DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DEGRADATION AND MINERALIZATION OF DIURON AND SIMAZINE IN AQUEOUS SOLUTION BY ADVANCED OXIDATION PROCESSES

by
Ebru Çokay ÇATALKAYA

October, 2010
İZMİR

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"DEGRADATION AND MINERALIZATION OF DIURON AND SIMAZINE IN AQUEOUS SOLUTION BY ADVANCED OXIDATION PROCESSES"** completed by **EBRU ÇOKAY ÇATALKAYA** under supervision of **PROF. DR. FİKRET KARGI** 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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I would like to dedicate this thesis to my family and the memory of my teacher, Prof. Dr. Füsun ŞENGÜL.

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DEGRADATION AND MINERALIZATION OF DIURON AND SIMAZINE IN AQUEOUS SOLUTION BY ADVANCED OXIDATION PROCESSES

ABSTRACT

The first part of the thesis consists of experimental studies on removal of pesticides from aqueous solution by advanced oxidation processes (Fenton, photo-Fenton and peroxone oxidation) using Box-Behnken statistical experiment design. Effects of pesticide (diuron or simazine), hydrogen peroxide and ferrous ion concentrations and initial pH on the extent of pesticide and total organic carbon (TOC) removals were investigated. Optimum reagent doses yielding the highest pesticide and TOC removals were determined. Complete removal of pesticides was accomplished within fifteen minutes while complete mineralization was not achieved even within sixty minutes indicating formation of some intermediate compounds. In photo-Fenton treatment, the highest complete pesticide removal and mineralization (eighty-five percent) were obtained for diuron-containing water. In advanced oxidation of simazine ozone/peroxide (peroxone) treatment yielded higher mineralization (ninety-four percent) although there were no differences in simazine removals. The initial rate of pesticide degradation was found to be first-order with respect to the initial pesticide concentration for Fenton and photo-Fenton processes.

The second part of the thesis was on treatment of pulp mill effluent by different AOPs. In the treatment of pulp mill effluent, photo-Fenton treatment yielded comparable TOC (eighty-five percent), color (eighty-two percent) and AOX (ninety-three percent) removals within five minutes due to oxidations by UV light in addition to the Fenton's reagent. When pulp mill effluent from different sources was used, the TiO_2-assisted photo-catalysis resulted in the highest TOC (eighty percent) and toxicity (ninety-five percent) removals under alkaline conditions within sixty minutes.

Keywords: Simazine, diuron, advanced oxidation processes (AOPs), box-behnken design.

İLERİ OKSİDASYON YÖNTEMLERİ İLE SULU ÇÖZELTİDE BULUNAN SİMAZİN VE DİURONUN MİNERALİZASYONU VE DEGRADASYONU

ÖZ

Tezin ilk bölümü, ileri oksidasyon yöntemleri (Fenton, foto-Fenton ve perokson oksidasyonu) ile pestisit arıtımı için Box-Behnken istatiksel deney metoduna göre tasarlanmış deneysel çalışmaları içermektedir. Başlangıç pH değeri ve pestisit, hidrojen peroksit ve demir (II) konsantrasyonlarının, pestisit ve TOK giderimine olan etkileri incelenmiştir. Pestisit ve TOK giderme verimlerini maximize eden optimum dozlar belirlenmiştir. Pestisit parçalanması onbeş dakikada tamamlanırken, mineralizasyon altmış dakika sonunda bile oluşan ara ürünler nedeni ile tamamen gerçekleşmemiştir. Foto-Fenton yöntemi ile diuron içeren suyun arıtılmasında, pestisit giderimi tamamen gerçekleşirken, TOK giderimi sadece yüzde seksenbeş olarak elde edilmiştir. Simazinin perokson yöntemi ile arıtılmasında, maksimum mineralizasyon (yüzde doksanbeş) sağlanırken, simazin gideriminde çok fazla farklılık elde edilmemiştir. Fenton ve foto-Fenton yöntemlerinde, pestisit parçalanmasının birinci derece reaksiyon kinetiğine uygun olduğu bulunmuştur.

Tezin ikinci bölümünde ileri oksidasyon yöntemleri ile kağıt sanayi atıksuyunun arıtılması incelenmiştir. Foto-Fenton yöntemi ile sadece beş dakikalık reaksiyon süresinde, yüzde seksen beş TOK, yüzde seksen iki renk ve yüzde doksan üç AOX giderimi elde edilmiştir. Fenton yöntemine UV ışığının ilavesi ile foto-Fenton yönteminin reaksiyon süresine olan etkisi gözlenmiştir. Farklı bir kağıt atıksuyunun arıtılmasında ise TiO_2 kullanılan foto-katalitik oksidasyon yöntemi ile bazik koşullarda atmış dakikalık reaksiyon süresinde yüzde seksen TOK ve yüzde doksan dört toksisite giderimi elde edilmiştir.

Anahtar sözcükler: Simazine, diuron, ileri oksidasyon prosesleri (İOP), box-behnken yöntemi.

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CHAPTER ONE
INTRODUCTION

1.1 The Problem Statement

Cultivation of plants for economical purposes requires a constant struggle against losses from pests promoted by weeds, insects and diseases. The most frequent agents used for this purpose are pesticides in their different forms such as insecticides, herbicides, fungicides that contribute to agricultural productivity to a great extent (Chiron *et al.,* 2000). However, concerns about the potential impacts of pesticides on human health have arisen because the extensive use of these substances leads to their presence, together with their metabolites, in surface wastewaters from agricultural activities and in drinking waters (Barbash *et al.,* 2001).

In Europe, pesticides are considered as hazardous substances in accordance with current legislation regarding water (Directive 2006/11/EC). Therefore, the EU has set pesticide standards for drinking water at a maximum permissible concentration of 0.1 mg/L for any particular pesticide, and 0.5 mg/L for the sum of all pesticides, including their degradation products (Council Directive 98/83/EC).

Herbicides are mainly present in water supplies near agricultural areas. Most widely used herbicides are triazines (specially atrazine), phenoxyalkyl acid derivatives (2,4-D and MCPA), nitrogenous herbicides, such as those included in the acetamide group, and phenyl-urea herbicides. Those compounds have received particular attention in recent years because of their toxicity and possible carcinogenic properties (Mackay *et al.,* 1997). Due to their bio-recalcitrant and toxic properties, herbicides cannot be effectively treated in conventional wastewater treatment plants based on the activity of a microbiological consortium. New technologies need to be developed for effective treatment of herbicide containing wastewaters. In recent years, advanced oxidation has become a promising alternative for mineralization and reducing recalcitrant organic compounds in water samples.

1.2 Characteristics of Diuron

Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) belongs to the family of halogeno-phenylurea representing an important class of herbicides used in pre-and post-emergence to control broadleaf and grass weeds (Gooddy *et al.,* 2002; Tom Lin, 1997). It is formulated as a wettable powder and as a flowable liquid suspension. Diuron is considered as a highly toxic, persistent priority substance by the EU (European Commission, 2001) and has a half-life of 300 days when applied to the soil (Malato *et al.,* 2003). It is resistant to hydrolysis at pH's 5, 7 and 9. This persistence is necessary to achieve the desired herbicidal activity during seed germination. Chemical structure of diuron is presented in Figure 1.1.

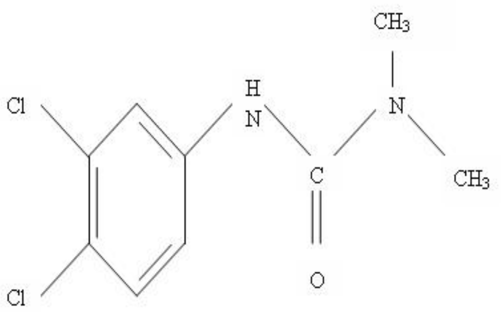

Figure 1.1 Chemical structure of diuron.

The physicochemical properties of diuron are given in Table 1.1.

Table 1.1 Physicochemical properties of diuron

Properties	
Chemical Name	N-(3,4-dichlophenyl)-N,N-dimethyl urea
CAS Number	[330-54-1]
Water solubility	42 ppm @ 20°C
Melting Point	158 °C - 159 °C
Vapor Pressure	2.97×10^{-3} (mm Hg) @ 50°C
Organic carbon partition coefficient (K_{oc})	2.77
Molecular Formula	$C_9H_{10}Cl_2N_2O$
Molecule Weight	233.1 g/mol
Density	0.619 g/mL @ 20°C

Diuron degrades by N-demethylation under aerobic conditions to metabolites including 3,4-dichloromethylphenylurea (DCPMU), 3,4-dichlorophenylurea (DCPU), and 3,4-dichloroaniline (DCA) (Dalton *et al.*, 1966). The degradation pathway for diuron and its metabolites, DCPMU, DCPU, and DCA, are shown in Figure 1.2.

