l	72.22	**88.89**	83.33	**94.44**	H_2O_2=500 mg/l	70.00	**80.00**	80.00	**90.00**
TiO_2=10.00 mg/l	77.78	**88.89**	83.33	**94.44**	TiO_2=10.00 mg/l	70.00	**80.00**	80.00	**90.00**
NaCl=2.50 g/l	72.22	**88.89**	77.78	**94.44**	NaCl=2.50 g/l	70.00	**80.00**	80.00	**90.00**
Fe^{+2}=8.00 mg/l	72.22	**88.89**	77.78	**94.44**	Fe^{+2}=8.00 mg/l	70.00	**80.00**	80.00	**90.00**
Fe^{+3}=20.00 mg/l	72.22	**88.89**	77.78	**94.44**	Fe^{+3}=20.00 mg/l	60.00	**70.00**	80.00	**90.00**
HCO_3^{-1}=1.00 g/l	72.22	**83.33**	77.78	**88.89**	HCO_3^{-1}=1.00 g/l	50.00	**70.00**	60.00	**80.00**
C_4H_9OH=0.50 g/l	72.22	**83.33**	77.78	**88.89**	C_4H_9OH=0.50 g/l	60.00	**70.00**	70.00	**80.00**

Appendix 7.24 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments after 60 min, 120 and 150 min sonication times at 25°C (n=3, mean values).

PAHs	Inf. (A) T=0 min PAHs (ng/ml) ± SD	Eff. (B) T=150 min PAHs (ng/ml) ± SD	T=60 min PAHs (%)	T=120 min PAHs (%)	T=150 min PAHs (%)	ZORKC (C)	ZORKC (R^2)	FORKC (D)	FORKC (R^2)	SORKC (E)	SORKC (R^2)
NAP	1012.93 ± 35.45	206.20 ± 7.22	27.30	30.49	70.21	4.741	0.88	0.047	0.98	35.10x10^{-4}	0.82
ACL	50.20 ± 1.76	10.22 ± 0.36	52.29	58.40	73.77	4.473	0.88	0.045	0.98	34.30x10^{-4}	0.82
ACT	66.82 ± 2.34	13.60 ± 0.48	51.48	57.49	87.04	4.220	0.88	0.042	0.98	33.00x10^{-4}	0.82
FLN	55.57 ± 1.95	11.31 ± 0.40	52.03	58.11	81.09	3.981	0.88	0.040	0.98	28.20x10^{-4}	0.82
PHE	125.58 ± 4.40	25.56 ± 0.90	48.80	54.50	79.35	3.755	0.88	0.037	0.98	22.10x10^{-4}	0.82
ANT	7.48 ± 0.26	1.52 ± 0.05	54.51	60.87	90.86	3.544	0.88	0.035	0.98	21.40x10^{-4}	0.82
CRB	14.20 ± 0.50	2.89 ± 0.10	54.15	60.47	64.86	3.342	0.88	0.034	0.98	20.70x10^{-4}	0.82
FL	19.36 ± 0.68	3.94 ± 0.14	53.87	60.17	83.52	3.153	0.88	0.032	0.98	20.10x10^{-4}	0.82
PY	15.54 ± 0.54	3.16 ± 0.11	54.08	60.39	82.46	2.975	0.88	0.030	0.98	19.50x10^{-4}	0.82
BaA	0.55 ± 0.19	0.11 ± 0.03	54.89	61.30	90.25	2.806	0.88	0.028	0.98	16.00x10^{-4}	0.82
CHR	2.68 ± 0.93	0.55 ± 0.19	54.77	61.17	83.73	1.373	0.88	0.027	0.98	15.40x10^{-4}	0.82
BbF	0.80 ± 0.28	0.16 ± 0.05	54.87	61.28	94.52	1.255	0.88	0.022	0.98	14.70x10^{-4}	0.82
BkF	0.80 ± 0.28	0.16 ± 0.05	54.87	61.28	88.94	1.249	0.88	0.018	0.98	14.00x10^{-4}	0.82
BaP	0.07 ± 0.02	0.02 ± 0.007	54.91	61.32	66.03	0.699	0.88	0.010	0.98	10.00x10^{-4}	0.82
IcdP	1.09 ± 0.38	0.22 ± 0.07	54.86	61.26	62.62	0.415	0.88	0.008	0.98	8.09x10^{-4}	0.82
DahA	4.58 ± 1.60	0.93 ± 0.32	54.67	61.05	77.74	0.218	0.88	0.003	0.98	1.60x10^{-4}	0.82
BghiP	0.51 ± 0.17	0.10 ± 0.03	54.89	61.30	78.72	0.150	0.88	0.002	0.98	0.19x10^{-4}	0.82

(A) Inf.= influent, (B) Eff. = effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

Appendix 7.25 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments after 60 min, 120 and 150 min sonication times at 30^{o}C (n=3, mean values).

PAHs	Inf. (A) T=0 min PAHs (ng/ml) ± SD	Eff. (B) T=150 min PAHs (ng/ml) ± SD	T=60 min PAHs (%)	T=120 min PAHs (%)	T=150 min PAHs (%)	ZORKC (C)	ZORKC (R^2)	FORKC (D)	FORKC (R^2)	SORKC (E)	SORKC (R^2)
NAP	1012.93 ± 35.50	101.88 ± 3.57	21.44	59.80	96.37	6.091	0.96	0.078	0.99	$38.70x10^{-4}$	0.61
ACL	50.20 ± 1.76	5.05 ± 0.18	41.86	78.18	93.11	5.746	0.96	0.074	0.99	$37.10x10^{-4}$	0.61
ACT	66.82 ± 2.34	6.72 ± 0.24	41.19	67.24	86.05	5.421	0.96	0.070	0.99	$35.60x10^{-4}$	0.61
FLN	55.57 ± 1.95	5.59 ± 0.20	41.64	77.87	90.44	5.114	0.96	0.066	0.99	$24.10x10^{-4}$	0.61
PHE	125.58 ± 4.40	12.63 ± 0.44	38.96	74.14	91.24	4.824	0.96	0.062	0.99	$22.80x10^{-4}$	0.61
ANT	7.48 ± 0.26	0.75 ± 0.03	43.71	60.74	80.20	4.551	0.96	0.058	0.99	$21.50x10^{-4}$	0.61
CRB	14.19 ± 0.15	1.43 ± 0.05	43.41	70.33	94.85	4.294	0.96	0.055	0.99	$20.20x10^{-4}$	0.61
FL	19.36 ± 0.68	1.95 ± 0.07	43.18	70.01	89.03	4.051	0.96	0.052	0.99	$19.10x10^{-4}$	0.61
PY	15.54 ± 0.54	1.56 ± 0.06	43.35	76.24	89.69	3.821	0.96	0.049	0.99	$18.00x10^{-4}$	0.61
BaA	0.55 ± 0.19	0.05 ± 0.01	44.02	61.18	81.46	3.605	0.96	0.046	0.99	$17.00x10^{-4}$	0.61
CHR	2.68 ± 0.93	0.27 ± 0.09	43.93	61.05	88.89	2.372	0.96	0.041	0.99	$13.00x10^{-4}$	0.61
BbF	0.80 ± 0.28	0.08 ± 0.02	44.01	51.17	67.03	2.264	0.96	0.035	0.99	$12.60x10^{-4}$	0.61
BkF	0.80 ± 0.28	0.08 ± 0.02	44.01	71.17	83.66	2.218	0.96	0.031	0.99	$4.80x10^{-4}$	0.61
BaP	0.07 ± 0.02	0.007 ± 0.002	44.05	81.21	94.68	1.567	0.96	0.030	0.99	$4.00x10^{-4}$	0.61
IcdP	1.09 ± 0.38	0.11 ± 0.03	44.00	76.15	95.16	1.414	0.96	0.028	0.99	$2.18x10^{-4}$	0.61
DahA	4.58 ± 1.60	0.46 ± 0.16	43.84	70.93	91.88	1.217	0.96	0.026	0.99	$1.83x10^{-4}$	0.61
BghiP	0.51 ± 0.17	0.05 ± 0.01	44.03	71.18	91.50	1.139	0.96	0.020	0.99	$0.50x10^{-4}$	0.61

(A) Inf.= influent, (B) Eff. = effluent, (C) ZORKC: Zero order reaction kinetic constant (mg/l . h), (D) FORKC: First order reaction kinetic constant (1/h), (E) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient.

Appendix 7.26 Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments in HCO_3^{-1}=1.00 g/l concentration after 60 min, 120 and 150 min sonication times at 30°C (n=3, mean values).