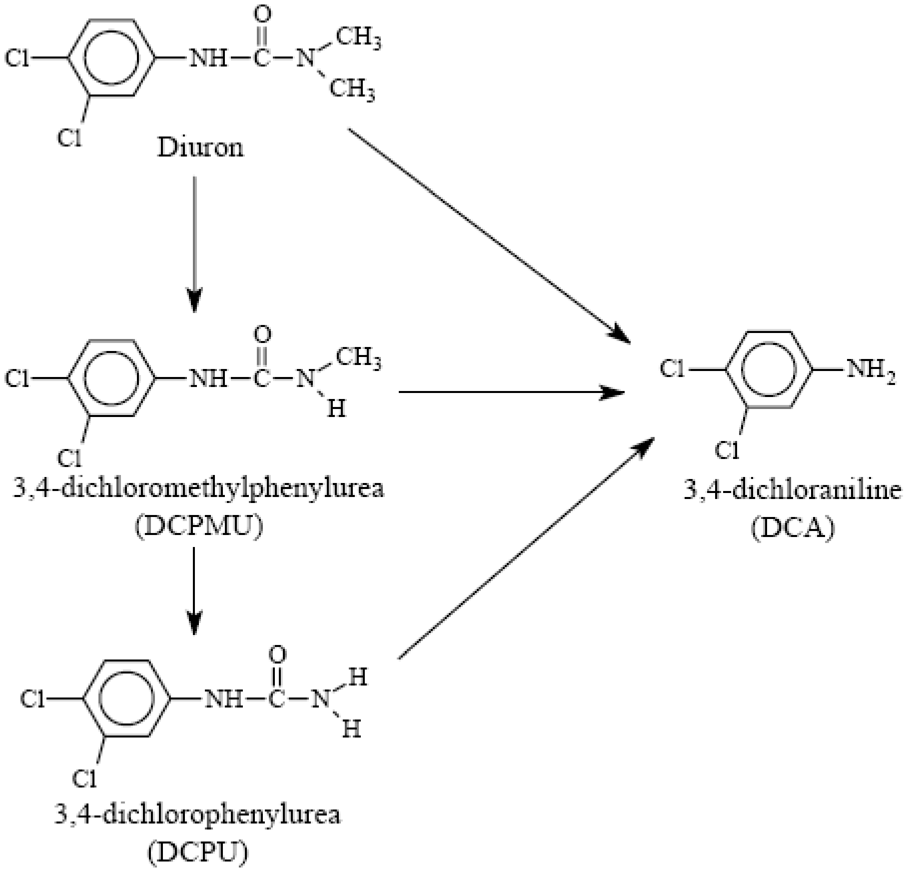

Figure 1.2 Pathways for degradation of diuron.

1.3 Characteristics of Simazine

Simazine (6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine), one of the most commonly used herbicides, belongs to the family of triazine. In addition to the aromatic carbon/nitrogen ring, simazine contains one chlorine and two ethylamine groups attached to the ring (Figure 1.3). Other chemicals of the triazine family include prometryn and atrazine (Ware, 2000). It is used to control broad-leaf weeds and annual grasses in crop fields. Fish farm ponds, aquariums, and cooling towers are some of the water systems where simazine was used to control algae before 1992 (Cremlyn, 1990). The herbicide is available as a commercial product in powder, liquid, and granular formulations.

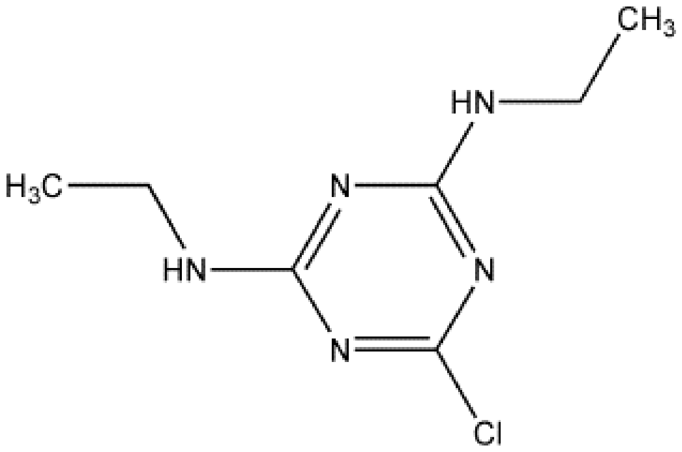

Figure 1.3 Chemical structure of simazine.

In addition to the aromatic carbon/nitrogen ring of simazine, the compound also contains chlorine and two ethylamine groups attached to the ring, physicochemical properties of simazine is presented in Table 1.2.

Table 1.2 Physicochemical properties of simazine

Properties	
Chemical Name	6-chloro-N_2,N_4-diethyl-1,3,5-triazine-2,4-diamine
CAS Number	[122-34-9]
Water solubility	5 mg/L @ 20° C
Melting Point	225° C - 227° C
Vapor Pressure	6.1×10^{-9} (mm Hg) @ 20° C 3.6×10^{-8} (mm Hg) @ 30° C 9.8×10^{-4} (mm Hg) @ 100° C
Organic carbon partition coefficient (K_{oc})	130
Molecular Formula	$C_7H_{12}ClN_5$
Molecule Weight	201.657 g/mol
Density	0.436 g/mL @ 20° C

The main photochemical degradation products of simazine were found to be 2-hydroxy-4,6-bis(ethylamino)-s-triazine, 2-chloro-4-amino-6-ethylamino)-s-triazine (deisopropylatrazine), and 2-chloro-4,6-diamino-s-triazine (diamino chlorotriazine) at basic conditions (Spurlock *et al.,* 2000; Evgenidou & Fytianos, 2002). The degradation pathway for simazine and its metabolites are shown in Figure 1.4.

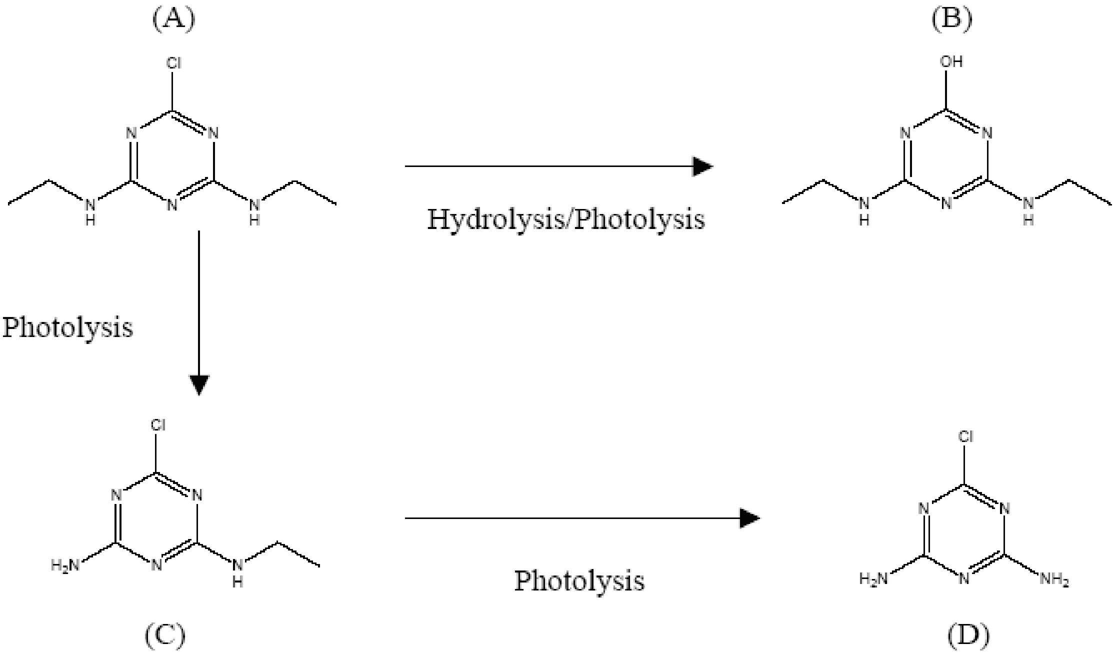

Figure 1.4 Pathways for degradation of simazine.

1.4 Treatment Methods used for Pesticide Removal

Different methods were developed for the removal of pesticides from wastewater. Conventional techniques commonly applied for the removal of pesticides from wastewater include chemical, biological and physical methods. Chemical methods are chemical precipitation/neutralization, coagulation/flocculation, solvent extraction, fixation, acid-base hydrolysis, chlorination. In chemical precipitation, chemicals such as ferrous sulfate, lime, caustic and sodium carbonate are commonly used. Physical methods are electrodialysis, reverse osmosis, ion exchange, membrane separation, adsorption (granular active carbon filters) and filtration. Biological methods are landfills, enziymatic treatment and activated sludge process. However, these chemical, biological and physical methods have significant disadvantages, including incomplete pesticide removal, producing large volume of sludge, requirements for expensive equipment and monitoring systems, high reagent or energy requirements and producing of toxic sludge or other waste products that require disposal. New technologies (such as advanced oxidation processes) are required that can reduce pesticide concentrations to environmentally acceptable levels at affordable costs.

1.4.1 Advanced Oxidation Processes

More stringenth discharge limits imposed by legislation to the treatment plants in the last years. Therefore, in recent years removal of harmful pollutants present in water supplies was investigated by means of a variety of chemical procedures instead of conventional wastewater treatment plants. Among them, AOPs, which are constituted by the combination of several oxidants such as UV radiation, ozone, hydrogen peroxide, etc (Meunier *et al.,* 2006), are characterized by the generation of very reactive and oxidizing free radicals in aqueous solutions, such as the hydroxyl radicals (OH•) (redox potential=2.8 V), with substantial destruction power (Masten & Davies, 1994).

Hydroxyl radicals react rapidly and usually indiscriminately with most organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom from aliphatic organic molecules (Buxton *et al.,* 1988). The resulting organic radicals then react with oxygen to initiate a series of degradative oxidation reactions that ultimately lead to mineralization products, such as CO_2 and H_2O (Legrini *et al.,* 1993). Therefore, advanced oxidation is a potential alternative for mineralization and to removal of recalcitrant organic compounds from polluted water. Several AOPs are currently used for elimination of pesticides. Among those are the O_3/H_2O_2 (Meijers *et al.,* 1995), O_3/UV (Kuo, 1998), photo-Fenton (Doong & Chang, 1998), TiO_2-assisted photocatalysis (Mills & Le Hunte, 1997) and electrochemical oxidation processes (Brillas *et al.*, 2000).

The advantages of advanced oxidation processes over biological and physical methods can be summarized as follows:

1. High treatment efficiencies enhanced by the fact that $OH^{\bullet}$ radicals may be produced by different mechanisms which can be adapted to specific treatment requirements,

2. Fast reaction rates yielding relatively small reactor volumes

3. High flexibility and the possibility of incorporation into water recycling processes,

4. Operation under mild conditions such as T = 20-30 °C and pH = 5-8

5. Advanced oxidation technologies as a pre-treatment or post-treatment combined with a conventional biological treatment is an alternative for non-biodegradable or toxic wastewater treatment

However, the destructive nature of AOPs have to be carefully compared with the high operation costs as well as the diffuculties encountered in the control of accumulation of the oxidation products (Colonna *et al.,* 1999).

One common problem for some of the AOPs is the high demand of electrical energy for UV lamps and ozone generator causing high operational costs. However, Fenton and solar-Fenton treatments are less costly. Minimization of the required irradiation time and the energy consumption by optimization of the other reaction conditions such as operational pH, chemicals used and concentrations, pollutant/oxidant ratio are very important.

1.5 Characteristics of Pulp and Paper Industry Wastewater

As with all major industries, the pulp and paper industry can have numerous potential environmental impacts. One of the major concerns is the potential damage caused by the effluents to receiving waters. Pulping processes utilize large amounts of water that reappear in the form of effluent. The most significant sources of pollution among various process stages are wood preparation, pulping, pulp washing, screening, washing, bleaching, and paper machine and coating operations. Among the processes, pulping generates a high-strength wastewater especially by chemical pulping.

Depending upon the type of the pulping process various toxic chemicals such as resin acids, unsaturated fatty acids, diterpene alcohols and chlorinated resin acids are generated in the pulp and paper making process (Pokhrel *et al.,* 2004). Major pollution factors in the effluents of pulp and paper industry are high suspended solids, dissolved oxygen demand, toxicity and color (Poole *et al.*, 1978). In order to meet increasingly stringent discharge limits, pulp mills are forced to adopt more efficient process schemes or technogicaly advanced treatment systems. Extensive research on wastewater treatment processes has generally reduced all of these parameters. However, toxicity and color reduction occurs to a greater or a lesser extent depending on the pulping process and the wastewater treatment process used. The majority of pulp mills use activated sludge and aerated lagoons to treat their effluents.

The major handicap to biological treatment is that the large molecule organic compounds, which are associated with toxicity are not completely degraded prior to effluent discharge and therefore pose a threat to the receiving waters. A solution to this problem may be the use of advanced oxidation processes before biological treatment as pre-treatment in order to reduce refractory organics and color in wastewater. Numerous studies have shown that advanced oxidation processes are effective in removing color, odor, and improves biological degradation by breaking down large molecules into smaller products that are more susceptible to biological degradation.

1.6 Objectives and Scope of the Thesis

Objectives of the proposed study can be summarized as follows:

1. To investigate the effectiveness of different advanced oxidation processes for the treatment of pesticide identified as priority pollutants by the European Water Framework Directive 2000/60/EC and pulp mill effluents.

2. To investigate the effects of environmental conditions on advanced oxidation of pesticides and pulp mill effluent. Effects of the following parameters would be investigated:

    - pH
    - Hydrogen peroxide concentration
    - Ferrous ion concentration
    - Pesticide dose
    - Ozone dose
    - UV light

3. To determine optimum catalyst and oxidant dosages and reaction time by using the Box-Wilson statistical experiment design and the response surface methodology yielding maximum pesticide and TOC removals.

4. To compare the oxidative performances of the selected advanced oxidation processes in terms of TOC and pesticide removals.

5. To determine the most appropriate advanced oxidation process as pre-treatment or post-treatment alternative for the industrial and synthetic wastewaters of concern.

6. To study the kinetics of pesticide degradation by different AOPs and to determine the major kinetic constants by using the experimental data.

CHAPTER TWO
LITERATURE REVIEW

Large number of studies was reported in literature for the removal of pesticides from wastewater by advanced oxidation process. Major studies may be summarized as follows:

2.1 Diuron Removal by AOPs

Benitez *et al.,* (2007) examined oxidation of four phenyl-urea herbicides (isoproturon, chlortoluron, diuron, and linuron) in some natural water systems (commercial mineral water, groundwater, and surface water from a reservoir) by ozone at pH 2, and by a combination of O_3/H_2O_2 at pH 9. The influence of operating conditions (initial ozone dose, nature of herbicides, and type of water systems) on herbicide removal efficiency was investigated. The partial contributions of direct ozone and radical pathways were evaluated, and the results showed that reaction with OH• radicals was the major pathway for the oxidative transformation of diuron and linuron, even when conventional ozonation was applied, while for chlortoluron and isoproturon, direct ozonation was the major pathway (Benitez *et al.,* 2007).

Farre *et al.,* (2007a) analyzed the intermediates generated during the chemical oxidation of diuron and linuron herbicides using a chemical oxidation (photo-Fenton) and a biological coupled system. Three combinations of reactant dose were used in the chemical oxidation step. Different degrees of elimination of total organic matter were achieved in the secondary biological treatment depending on the by-products generated in the chemical stage. Formic, oxalic and acetic acids appear at different concentration during the photo-Fenton experiments. The presence of acetic acid was found to be higher under soft oxidant conditions while an increase in OH• concentration produces a higher concentration of oxalic acid. 3,4-dichloroaniline and 3,4-dichlorophenyl isocyanate have been found as intermediates in the oxidation processes among other hydroxilated by-products (Farre *et al.*, 2007a).

Farre *et al.,* (2007b) used a preliminary chemical treatment of pentachlorophenol, isoproturon, diuron, alachlor and atrazine pesticide aqueous solutions (all them belonging to the list of priority pollutants of the European Union) based on a combination of ozone and photo-Fenton reagents to generate intermediates of partial degradation that could be more conveniently degraded with a secondary biological treatment. Quantification of the biodegradability and the toxicity of the treated solutions have been carried out in order to ascertain the suitability of the coupling between the chemical and the biological step. PCP, isoproturon, diuron, alachlor and atrazine pesticide solutions have been partially degraded by using a chemical pretreatment method based on a combination of ozone and photo-Fenton reagents. The removal of the parent pesticide takes place in a few minutes, but the complete mineralization of all the organic content takes longer times (Farre *et al.,* 2007b).

Lapertot *et al.,* (2006) evaluated the results of photo-Fenton treatment in a solar pilot-plant scale of several EU priority hazardous substances (Alachlor, Atrazine, Chlorfenvinphos, Diuron and Isoproturon) dissolved not only from the point of view of contaminant disappearance and mineralization, but also of toxicity reduction and enhancement of biodegradability. Photo-Fenton at low iron concentrations (10-20 mg/L) is an effective method for treating priority substances. Complete disappearance and total dechlorination of all pesticides was attained very easily at different initial concentrations, alone and in mixtures. Biodegradability was enhanced (70% considered biodegradable) by the photo-Fenton treatment after 12-25 min (Lapertot *et al.,* 2006).