PAHs	**Inf. (A) T=0 min PAHs (ng/ml) ± SD**	**Eff. (B) T=150 min PAHs (ng/ml) ± SD**	**T=60 min PAHs (%)**	**T=120 min PAHs (%)**	**T=150 min PAHs (%)**	**ZORKC (C)**	**ZORKC (R^2)**	**FORKC (D)**	**FORKC (R^2)**	**SORKC (E)**	**SORKC (R^2)**
NAP	4286.12 ±150.01	190.04 ± 6.65	79.80	90.39	95.57	6.833	0.91	0.110	0.99	$47.10x10^{-4}$	0.84
ACL	111.90 ± 3.92	9.42 ± 0.33	61.66	81.76	91.58	6.450	0.91	0.104	0.99	$44.50x10^{-4}$	0.81
ACT	73.57 ± 2.58	12.54 ± 0.44	22.37	63.07	82.96	6.081	0.98	0.097	0.99	$42.00x10^{-4}$	0.75
FLN	89.29 ± 3.13	10.43 ± 0.37	46.80	74.69	88.32	5.740	0.98	0.092	0.99	$39.60x10^{-4}$	0.98
PHE	220.38 ± 7.71	23.56 ± 0.83	51.30	76.83	89.31	5.412	0.96	0.087	0.99	$37.20x10^{-4}$	0.80
ANT	18.58 ± 0.65	1.40 ± 0.05	65.61	83.64	92.45	5.106	0.89	0.082	0.99	$35.20x10^{-4}$	0.82
CRB	42.36 ± 1.48	2.66 ± 0.09	71.37	86.38	93.72	4.817	0.86	0.077	0.99	$33.40x10^{-4}$	0.83
FL	27.12 ± 0.95	3.63 ± 0.13	38.97	70.96	86.60	4.550	0.89	0.073	0.99	$31.30x10^{-4}$	0.78
PY	23.16 ± 0.81	2.92 ± 0.10	42.64	72.71	87.41	4.287	0.98	0.069	0.99	$29.60x10^{-4}$	0.78
BaA	1.41 ± 0.05	0.10 ± 0.004	66.32	83.98	92.61	4.045	0.89	0.065	0.99	$29.80x10^{-4}$	0.82
CHR	3.71 ± 0.13	0.50 ± 0.02	38.18	70.59	86.43	3.416	0.98	0.054	0.99	$19.30x10^{-4}$	0.78
BbF	2.41 ± 0.08	0.15 ± 0.005	71.79	86.58	93.81	2.703	0.96	0.047	0.99	$14.70x10^{-4}$	0.83
BkF	2.12 ± 0.07	0.15 ± 0.005	67.74	84.65	92.92	2.566	0.98	0.044	0.99	$8.90x10^{-4}$	0.82
BaP	0.21 ± 0.007	0.01 ± 0.0004	70.39	85.91	93.50	2.044	0.96	0.042	0.99	$6.50x10^{-4}$	0.83
IcdP	3.47 ± 0.12	0.21 ± 0.007	73.09	87.20	94.09	1.780	0.95	0.039	0.99	$4.76x10^{-4}$	0.83
DahA	8.66 ± 0.30	0.86 ± 0.03	54.82	78.50	90.08	1.385	0.95	0.034	0.99	$3.31x10^{-4}$	0.80
BghiP	0.93 ± 0.03	0.10 ± 0.004	52.73	77.51	89.62	1.280	0.96	0.031	0.99	$1.70x10^{-4}$	0.80

Appendix 7.27 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies after 150 min sonication time at 25°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	42779 ± 1497	60.91	444.690	0.95	0.006	0.99	$8.87x10^{-8}$	0.83
TOC (E)	66488 ± 2327	27074 ± 947	59.28	262.990	0.95	0.006	0.99	$1.37x10^{-7}$	0.84
Color (F)	99.80 ± 3.493	50.20 ± 1.76	49.70	0.326	0.88	0.005	0.99	$6.67x10^{-5}$	0.96
Phenol (G)	4090 ± 143.15	1707.50 ± 59.76	58.25	16.580	0.98	0.006	0.99	$2.42x10^{-6}$	0.97
TAAs (H)	3000 ± 105	1105 ± 38.68	63.17	12.010	0.97	0.006	0.99	$3.50x10^{-6}$	0.92
TFAs (J)	5200 ± 182	3249.66 ± 113.74	37.51	11.560	0.89	0.003	0.99	$6.65x10^{-7}$	0.81

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.28 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies after 150 min sonication time at 30°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	40967 ± 1434	62.57	450.240	0.96	0.006	0.99	9.37×10^{-8}	0.82
TOC (E)	66488 ± 2327	25515 ± 893	61.62	271.850	0.96	0.006	0.99	1.49×10^{-7}	0.83
Color (F)	99.80 ± 3.493	25.50 ± 0.89	74.45	0.461	0.96	0.008	0.99	2.00×10^{-3}	0.80
Phenol (G)	4090 ± 143.15	1661 ± 58.14	59.40	16.864	0.97	0.006	0.99	2.53×10^{-6}	0.97
TAAs (H)	3000 ± 105	1051 ± 36.79	64.98	12.711	0.96	0.007	0.99	3.97×10^{-6}	0.97
TFAs (J)	5200 ± 182	2826 ± 98.91	45.66	13.981	0.88	0.004	0.99	9.17×10^{-7}	0.77