Benitez *et al.,* (2006) examined photo-oxidation of four phenyl-urea herbicides (linuron, chlorotoluron, diuron, and isoproturon) using monochromatic UV radiation in ultra-pure aqueous solutions. The influence of pH and temperature on the photodegradation process was established, and the first-order rate constants and quantum yields were evaluated. A kinetic study was performed using a competitive kinetic model that allowed various rate constants to be evaluated for each herbicide. The simultaneous photo-oxidation of mixtures of these phenyl-ureas in different types of water (ultra-pure water, commercial mineral water, groundwater, and lake water) showed the same trend of reactivities to both UV radiation alone and the

UV/H_2O_2 combination: i.e., linuron > chlorotoluron > diuron > isoproturon (Benitez *et al.*, 2006).

Farre *et al.*, (2005) reported a rapid decrease of the concentration of the biorecalcitrant pesticides, alachlor, atrazine, chlorfenvinfos, diuron and PCP in aqueous solutions using Photo-Fenton/ozone (PhFO) and TiO_2-photocatalysis/ozone (PhCO) coupled systems as advanced oxidation processes. The degradation processes follow a first and zero-order kinetics, when PhFO and PhCO are applied respectively. The application of PhFO, PhCO and ozone+UV systems to the pesticide aqueous solutions leads to a strong TOC reduction, except for atrazine (Farre *et al*., 2005).

Paterlini *et al.*, (2005) investigated the degradation of tebuthiuron, diuron and 2,4-D in aqueous solution by photo-Fenton process using ferrioxalate complex (FeOx) as source of Fe(II) under blacklight irradiation. The multivariate analysis, more precisely, the response surface methodology was applied to evaluate the role of FeOx and hydrogen peroxide concentrations as variables in the degradation process to define the concentration ranges that result in the most efficient degradation of the herbicides. Under optimized conditions, 20 min were sufficient to mineralize 93% of TOC from 2,4-D and 90% of diuron, including oxalate. Complete dechlorination of these compounds was achieved after 10 min reaction (Paterlini *et al.,* 2005).

Hincapie *et al.*, (2005) investigated degradation of different pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol) considered PS (priority substances) by the European Commission at pilot plant scale using photo-Fenton and TiO_2 photocatalysis driven by solar energy. Two different iron concentrations (2 and 55 mg/L) and TiO_2 at 200 mg/L have been tested and discussed, using mainly TOC mineralization for comparison of treatment effectiveness. Almost complete mineralization and total detoxification were always attained. It has been demonstrated that evolution of chloride could be a key-parameter for predicting toxicity of chlorinated compounds (Hincapie *et al.*, 2005).

Malato *et al.*, (2002) studied the technical feasibility and performance of photocatalytic degradation of four water-soluble pesticides (diuron, imidacloprid, formetanate and methomyl) at pilot scale in two well-defined systems, which consist of heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by photo-Fenton. Experimental conditions allowed disappearance of pesticide and degree of mineralization achieved in the two photocatalytic systems to be compared. Total disappearance of the parent compounds and 90% mineralization have been attained with all pesticides tested, methomyl being the most difficult to be degraded with both treatments. First-order rate constants, initial rate, time necessary for mineralising 90% of the initial TOC and hydrogen peroxide consumption were calculated in all cases, enabling comparison both of treatments and of the selected pesticide reactivity. AOPs driven by solar energy appear to be an efficient method of removing pesticides from water (Malato *et al.,* 2002).

The photocatalytic degradation of diuron was executed in the presence of platinized TiO_2 photocatalyst. It was found that the first-order rate constant for diuron degradation by Pt–TiO_2 was ca. 4 times higher than P-25 TiO_2. Based on these results, the photocatalytic reaction by Pt–TiO_2 could be useful technology for the treatment of wastewater containing diuron (Katsumata *et al.,* 2009).

The Catalytic Wet Air Oxidation (CWAO) of diuron has been investigated in aqueous solution in the presence of a Ru/TiO_2 catalyst at 140-180 ^oC and 5 MPa total air pressure. Thermal degradation is the main initial process yielding mainly 3,4-dichloroaniline (DCA) and dimethylamine (DMA). In addition to this, the mineralization is incomplete compared to other advanced oxidation processes (Carrier *et al.,* 2009).

The efficiency of low pressure UV photolysis and advanced oxidation processes (using hydrogen peroxide and titanium dioxide) for the degradation of pesticides (ısoproton, alachlor, pentachlorophenol, atrazine, chlorfenvinphos and diuron) was investigated by Sanches *et al.,* 2010. Photolysis of the pesticides followed the same trend: isoproturon degradation was negligible, alachlor, pentachlorophenol, and atrazine showed similar degradation rate constants, whereas diuron and chlorfenvinphos were highly removed.

Effects of pH, persulphate and Fe (II) concentration on the destruction of diuron by heat-assisted persulphate were examined by Romero *et al.,* 2010. Experiments were performed at 50 ^{o}C and an initial diuron concentration of 0.09 mM. For the higher persulphate concentration (2.1 mM), complete diuron oxidation was achieved at 0.72 mM Fe(II) concentration in a few minutes.

2.2 Simazine Removal by AOPs

Gora *et al.,* (2006) studied the photocatalytic oxidation (PCO) of the herbicides isoproturon, simazine and propazine over irradiated TiO_2 suspensions in single-component and in multicomponent systems. The initial herbicide concentration ranged from 70 mg/L to 3 mg/L in order to approach typical concentrations found in contaminated ground and surface waters. The time-dependent degradation profiles of each herbicide were successfully modelled using an approximation of the Langmuir-Hinshelwood (L-H) rate equation, which takes into account the direct effect of the intermediate reaction products. A direct comparison of the binding constants of the herbicides observed under dark adsorption and under PCO shows that these are very similar suggesting that the degradation of isoproturon, simazine and propazine mixtures follows a surface or near-surface reaction according to a competitive L-H mechanism (Gora *et al.,* 2006).

Rivas *et al.,* (2004) carried out the removal of the herbicide simazine in aqueous phase by means of Fenton’s reagent. The influence of the main operating parameters, Fe(II) concentration (5.0×10^{-5} to 4.0×10^{-4} M), pH (2-6) and temperature (10-30°C) has been studied. The optimum working pH was 3.0. The operating temperature exerts a minor influence in the interval tested in this work (10-30°C). An excess of Fe(II) fed to the reactor leads to a decrease in the effectiveness of the process, probably due to the scavenging nature of Fe(II) (Rivas *et al.,* 2004).

Rivas *et al.,* (2001) ozonized simazine, a common herbicide found in surface and ground water in continuous flow mode. The ozone dose fed to the system exerted a positive effect, while the gas flow rate did not influence the efficiency of the process provided ozone mass flow rate was constant. Increasing the pH led to a higher extension of the free radical degradation of simazine and, therefore, to a higher efficiency of the process. Addition of free radical promoters, i.e. hydrogen peroxide, did result in a significant improvement of the simazine removal rate. A first approach to process economy showed the system ozone/hydrogen peroxide as the most advantageous in terms of electrical energy requirements (Rivas *et al.*, 2001).

Huston *et al.*, (1999) investigated the destruction of pesticide active ingredients (AI) and commercial formulations in acidic aqueous solution with the catalytic photo-Fenton, Fe(III)/H_2O_2/UV. The AIs are alachlor, aldicarb, atrazine, azinphos-methyl, captan, carbofuran, dicamba, disulfoton, glyphosate, malathion, methoxylchlor, metolachlor, picloram and simazine. Complete loss of pure AI occurred in most cases in <30 min under the following conditions: $5.0*10^{-5}$ M Fe(III), $1.0*10^{-2}$ M H_2O_2, T=25.0°C, pH 2.8 and $1.2*10^{19}$ quantal^{-1} s^{-1} with fluorescent blacklight UV irradiation (300±400 nm). Considerable mineralization over 120 min occurred in most cases as evidenced by the appearance of inorganic ions and the decline in total organic carbon (TOC) of the solution. Intermediate products such as formate, acetate and oxalate appeared in early stages of degradation insome cases (Huston *et al.*, 1999).

Most of the literature studies on the photooxidation of mixtures of the selected herbicides in several types of waters the treatment of pesticides was performed using advanced oxidation processes, which are based on only pesticide degradation. Toxic effects and inhibition of only one pesticide on degradation, mineralization and dehalogenation in advanced oxidation processes were not investigated and reported in literature. Therefore, the objective of the first part of this thesis was to investigate the performance of advanced oxidation processes treating one selected pesticide to evaluate TOC, pesticide and AOX removals as function of the operating parameters.

Many investigators have studied removal of pesticides from wastewater by oxidation processes extensively. Limited number of studies was reported in literature on photolysis (Rivas *et al.*, 2001), photo-catalytic degradation (Gora *et al.*, 2006), and oxidation of pesticide (Rivas *et al.*, 2004). However, the reported studies were mainly focused on the analysis and identification of the main products with proposals for the reaction mechanisms for the photoreactions. The effects of reagent doses on pesticide (simazine, diuron) degradation and mineralization by the different advanced oxidation processes (Fenton, photo-Fenton and peroxone oxidations) were not reported in literature. The objective of the second part of this thesis was to investigate the performance of different advanced oxidation processes (Fenton, photo-Fenton and peroxone process) on TOC, pesticide and AOX removals.

There is no sound mathematical model describing the effects of different independent parameters on performance of advanced oxidation processes (degradation, mineralization and dehalogenation of pesticides) used to treat pesticides. Therefore, another objective of the third part of thesis was to develop a sound mathematical model. The Box-Behnken statistical experiment design was used in this study to investigate the effects of independent variables (H_2O_2, ferrous ion, pesticide dose and pH) on pesticide, TOC (mineralization) and AOX (dehalogenation) removals by the different advanced oxidation processes (Fenton, photo-Fenton, peroxone treatments). Optimum reactive concentrations maximizing the pesticide, TOC and AOX removals were also determined by using an optimization program.

2.3 Pulp and Paper Industry Wastewater Treatment by AOPs

Application of advanced oxidation processes on wastewater treatment was also investigated in the thesis. Pulp and paper industry was selected due to presence of toxic chemicals and pesticides. A number of studies were reported in literature for the treatment of pulp and paper mill wastewater by advanced oxidation process. Major studies may be summarized as follows:

Perez *et al.*, (2002a) investigated the degradation of the organic content of a bleaching kraft mill effluent (BKME) using Fenton’s reagent and irradiation providing the conditions needed for the simultaneous occurrence of Fenton and photo-Fenton reactions. The main parameters that govern the complex reactive system, i.e. light intensity, temperature, pH, Fe(II) and H_2O_2 initial concentrations, and O_2 presence in solution have been studied. The presence of small amounts of O_2 seems to be enough to ensure the reaction progress. The combination of Fenton and photo-Fenton reactions was proven highly effective for the treatment of pulp and paper industry wastewaters (Perez *et al.*, 2002a).

Hassan & Hawkyard (2002) studied the removal of color by combined oxidation with ozone and Fenton's reagent and stated that 100% color removal was achieved at a pH of 4-5 when of ferral (derived from natural clay sources, which contains 2% ferric sulfate and 6% aluminum sulfate) and ferric sulfate were used (Hassan & Hawkyard, 2002).

Fierre *et al.,* (2001) conducted experiments where ozone at high (11) and low (3) pH with and without UV or H_2O_2 was applied to kraft paper mill effluent. It was found that pH 11 provided the better conditions for treatment of color, TOC, total phenols, and acute toxicity. O_3/pH=11/UV treatment provided the best conditions for color removal, in which 45% reduction was achieved (Fierre *et al.,* 2001).

Zamora *et al.*, (1998) reported on the use of horseradish peroxide to decolorize Kraft effluent by 50% within three hours of reaction time. The degradation of phenolic and polyphenolic compounds present in the bleaching effluent was studied using advanced oxidation systems such as photocatalysis with O_2/ZnO/UV, O_2/TiO_2/UV, O_3 and O_3/UV. O_2/ZnO/UV and O_2/TiO_2/UV were the best systems to oxidize the effluent in a short period of time. Balcioglu & Ferhan (1999) reported on photo-catalytic oxidation of kraft pulp bleaching wastewater showing that the removal largely depended on the concentration of COD and chloride below a certain level.

Hostacy *et al.,* (1997) investigated the use of ozonation to treat bleaching effluents in an attempt to reduce AOX, COD, BOD and acute toxicity. All parameters were more efficiently treated in alkaline conditions rather than acidic. 80% reduction in AOX and nearly total destruction of chlorophenols was observed in alkaline conditions. Nearly 60% reduction of both BOD and COD were also observed in alkaline conditions. This is likely due to the formation of hydroxyl radicals at high pHs, which is a stronger oxidizer than ozone (Hostacy *et al.,* 1997).

Zhou & Smith (1997a) showed that at an ozone dose over 40 mg/L, the ozonation of biologically pretreated pulp mill effluents resulted in up to 80% reduction in color and 60% reduction in adsorbable organic halogens (AOX). An improvement of biodegradability was also observed, as the ratio of BOD_5 to chemical oxygen demand

(COD) increased with an increase in the amount of consumed ozone. After storing for 2 days, up to 15% of color rebound in the treated effluents was observed (Zhou & Smith, 1997a).

Tuhkamen *et al*., (1997) evaluated the use of ozonation as a pretreatment to activated sludge. An increase in the biodegradability of the ozone-pretreated effluent was observed as an increase in the BOD/COD ratio. In other words, an increase in biodegradability is correlated to a conversion of COD to BOD. Other results for the ozone pretreated samples include overall removal efficiencies of up to 91% BOD removal and 85% COD removal. This was compared to 22 to 60% BOD and 47 to 62% COD removals without the ozonation pretreatment. They concluded that ozonation prior to biological treatment is an effective method to eliminate aquatic toxicity (Tuhkamen *et al*., 1997).

Mobius & Cordes-Tolle (1996) investigated the use of ozone as a pretreatment to biological treatment. An average ozone dose of 285 mg/L was applied to an industrial waste flowing through an ozonation reactor with a hydraulic retention time of 1 hour. An average COD of approximately 500 mg/L and BOD5 of about 30 mg/L. characterized the wastewater. It was noted that ozone caused partial oxidation of persistent organic compounds, which in turn lead to improve biological degradability. Other results include a 90% decrease in color, 67% AOX elimination and 50% COD removal (Mobius & Cordes-Tolle, 1996).

Nakamura *et al.,* (1996) conducted tests whereby kraft pulp wastewaters was treated with a combination of ozone and activated sludge. Ozone was applied to the effluent at a feed concentration of 20 mg/L. It was found that the consecutive treatment with ozone followed by activated sludge was effective at degrading the lignin compounds found in the effluent. Strong alkaline conditions (pH=12) further enhanced the degradation of the lignin (Nakamura *et al.,* 1996).

Murphy *et al.,* (1993) studied the removal of color from three effluent streams from a pulp and paper mill. They reported that the O_3/H_2O_2 process could achieve color removal up to 85% for the caustic extract stream, up to 90% for the acidic stream, and up to 50% in the final effluent. The optimum H_2O_2 to O_3 ratio usually ranges from 0.3 to 0.6 (Murphy *et al.*, 1993).

Results from the study conducted by Mohammed & Smith (1992) include a 65% and 100% increase in BOD for ozone doses of 50 and 100 mg/L, respectively. Color was also reduced by 58 to 67% for a 50 mg/L ozone dose and 77 to 85 % with ozone dose of 100 mg/L. Unlike BOD and color, there was no clear relationship for the reduction in levels of suspended solids, COD and TOC, using various ozone doses (Mohammed & Smith, 1992).

Extensive research on wastewater treatment processes has generally reduced all of these parameters. However, toxicity and color reduction occurs to a greater or a lesser extent depending on the pulping processes. The majority of pulp mills use activated sludge and aerated lagoons to treat their effluents. The major handicap to biological treatment is that the large molecule organic compounds that are associated with toxicity are not fully degraded prior to effluent discharge and therefore pose threat to the receiving waters. Therefore, the objective of the last part of the thesis was to investigate the reduction of refractory organics in pulp mill effluents using a combination of advanced oxidation processes and biological process in order to improve the performance of an activated sludge unit. Fenton, photo-Fenton and peroxone treatments were used for TOC, color and AOX removals from pulp mill effluent after biological treatment.

CHAPTER THREE
THEORETICAL BACKGROUND

3.1 General

The presence of toxic and refractory pollutants in the discharge of wastewaters and in some cases in water supplies is a topic of global concern. Conventional plants for biological wastewater treatment are no longer sufficient, since many of these contaminants are not biodegradable. As physical-chemical methods (e.g. flocculation, filtration, adsorption by granulated activated carbon, air stripping) achieve the removal by separation, they merely transfer the pollutants from one phase to another, leaving a problem of disposal of the transferred material. For that reason, new treatment technologies were investigated. Most of the limitations given above can be eliminated by using oxidation technologies (Gulyas, 1997).

3.2 Theory of Advanced Oxidation Processes

Advanced oxidation is used to convert pollutants to products such as CO_2 and H_2O or to intermediate products that are more readily biodegradable or removable by adsorption (Eckenfelder, 1989). In recent years, advanced oxidation processes (AOPs) have emerged as potentially powerful methods which are capable of transforming the pollutants into harmless substances (Esplugas *et al.*, 1994). These methods almost all rely on the generation of very reactive nonselective transient oxidizing species such as the hydroxyl radical, $OH^{\bullet}$, which has also been identified as the dominant oxidizing species (Masten & Davies, 1994).

When generated, these radicals react rapidly and usually indiscriminately with most organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom from aliphatic organic molecules (Buxton *et al.*, 1988). Although the hydroxyl radicals are short lived, they have a higher oxidation potential than ozone, chlorine, or hydrogen peroxide, and their unstable nature increases their reaction speed. Table 3.1 lists the redox potential of several oxidative species commonly used in water and wastewater treatment.