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.29 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Inf.** (A) **T=0 min** **Conc. ± SD**	**Eff.** (B) **T=150 min** **Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC** (A)	**ZORKC (R^2)**	**FORKC** (B)	**FORKC (R^2)**	**SORKC** (C)	**SORKC (R^2)**
COD (D)	109444 ± 3831	36298 ± 1270	66.83	483.67	0.97	0.007	0.99	$1.13x10^{-7}$	0.82
TOC (E)	66488 ± 2327	22660 ± 793	65.92	287.79	0.97	0.007	0.99	$1.77x10^{-7}$	0.82
Color (F)	99.80 ± 3.493	16.20 ± 0.57	83.77	0.546	0.98	0.012	0.99	$3.00x10^{-4}$	0.84
Phenol (G)	4090 ± 143.15	1585.41 ± 55.49	61.24	17.336	0.97	0.007	0.99	$2.73x10^{-6}$	0.97
TAAs (H)	3000 ± 105	884.52 ± 30.96	70.52	13.850	0.97	0.008	0.99	$5.08x10^{-6}$	0.95
TFAs (J)	5200 ± 182	2660.22 ± 93.11	48.84	15.025	0.89	0.004	0.99	$1.04x10^{-6}$	0.77

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.30 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of 1 h Aeration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC [(A)]**	**ZORKC (R^2)**	**FORKC [(B)]**	**FORKC (R^2)**	**SORKC [(C)]**	**SORKC (R^2)**
COD (D)	109444 ± 3831	14970.50 ± 523.97	86.32	619.300	0.98	0.012	0.99	3.38×10^{-7}	0.74
TOC (E)	66488 ± 2327	9799.50 ± 342.98	85.26	372.280	0.98	0.012	0.99	5.13×10^{-7}	0.76
Color (F)	99.80 ± 3.493	16.20 ± 0.57	88.48	0.546	0.98	0.012	0.99	3.00×10^{-4}	0.84
Phenol (G)	4090 ± 143.15	1116.88 ± 39.10	72.69	20.121	0.93	0.009	0.99	4.61×10^{-6}	0.97
TAAs (H)	3000 ± 105	815.10 ± 28.53	72.83	13.750	0.83	0.008	0.99	5.59×10^{-6}	0.96
TFAs (J)	5200 ± 182	1126.92 ± 39.44	78.33	27.307	0.98	0.011	0.99	4.48×10^{-6}	0.92

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.31 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	16953 ± 593.36	84.51	585.790	0.98	0.011	0.99	$2.84x10^{-7}$	0.72
TOC (E)	66488 ± 2327	10798 ± 377.93	83.76	368.200	0.93	0.012	0.99	$4.72x10^{-7}$	0.83
Color (F)	99.80 ± 3.493	8.10 ± 0.28	91.88	0.570	0.78	0.016	0.99	$7.00x10^{-4}$	0.91
Phenol (G)	4090 ± 143.15	859.60 ± 30.09	78.98	21.439	0.98	0.010	0.99	$5.86x10^{-6}$	0.91
TAAs (H)	3000 ± 105	763.16 ± 26.71	74.56	14.318	0.89	0.009	0.99	$6.21x10^{-6}$	0.98
TFAs (J)	5200 ± 182	1030.45 ± 36.07	80.18	28.147	0.98	0.011	0.99	$5.07x10^{-6}$	0.92

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.32 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies at pH=10.0 after 150 min sonication time at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Intitial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	11694.50 ± 409.31	89.31	616.780	0.93	0.014	0.99	4.37x10^{-7}	0.74
TOC (E)	66488 ± 2327	7872.50 ± 275.54	88.16	369.540	0.93	0.013	0.99	6.44x10^{-7}	0.76
Color (F)	99.80 ± 3.493	7.60 ± 0.27	92.38	0.572	0.85	0.015	0.99	7.00x10^{-4}	0.73
Phenol (G)	4090 ± 143.15	592.50 ± 20.74	85.51	23.366	0.97	0.013	0.99	9.17x10^{-6}	0.89
TAAs (H)	3000 ± 105	412.50 ± 14.43	86.25	15.528	0.87	0.011	0.99	1.14x10^{-5}	0.71
TFAs (J)	5200 ± 182	1140.89 ± 39.93	78.06	27.042	0.98	0.010	0.99	4.40x10^{-6}	0.92