Table 3.1Redox potential for commonly used oxidants in water

Oxidant	Oxidation Potential, V
Fluorine	3.0
Hydroxyl Radical	2.8
Ozone	2.1
Hydrogen Peroxide	1.8
Potassium Permanganate	1.7
Chlorine Dioxide	1.5
Chlorine	1.4

Generation of $OH^{\bullet}$ radicals is commonly accelerated by combining ozone, hydrogen peroxide, UV radiation, ferrous and ferric salts (Fe(II) and Fe(III)). Of these, UV plus hydrogen peroxide, lighted photo-Fenton, darked photo-Fenton, O_3/H_2O_2 and O_3 /UV hold the greatest promise to detoxify water and wastewater.

3.2.1 H_2O_2 Treatment

Hydrogen peroxide (H_2O_2) is one of the most powerful oxidizer and is stronger than chlorine, chlorine dioxide, and potassium permanganate. H_2O_2 can be converted into hydroxyl radicals ($OH^{\bullet}$) with high reactivity. Its applications on industrial wastewater are very effective, such as treatment of paper mill effluent, drilling mud, treatment of wastewater, which contains toxic and refractory organic substances.

3.2.2 Fenton Treatment

The Fenton reaction is a widely used catalytic oxidation method based on electron transfer between H_2O_2 and metal ions (Fe(II)) serving as homogeneous catalyst. The efficiency of the Fenton's reagent is based on the hydroxyl radical generation by a mixture of H_2O_2 and Fe(II) ions as shown in the following reaction (Ashraf *et al.*, 2006).

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + OH^{\bullet} \qquad \text{Eqn 3.1}$$

3.2.3 UV/H_2O_2 Treatment

Ultraviolet photolysis combined with hydrogen peroxide (UV/H_2O_2) is one of the most appropriate AOPs technologies for degradation of toxic organics since this process may occur in nature itself. The $OH^{\bullet}$ radicals produced through UV/H_2O_2 system as shown below activate organic compounds for oxidations by subtracting hydrogen atoms or by adding to double bonds (Ogata *et al.*, 1981; Crittenden *et al.*, 1999).

$H_2O_2 + h\nu \rightarrow 2OH\bullet$ Eqn 3.2

3.2.4 Photo-Fenton Treatment

The recently developed photo-Fenton treatment was shown to be an effective AOP for oxidation of recalcitrant organic compounds (Ruppert *et al.*, 1993). The mechanism of the photo-Fenton treatment is based on the hydroxyl radical generation by a mixture of H_2O_2 and Fe(II) ions (Fenton reaction) as shown in the following reaction (Ashraf *et al.*, 2006):

$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + OH^{\bullet}$ Eqn 3.3

Another reaction also produces additional hydroxyl radicals and regenerates Fe(II) ions under illumination which is known as the photo-Fenton reaction (Faust *et al.*, 1990).

$Fe(III) + H_2O + h\nu \rightarrow Fe(II) + H^+ + OH^{\bullet}$ Eqn 3.4

Consequently, higher concentrations of $OH^{\bullet}$ radicals and Fe(II) can be attained with the UV/H_2O_2/Fe(II) treatment as compared to the conventional Fenton’s reagent treatment. The reaction time needed for the photo-Fenton process is extremely low and depends on the operating pH and the concentrations of H_2O_2 and Fe(II).

3.2.5 Ozone Treatment

Ozone is also a source of hydroxyl radicals especially with the combination of peroxide (O_3/H_2O_2) which is very effective in elimination of refractory micropollutants, including most pesticides, chlorinated solvents, aliphatic hydrocarbons and aromatic compounds (Report U.S. EPA/600/R- 06/072, 2006, Report U.S. EPA542-R-98-008, 1998). Ozone is a specific and efficient oxidant with a standard oxidation potential of 2.1 V. Oxidation of organic compounds by ozone treatment can be realized by two different mechanisms.

a. Through direct oxidation by ozone as described below

$O_3 + RC = CR \rightarrow RCOCR + O_2$ Eqn 3.5

b. Through indirect oxidation based on the ozone decomposition and formation of hydroxyl radicals. These radicals can be formed because of ozone reaction with hydroxide ions (OH^-) at neutral or basic pHs via reactions of Eqn 3.6 and Eqn 3.7:

$O_3 + OH^- \rightarrow O_2 + HO_2^-$ Eqn 3.6

$O_3 + HO_2^- \rightarrow O_2 + O_2^{\bullet -} + \bullet OH$ Eqn 3.7

Usually the indirect oxidation process by hydroxyl radicals is faster than direct oxidation (Singh *et al.*, 1995). In the presence of hydrogen peroxide, ozone oxidation is enhanced by the following reaction due to fast and effective hydroxyl radical formation (Sanchez-Lafuente *et al.*, 2002):

$2\ O_3 + 3\ H_2O_2 \rightarrow 4\ O_2 + 2\ OH\bullet + 2\ H_2O$ Eqn 3.8

Ozone-peroxide oxidation called as the peroxone treatment has been widely used for degradation of microorganic pollutants such as pecticides because of its effectiveness and simplicity. After the hydroxyl radicals are formed, propagation of radical chain reactions and oxidation of contaminants follow the same mechanisms as those occurring in ozonation at the elevated pH condition.

3.2.6 UV/TiO_2 Treatment

Semiconductor materials used in environmental applications include titanium oxide (TiO_2), strontium titanium trioxide and zinc oxide (ZnO). TiO_2 is generally preferred for use in commercial AOP applications because of its high level of photoconductivity, availability, low level of toxicity, low cost and relatively high chemical stability (Konstantinou & Albanis, 2004). Photo-catalytic degradation of recalcitrant organic contaminants in the presence of TiO_2 has been recently developed and investigated (Carraway *et al.*, 1994; Maugans & Akgerman, 1997). A large number of aliphatic and aromatic compounds can be mineralized by UV/TiO_2 treatment under suitable conditions. The process is initiated upon UV irradiation of the semiconductor with the formation of high energy electron/hole pairs by exciting an electron from the valence band (VB) to the conduction band (CB).

$$TiO_2 + hv \rightarrow e_{CB-} + h_{VB+} \qquad \text{Eqn 3.9}$$

The highly oxidative h_{VB}^+ (E_0 = 2.8 V) may directly react with the surface-sorbed organic molecules to form R^+ or indirectly via the formation of $OH^\bullet$ radicals (Konstantinou & Albanis, 2004; Gimenez *et al.*, 1997). The reaction of the photo-generated holes with water molecules and hydroxyl ions adsorbed on the surface of TiO_2 yields formation of hydroxyl radicals (San *et al.*, 2002; Gomes da Silva & Faria, 2003):

$$h_{VB+} + OH^- \rightarrow \bullet OH \qquad \text{Eqn 3.10}$$

$$h_{VB}^+ + H_2O(ads) \rightarrow \bullet OH + H^+ \qquad \text{Eqn 3.11}$$

$$e_{CB-} + O_2 \rightarrow {}^\cdot O_2^- \qquad \text{Eqn 3.12}$$

The resulting hydroxyl radicals are strong oxidizing agents and can oxidize most of the organic compounds (Maurino *et al.*, 1999). Major drawback of photo-catalytic processes is the need to remove the catalyst after treatment and the limited surface area of semiconductors.

3.2.7 UV/TiO₂/H₂O₂ Treatment

Titanium dioxide (TiO_2) is known to be more effective due to the formation of electron-hole pairs under illumination with UV light. Nevertheless, combination of electrons and holes inhibit the photo-catalytic reaction process as mentioned in UV/TiO_2 treatment. Some oxidants (oxygen, hydrogen peroxide, oxyhalogens) improve the performance of UV/TiO_2 treatment by capturing the electrons ejected from TiO_2 and therefore, reducing the probability of recombination of e^- and h_{VB}^+, yielding higher available number and the survival time of h_{VB}^+ (Irmak *et al.*, 2004). Recently, some investigators examined the effect of H_2O_2 on oxidation of organic pollutants, such as chlorophenols and atrazine mediated by TiO_2 (Wong & Chu, 2003). Addition of small amounts of hydrogen peroxide can significantly increase the generation rate of hydroxyl radicals, thereby enhancing the oxidation efficiencies of organic pollutants mediated by TiO_2.

At high H_2O_2 concentrations, photo-catalytic oxidation was inhibited by the reactions of excess H_2O_2 with $OH^\bullet$ radicals and h_{VB}^+ (Tanaka *et al.*, 2000; Konstantinou & Albanis, 2004).

$$H_2O_2 + \bullet OH \rightarrow H_2O + HO_2^\bullet \qquad \text{Eqn 3.13}$$

$$HO_2^\bullet + \bullet OH \rightarrow H_2O + O_2 \qquad \text{Eqn 3.14}$$

$$H_2O_2 + 2h_{VB}^+ \rightarrow O_2 + 2H^+ \qquad \text{Eqn 3.15}$$

3.3 Box-Behnken Statistical Experiment Design

Design of experiments by using statistical methods can be used for optimization of the process variables in multivariable systems. The response surface methodology (RSM) is a useful tool used for analysis of complex systems involving many variables and objective functions. The RSM and statistical experiment design comprises a group of statistical techniques for model building and prediction of the system behavior (Sastry & Khan, 1998; Hamed & Sakr, 2001). The RSM has been used by many investigators as an efficient statistical technique for optimization of multi-variable systems with minimum number of experiments (Francis *et al.*, 2000; Krishna *et al.*, 2000; Vohra & Satyanarayana, 2002).