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.33 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of Fe^{+2}=20.00 mg/l concentration after 150 min sonication time at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	10555 ± 369.43	90.36	641.180	0.91	0.015	0.99	5.26x10^{-7}	0.86
TOC (E)	66488 ± 2327	6903.50 ± 241.63	89.62	386.040	0.91	0.015	0.99	7.96x10^{-7}	0.86
Color (F)	99.80 ± 3.493	6.10 ± 0.21	93.89	0.585	0.83	0.017	0.99	8.72x10^{-3}	0.74
Phenol (G)	4090 ± 143.15	423.68 ± 14.83	89.64	24.906	0.97	0.015	0.99	1.37x10^{-5}	0.88
TAAs (H)	3000 ± 105	423.68 ± 14.83	85.88	15.928	0.79	0.012	0.99	1.19x10^{-5}	0.90
TFAs (J)	5200 ± 182	1643.45 ± 57.52	68.40	22.902	0.98	0.007	0.99	2.56x10^{-6}	0.91

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.34 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of Fe^{+3}=50.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC [(A)]**	**ZORKC (R^2)**	**FORKC [(B)]**	**FORKC (R^2)**	**SORKC [(C)]**	**SORKC (R^2)**
COD (D)	109444 ± 3831	10125.50 ± 354.39	90.75	643.950	0.89	0.015	0.99	$5.58x10^{-7}$	0.89
TOC (E)	66488 ± 2327	6917.50 ± 242.11	89.60	382.540	0.89	0.014	0.99	$7.88x10^{-7}$	0.86
Color (F)	99.80 ± 3.493	8.90 ± 0.31	91.08	0.568	0.81	0.015	0.99	$6.02x10^{-4}$	0.86
Phenol (G)	4090 ± 143.15	303.32 ± 10.62	92.58	25.475	0.96	0.017	0.99	$1.91x10^{-5}$	0.83
TAAs (H)	3000 ± 105	313.32 ± 10.97	89.56	16.356	0.83	0.013	0.99	$1.58x10^{-5}$	0.75
TFAs (J)	5200 ± 182	1771.74 ± 62.01	65.93	21.836	0.98	0.007	0.99	$2.27x10^{-6}$	0.90

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.35 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of HCO$_3^{-1}$=5.00 g/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	16188.52 ± 566.60	85.21	581.750	0.91	0.012	0.99	3.04×10^{-7}	0.78
TOC (E)	66488 ± 2327	10026.39 ± 350.92	84.92	351.420	0.91	0.011	0.99	4.87×10^{-7}	0.79
Color (F)	99.80 ± 3.493	8.20 ± 0.29	91.78	0.565	0.76	0.015	0.99	6.44×10^{-4}	0.86
Phenol (G)	4090 ± 143.15	256.68 ± 8.98	93.72	25.693	0.95	0.018	0.99	2.28×10^{-5}	0.82
TAAs (H)	3000 ± 105	456.68 ± 15.98	84.78	15.642	0.77	0.011	0.99	1.08×10^{-5}	0.90
TFAs (J)	5200 ± 182	1980.70 ± 69.32	61.91	20.188	0.97	0.006	0.99	1.87×10^{-6}	0.88

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.36 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in OMI ww at maximum removal efficiencies in the presence of C_4H_9OH=2.00 g/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC** **(A)**	**ZORKC (R^2)**	**FORKC** **(B)**	**FORKC (R^2)**	**SORKC** **(C)**	**SORKC (R^2)**
COD (D)	109444 ± 3831	10178.52 ± 356.25	90.70	616.840	0.91	0.014	0.99	$4.97x10^{-7}$	0.69
TOC (E)	66488 ± 2327	7200.65 ± 252.02	89.17	370.450	0.91	0.013	0.99	$7.02x10^{-7}$	0.73
Color (F)	99.80 ± 3.493	10.20 ± 0.36	89.78	0.569	0.85	0.014	0.99	$5.38x10^{-4}$	0.90
Phenol (G)	4090 ± 143.15	389.68 ± 13.64	90.47	25.092	0.95	0.016	0.99	$1.57x10^{-5}$	0.91
TAAs (H)	3000 ± 105	389.68 ± 13.64	87.01	16.058	0.82	0.012	0.99	$1.28x10^{-5}$	0.84
TFAs (J)	5200 ± 182	1551.81 ± 54.31	70.16	23.667	0.98	0.008	0.99	$2.81x10^{-6}$	0.91

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), Phenol (G): Total phenol (mg/l), TAAs (H): TAAs (mg benzidine/l), TFAs (J): TFAs (mg/l).