Different types of statistical experiment designs include 3-level factorial; central composite (CCD) (Boza *et al.*, 2000; Box & Wilson, 1951), Box- Behnken (Singh *et al.*, 1995) and D-optimal designs (Sanchez-Lafuente *et al.*, 2002). A modified central composite experimental design known as the Box-Behnken design (BBD) is an independent, rotatable quadratic design containing no embedded factorial or fractional factorial design (Ragonese *et al.*, 2002). Among all the statistical experiment design methods, Box-Behnken design requires fewer runs than the other design methods, such as 15 runs for a 3-factor experiment design. Moreover, the method allows calculation of the response function at intermediate levels which are not experimentally studied (Sastry & Khan, 1998; Hamed & Sakr, 2001). A comparison of BBD with the other response surface designs (central composite, Doehlert matrix and three-level full factorial design) has shown that the BBD and Doehlert matrix are slightly more efficient than the central composite design, but much more efficient than the three-level factorial designs (Ferreira *et al.*, 2007). The Box-Behnken statistical experiment design and the RSM were reported to be useful in optimization of the three variable response functions (Hamed & Sakr, 2001; Charles & Kennneth, 1998). The optimization process involves studying the response of the statistically designed combinations, estimating the coefficients by fitting the experimental data to the response function, predicting the response of the fitted model and checking the adequacy of the model by the ANOVA tests.

The independent variables were the dose of pesticide (X_1), hydrogen peroxide (X_2), and ferrous ion (X_3). The low, center and high levels of each variable are designated as -1, 0, and +1, respectively. Response functions describing variations of dependent variables (percent pesticide, TOC or AOX removals) with the independent variables (*X*;) can be written as follows:

$$Y = \overbrace{\underbrace{b_o+}}\sum b_i*\overbrace{\underbrace{X_i+\ \sum}} b_{ij}*X_i*\overbrace{\underbrace{X_j+}}\ \sum b_{ii}*X_i^2 \qquad \text{Eqn 3.16}$$

where *Y* is the predicted response (percent pesticide, TOC and AOX removals), b_0 is the offset term and b_i is the linear effect while b_{ii} and b_{ij} are the square and the interaction effects, respectively. The application of RSM offers an empirical relationship between the response function and the independent variables. The mathematical relationship between the response function (Y) and the independent variables (X) can be approximated by a quadratic polynomial equation as follows:

$$Y=b_0+b_1X_1+b_2X+b_3X_3+b_{12}X_1X_2+b_{13}X_1X_3+b_{23}X_2X_3+b_{11}X_1^2+b_{22}X_2^2+ b_{33}X_3^2$$

Eqn 3.17

This approach was selected because relatively fewer combinations of the variables were used to estimate a potentially complex response function. Fifteen experiments are needed to calculate 9 coefficients of the second-order polynomial regression model. This model contains one block term, three linear, three quadratic and three interaction terms. The response function coefficients were determined by regression using the experimental data and the Stat-Ease Design Expert 7.0.1computer program.

Coded points used in Box-Behnken statistical design are presented in Table 3.2. The results of analysis of variance (ANOVA) are also presented in tables indicating the fact that that the predictability of the model is at >95% confidence interval. Response function predictions are in good agreement with the experimental data with a coefficient of determination (R^2) of larger than 0.99. Furthermore, the computed F value is much greater than that of the tabular $F_{0.01\,(14,\,14)}$ value of 3.70 suggesting that the treatment is highly significant. P values of less than 0.05 for any factor in analysis of variance (ANOVA) indicated a significant effect of the corresponding variable on the response.

Table 3.2 Coded levels of the experimental data points used in Box-Behnken statistical design

Run	X_1 Pesticide,	X_2 H_2O_2,	X_3 Fe(II) or pH,
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0

3.4 Kinetics of Pesticide Degradation

Time course of variations of pesticide concentrations for different experiments of the Box-Behnken design were drawn. Pesticide degradation by Fenton/photo-Fenton oxidation can be described by the following reaction,

$$\text{Pesticide} + H_2O_2 + \text{Fe(II)} \xrightarrow{h\nu} \text{Products} + H_2O + CO_2 \qquad \text{Eqn 3.18}$$

The initial reaction rates of pesticide degradation can be expressed in terms of initial pesticide, H_2O_2 and Fe(II) concentrations as follows,

$$R_o = (-dP/dt)_o = k\, P_o^{\alpha}\ HP_o^{\ \beta}\ Fe_o^{\ \gamma} \qquad \text{Eqn 3.19}$$

where, R_o is the initial rate of pesticide degradation (mg P L^{-1} min^{-1}); k is the rate constant; P_o, HP_o and Fe_o are the initial simazine, peroxide and Fe(II) concentrations, respectively (mg/L)

In linearized form, the rate equation can be written as follows

$$\text{Ln } R_o = \text{Ln } k + \alpha \text{ Ln } P_o + \beta \text{ Ln } HP_o + \gamma \text{ Ln } Fe_o \qquad \text{Eqn 3.20}$$

The coefficients of eqn 3.17 were determined by correlation with the experimental data.

CHAPTER FOUR
MATERIALS AND METHODS

4.1 Diuron Removal by the AOPs

4.1.1 Chemicals

High purity grade (99.4%) of diuron was purchased from Riedel-de-Haen (Germany). Physico-chemical characteristics of diuron are summarized in Table 1.1. Chromatographic grade acetonitrile and analytical grade hydrogen peroxide solution (30% (w/w)), H_2SO_4 (98–99%) and NaOH were all purchased from Merck (Germany). Ferrous sulphate ($FeSO_4 \cdot 7H_2O$) used as source of Fe(II) in the Fenton and photo-Fenton treatment, was analytical grade and purchased from Merck. Concentrated stock solution of Fe(II) (5000 mg/L) was prepared for further dilution to obtain solutions of desired concentrations. Fe(II) stock solution was stored in dark to prevent oxidation of Fe(II). pH adjustments were done by using either sodium hydroxide or sulfuric acid solutions. All other chemicals were of analytical grade and used without any further purification. Water used for chemical solutions was purified using a Mili-Q system (milipore filtration).

4.1.2 Experimental Procedure

Fenton's reagent experiments were carried out at room temperature (23-25^{o}C) using different diuron, hydrogen peroxide and ferrous ion doses at the natural pH of pesticide solution (pH = 4.2) which is suitable for Fenton treatment (Hsueh *et al.*, 2005). Temperature changes during reactions were negligible. Predetermined amounts of oxidant (1.5-340 mg/L H_2O_2) and the catalyst (0.25-56 mg/L Fe(II)) were injected to the agitated reactors (150 rpm) containing diuron solution (1-25 mg/L) at the beginning of each experiment. The iron salt was mixed well with diuron solution before the addition of hydrogen peroxide solution. Samples withdrawn from the reactor at certain time intervals were analyzed immediately to avoid further reactions. Samples (30 ml) of raw and treated pesticide solutions were analyzed for pesticide and TOC contents. pH and conductivity levels were also recorded.

Photo-Fenton experiments were carried out at room temperature (23 ± 2 ^oC) using different hydrogen peroxide and ferrous ion doses at the natural pH of pesticide solution (pH 4.2) which is suitable for photo-Fenton treatment (Hsueh *et al.*, 2005). Pesticide solution with desired concentration of the pesticide (1-25 mg/L) was placed in the reactor and predetermined amounts of oxidant (1.5-340 mg/L H_2O_2) and the catalyst (0.25-56 mg/L Fe (II)) were injected to the reactor at the beginning of each experiment. In batch experiments, Fe(II) (catalyst) was mixed well with wastewater before the addition of hydrogen peroxide (oxidant). The experiments were started by addition of the H_2O_2 to the reactor. Samples withdrawn from the reactor at certain time intervals were analyzed immediately to avoid further reactions. Samples (30 ml) of raw and treated pesticide solutions were analyzed for pesticide and TOC contents. pH and conductivity levels were also recorded.

In batch peroxone oxidation experiments, the pH was manually adjusted to desired level (3-11) using dilute sulfuric acid or sodium hydroxide then, predetermined amounts of oxidant (0-340 mg/L H_2O_2) were injected to the reactor at the beginning of each experiment. The experiments were started by turning the ozone generator on. Samples withdrawn from the reactor at certain time intervals were analyzed immediately to avoid further reaction. Samples (30 ml) of raw and treated pesticide solutions were analyzed for pesticide and organic content (TOC, total organic carbon). pH variations were recorded throughout the experiments. All experiments were carried out in batch mode.