Appendix 7.37 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies after 150 min sonication time at 25°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	247.75 ± 8.67	74.27	4.601	0.92	0.009	0.99	$1.78x10^{-5}$	0.81
TOC (E)	587.84 ± 20.57	159.01 ± 5.56	72.95	2.719	0.98	0.008	0.99	$2.71x10^{-5}$	0.80
Color (F)	88.56 ± 3.10	38.01 ± 1.33	57.09	0.372	0.94	0.006	0.99	$1.10x10^{-4}$	0.90
TAAs (G)	1620 ± 56.70	1183 ± 41.41	26.98	2.685	0.92	0.002	0.99	$1.39x10^{-6}$	0.94

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.38 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies after 150 min sonication time at 30°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	177.83 ± 6.22	81.53	5.132	0.98	0.011	0.99	$2.81x10^{-5}$	0.85
TOC (E)	587.84 ± 20.57	112.93 ± 3.95	80.79	3.123	0.98	0.011	0.99	$4.42x10^{-5}$	0.86
Color (F)	88.56 ± 3.10	18.50 ± 0.65	78.26	0.468	0.90	0.011	0.99	$3.03x10^{-4}$	0.97
TAAs (G)	1620 ± 56.70	1071 ± 37.49	33.89	3.489	0.95	0.003	0.99	$2.00x10^{-6}$	0.97

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.39 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies after 150 min sonication time at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC** (A)	**ZORKC (R^2)**	**FORKC** (B)	**FORKC (R^2)**	**SORKC** (C)	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	145.24 ± 5.08	84.92	5.127	0.95	0.011	0.99	$3.34\text{x}10^{-5}$	0.75
TOC (E)	587.84 ± 20.57	98.67 ± 3.45	83.22	3.056	0.95	0.011	0.99	$4.83\text{x}10^{-5}$	0.75
Color (F)	88.56 ± 3.10	10.50 ± 0.37	87.66	0.486	0.75	0.013	0.99	$5.15\text{x}10^{-4}$	0.86
TAAs (G)	1620 ± 56.70	962 ± 33.67	40.62	4.150	0.97	0.003	0.99	$2.62\text{x}10^{-6}$	0.96

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.40 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of 1 h aeration after 150 min sonication time at 60^{o}C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	151.39 ± 5.30	84.28	5.028	0.93	0.011	0.99	$3.16x10^{-5}$	0.75
TOC (E)	587.84 ± 20.57	98.37 ± 3.44	83.27	3.021	0.94	0.011	0.99	$4.79x10^{-5}$	0.75
Color (F)	88.56 ± 3.10	8.30 ± 0.29	90.25	0.536	0.94	0.016	0.99	$7.01x10^{-4}$	0.89
TAAs (G)	1620 ± 56.70	658.03 ± 23.03	59.38	6.428	0.98	0.006	0.99	$5.80x10^{-6}$	0.92

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.41 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of 30 min $N_2(g)$ (6.00 mg/l N_2) sparging after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC [(A)]**	**ZORKC (R^2)**	**FORKC [(B)]**	**FORKC (R^2)**	**SORKC [(C)]**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	17.01 ± 0.60	98.23	6.187	0.93	0.025	0.99	$3.14x10^{-4}$	0.54
TOC (E)	587.84 ± 20.57	10.21 ± 0.36	98.26	3.791	0.93	0.025	0.99	$5.23x10^{-4}$	0.54
Color (F)	88.56 ± 3.10	4.00 ± 0.15	95.30	0.525	0.76	0.019	0.99	$1.36x10^{-3}$	0.80
TAAs (G)	1620 ± 56.70	517.03 ± 18.10	68.08	7.356	0.98	0.007	0.99	$8.20x10^{-6}$	0.85

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.42 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies at pH=10.0 after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	51.07 ± 1.79	94.70	6.067	0.93	0.019	0.99	$1.60\text{x}10^{-4}$	0.82
TOC (E)	587.84 ± 20.57	41.09 ± 1.44	93.01	3.622	0.92	0.018	0.99	$1.44\text{x}10^{-4}$	0.87
Color (F)	88.56 ± 3.10	4.20 ± 0.15	95.06	0.524	0.72	0.018	0.99	$1.35\text{x}10^{-3}$	0.92
TAAs (G)	1620 ± 56.70	568.71 ± 19.91	64.89	6.886	0.98	0.007	0.99	$7.00\text{x}10^{-6}$	0.83

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.43 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of DO=10.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC [(A)]**	**ZORKC (R^2)**	**FORKC [(B)]**	**FORKC (R^2)**	**SORKC [(C)]**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	57.06 ± 2.00	94.07	5.812	0.93	0.017	0.99	9.31×10^{-5}	0.67
TOC (E)	587.84 ± 20.57	42.50 ± 1.50	92.77	3.510	0.93	0.016	0.99	1.26×10^{-4}	0.72
Color (F)	88.56 ± 3.10	2.00 ± 0.07	97.65	0.540	0.72	0.024	0.99	2.89×10^{-3}	0.87
TAAs (G)	1620 ± 56.70	460.70 ± 16.12	71.56	7.440	0.84	0.008	0.99	9.12×10^{-6}	0.75

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.44 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of Fe^{+3}=50.00 mg/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC (A)**	**ZORKC (R^2)**	**FORKC (B)**	**FORKC (R^2)**	**SORKC (C)**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	6.11 ± 0.21	99.37	6.326	0.95	0.031	0.99	8.48x10^{-4}	0.45
TOC (E)	587.84 ± 20.57	3.83 ± 0.13	99.35	3.858	0.95	0.030	0.99	1.36x10^{-3}	0.45
Color (F)	88.56 ± 3.10	5.90 ± 0.21	93.07	0.516	0.71	0.017	0.99	9.97x10^{-4}	0.95
TAAs (G)	1620 ± 56.70	482.06 ± 16.87	70.24	7.591	0.98	0.008	0.99	8.97x10^{-6}	0.82

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.45 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of HCO_3^{-1}=5.00 g/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial** **T=0 min** **Conc. ± SD**	**Effluent** **T=150 min** **Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC** **(A)**	**ZORKC (R^2)**	**FORKC** **(B)**	**FORKC (R^2)**	**SORKC** **(C)**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	168.52 ± 5.90	82.50	5.275	0.97	0.011	0.99	$2.85x10^{-5}$	0.69
TOC (E)	587.84 ± 20.57	18.64 ± 0.65	83.84	3.632	0.92	0.021	0.99	$2.82x10^{-4}$	0.57
Color (F)	88.56 ± 3.10	3.30 ± 0.12	96.12	0.530	0.73	0.020	0.99	$1.70x10^{-3}$	0.86
TAAs (G)	1620 ± 56.70	559.09 ± 19.57	65.49	6.815	0.93	0.007	0.99	$7.11x10^{-6}$	0.86

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.46 The pseudo zero, first and second order reaction kinetic constants of experimental parameters in TI ww at maximum removal efficiencies in the presence of C_4H_9OH=2.00 g/l concentration after 150 min sonication time at 60°C (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values ± SD).

Parameters	**Initial T=0 min Conc. ± SD**	**Effluent T=150 min Conc. ± SD**	**T=150 min Rem. (%)**	**ZORKC** **(A)**	**ZORKC (R^2)**	**FORKC** **(B)**	**FORKC (R^2)**	**SORKC** **(C)**	**SORKC (R^2)**
COD (D)	962.99 ± 33.71	169.52 ± 5.93	82.40	5.532	0.97	0.012	0.99	$3.04x10^{-5}$	0.81
TOC (E)	587.84 ± 20.57	18.64 ± 0.65	83.84	3.633	0.92	0.021	0.99	$2.82x10^{-4}$	0.57
Color (F)	88.56 ± 3.10	4.70 ± 0.17	94.48	0.523	0.72	0.018	0.99	$1.23x10^{-3}$	0.95
TAAs (G)	1620 ± 56.70	558.59 ± 19.55	65.52	6.775	0.98	0.007	0.99	$7.07x10^{-6}$	0.85

(A) ZORKC: Zero order reaction kinetic constant (mg/l . h), (B) FORKC: First order reaction kinetic constant (1/h), (C) SORKC: Second order reaction kinetic constant (l/mg . h), R^2: Regression coefficient, COD (D): COD (mg/l), TOC (E): TOC (mg/l), Color (F): Color (m^{-1}), TAAs (G): TAAs (mg benzidine/l).

Appendix 7.47 The Evaluation of specific energies in COD_{dis} (E_s), electric energy per unit volume in COD_{dis} (EE/O) and electrical energy per unit mass in COD_{dis} (EE/M) values in PCI ww, OMI ww and TI ww during sonication process with only sonication process (sonication power=640 W, sonication frequency=35 kHz, n=3, mean values).

Wastewater	**E_s [a] (kWh/kg COD_{dis})**	**Cost for E_s (TL/kg COD_{dis})**	**EE/O [b] (kW/m^3/ COD_{dis})**	**Cost for EE/O (TL/m^3/ COD_{dis})**	**EE/M [c] (kWh/kg/ COD_{dis})**	**Cost for EE/M (TL/kg/ COD_{dis})**
PCI ww	3.12	0.52	4481.80	741.53	3995.41	661.06
OMI ww	0.03	0.005	7804.88	1291.35	48.00	7.94
TI ww	3.32	0.55	5427.33	897.97	4474.02	740.25

a: Specific enegy (E_s) in COD_{dis} (kWh/kg COD_{dis}); b: Electric energy per unit volume in COD_{dis} (EE/O), (kW/m^3/ COD_{dis}); c: Electrical energy per unit mass in COD_{dis} (EE/M), (kWh/kg/ COD_{dis})

Appendix 7.48 The evaluation of cost in PCI ww, OMI ww, TI ww during sonication process with only sonication

Parameters	Costs with only Sonication				
	Annual (TL/year)	Monthly (TL/month)	Weekly (TL/week)	Daily (TL/day)	Hourly (TL/hour)
Total labor cost	3120	260	60	12	2.40
Total analysis cost	3120	260	60	12	2.40
Total chemical cost	-	-	-	-	-
Total electrical cost	193808.32	1146.80	71.675	13.761	0.114
Total part replacement cost	7.50	0.63	0.14	0.03	0.006
Total O&M cost with only sonication	200055.82	16671.32	3847.23	769.45	153.89
Amortized capital cost	120	10	2.31	0.46	0.09
Total capital cost	1500	125	28.85	5.77	1.15
Total amortized capital cost	1620	135	31.15	6.23	1.25
Total operating cost with only sonication	201675.82	16806.32	3878.38	775.68	155.14
Total cost with only sonication	201555.82	16796.32	3876.07	775.22	155.04

(* *): TL 500 ml/year=$5 * 10^{-4}$ TL m^3/year ; If these results multiple with $5 * 10^{-4}$, cost results to convert TL m^3/year.

Appendix 7.49 The evaluation of cost in PCI ww, OMI ww, TI ww during sonication process with the addition of O_2(g) sparging.

Parameters	**Costs with the Addition of O_2(g) Sparging**				
	Annual (TL/year)	**Monthly (TL/month)**	**Weekly (TL/week)**	**Daily (TL/day)**	**Hourly (TL/hour)**
Total labor cost	3120	260	60	12	2.40
Total analysis cost	3120	260	60	12	2.40
Total chemical cost of O_2(g) sparging	650 *	54.17	12.50	2.50	0.50
Total electrical cost	193808.32	1146.80	71.675	13.761	0.114
Total part replacement cost	7.50	0.63	0.14	0.03	0.006
Total O&M cost	200705.82	16725.49	3859.73	771.95	154.39
Amortized capital cost	120	10	2.31	0.46	0.09
Total capital cost	1500	125	28.85	5.77	1.15
Total amortized capital cost	1620	135	31.15	6.23	1.25
Total operating cost	202325.82	16860.49	3890.88	778.18	155.64
Total Cost	202205.82	16850.49	3888.57	777.72	155.54

(*): TL/500 ml wastewater in bottle for 1 year.

(* *): TL 500 ml/year=5 * 10^{-4} TL m^3/year; If these results multiple with 5 * 10^{-4} , cost results to convert TL m^3/year.

Appendix 7.50 The comparison of Anaerobic, Aerobic, UV, O_3 and Sonication treatment processes (Eckenfelder, 1989; Eckenfelder et al., 2008).

Parameters	**Anaerobic Treatment**	**Aerobic Treatment**	**UV Treatment**	**O_3 Treatment**	**Sonication Treatment**
Energy requirements	Low	High	High	Medium	Low
Degree of treatment	Moderate (60.00 to 90.00%)	High (95.00% +)	High (95.00% +)	High (95.00% +)	High (95.00% +)
Sludge production	Low	High	No	No	No
Process stability (to toxic compounds and load changes)	Low to moderate	Moderate to high	Moderate to high	Moderate to high	Moderate to high
Start up time	2 to 4 months	2 to 4 weeks	1 to 2 weeks	2 to 4 weeks	Lower than 1 hour
Nutrient requirements	Low	High (for certain industrial wastes)	No	No	No
Odor	Potential odor problems	Less opportunity for odors	No	No	No
Alkalinity requirements	High (for certain industrial wastes)	Low	No	No	Low
Biogas production	Yes (net benefit is contingent on the need for reactor heating)	No	No	No	No
Capital cost	Medium	High	High	Medium	Low