4.1.3 Experimental Set-up

4.1.3.1 Configuration of UV Reactor

Figure 4.1 depicts a schematic diagram of the laboratory-scale photochemical reactor used in UV oxidations. All batch photo-oxidation experiments were performed in the completely mixed cylindrical photo-reactor made of glass with a total volume of 2.2 liter. The reactor was covered with an aluminum foil to avoid any light leakage to the outside. The reactor was placed on a magnetic stirrer and contained inlets for feeding the reactants, and ports for sample removal and temperature measurements. The UV irradiation source was a 16 watt low-pressure mercury vapor lamp (maximum emission at 254 nm) placed in a quartz tube. The intensity of the UV radiation was measured using the ferrioxalate actinometry method and estimated to be 4.98*10^{-6} einstein/s (mole of photons/second). The lamp was surrounded with a water-cooling jacket to remove the heat produced by the lamp and to maintain a constant temperature. The lamp tube was immersed in aqueous solution.

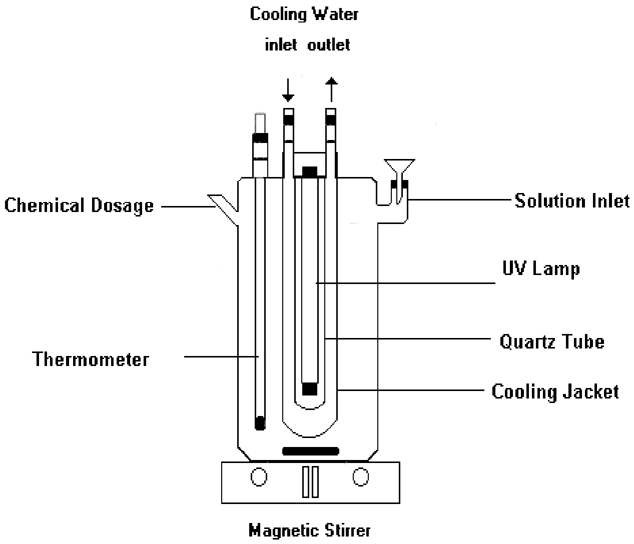

Figure 4.1 A schematic diagram of experimental set-up for the UV reactor.

4.1.3.2 Configuration of Ozone reactor

A schematic diagram of the laboratory-scale ozone reactor is depicted in Figure 4.2. Ozone system used in experimental studies has five basic components: a gas feed system (pure oxygen tube as a source of ozone), an ozone generator; ozone reactor, ozone monitor (to measure output of gaseous ozone) and ozone destruction unit (to kill excess amount of ozone before release air, O_3 is converted to O_2). The reactor was made of pyrex glass with a total reactor volume of 3 liter. Ozone was produced by a corona discharge of OZO 3VTT model ozone generator with a maximum capacity of 15 g/h. The ozone produced from oxygen with a purity of 99.5% was bubbled through the reactor with different rates using a diffuser of diameter 15 mm. At the top of ozone reactor, three port is located. Two ports are used for the ozone gaseous inlet and outlet. Also, one port of the bottom of the reactor is used for withdrawing samples. An ozone monitor (Eco sensors) measured the concentration of ozone in the effluent of the ozone reactor. A catalytic ozone-destruction unit destroyed excess ozone leaving the reactor.

In order to determine and calibrate exact O_3 input and output rates, some experiments were carried out. In separate runs, two separate gas washing bottles containing 2% KI solution was connected in series to collect all off-gas ozone passing through the wastewater and to determine off gas ozone concentration. Another single gas washing bottle with 20% KI was employed for measuring the (input) ozone concentration in the feed gas. The introduced ozone feed and effluent rates were measured by the standard potassium iodide absorption method (APHA,1992).

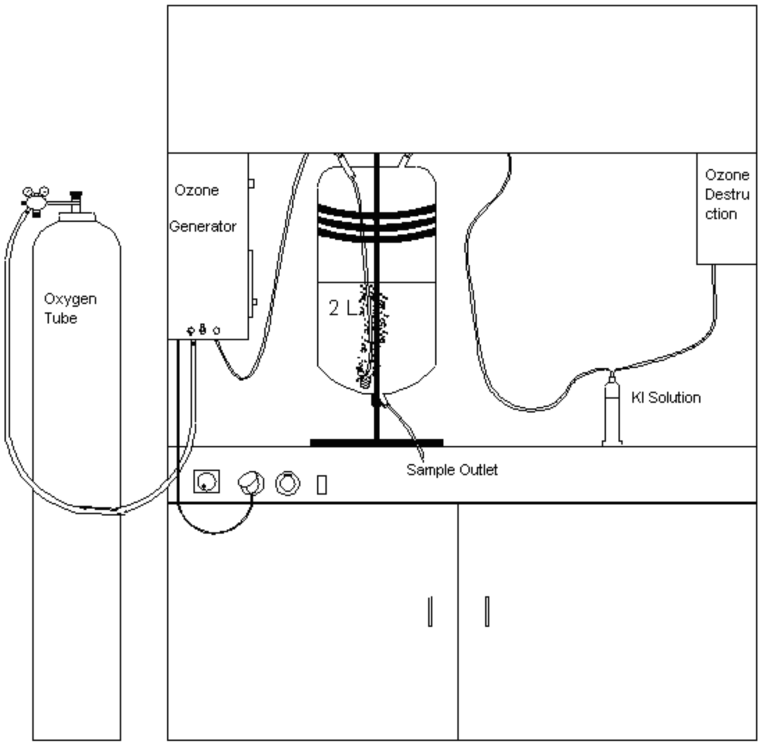

Figure 4.2 A schematic diagram of the laboratory-scale ozone reactor.

4.1.4 Analytical Methods

Samples were removed from the jar tests, UV and ozone reactors at pre-determined time intervals for immediate analysis of pesticide and TOC. The temperature of the solution was kept constant at 25 ± 2°C throughout all experiments.

Diuron was analyzed using an HPLC (Agilent 1100 model, USA), equipped with a UV-detector and a C18 column. The mobile phase composition was H_2O/acetonitrile with a ratio 40/60. The UV-detection was operated at 214 nm. The flow rate was 1 mL min^{-1} and the injection volume was 20 μL. Under these conditions, the retention time for diuron was 4 min. The calibration curve for diuron was constructed using the peak areas of the standard samples and were analyzed under the same conditions as that of the experimental samples. Stock solution of diuron was prepared by dissolving the proper amount of the herbicide in 1 liter water and was stored properly by protecting from the light. The calibration curve was prepared for concentrations between 30 mg/L and 0.0015 mg/L diuron with a linearity of $R^2= 0.999$.

A pH meter (WTW Scientific, Germany) was used to monitor pH. A DOHRMAN DC 190 TOC Analyzer (USA) was used to determine the total organic carbon (TOC) content of the samples. For the TOC measurements, potassium phthalate solution was used as the calibration standard with the concentrations 0, 5, 10, 15, 20 and 25 mg/L.

4.2 Simazine Removal by the AOPs

4.2.1 Chemicals

Simazine of high purity (99.4%) grade was purchased from Riedel-de-Haen (Germany). Chromatographic grade acetonitrile and analytical grade Ferrous ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide solution (30% (w/w)), H_2SO_4 (98–99%) and NaOH were all purchased from Merck (Germany). Concentrated stock solution of Fe(II) (3000 mg/L) was prepared for further dilution to obtain solutions of desired concentrations and was stored at dark. pH adjustments were done by using either sodium hydroxide or sulfuric acid solutions. All other chemicals were of analytical grade and used without any further purification. Water used for chemical solutions was purified using a Mili-Q system (milipore filtration).

4.2.2 Experimental Procedure

Fenton's reagent experiments were carried out at room temperature (23 ± 2 ^oC) using different H_2O_2 and Fe(II) doses at pH= 3.5 which is reported to be the most suitable pH for Fenton treatment (Hsueh *et al.,* 2005). Pesticide solution with desired concentration of the pesticide (0.5-5 mg/L) was placed in the reactor and predetermined amounts of oxidant (10-100 mg/L H_2O_2) and the catalyst (0-30 mg/L Fe (II)) were injected to the reactor at the beginning of each experiment. In batch experiments, Fe(II) (catalyst) was mixed well with wastewater before the addition of hydrogen peroxide (oxidant). The experiments were started by addition of the H_2O_2 to the reactor. Samples withdrawn from the reactor at certain time intervals were analyzed immediately to avoid further reaction. Samples (20 mL) of raw and treated pesticide solutions were analyzed for pesticide and TOC concentrations. pH levels were also determined for every sample.

Photo-Fenton experiments were carried out at room temperature (23 ± 2^oC) using different hydrogen peroxide and ferrous ion doses at the pH 3 which was reported to be a suitable pH for photo-Fenton treatment (Hsueh *et al.,* 2005). Pesticide solution with desired concentration of the pesticide (0.5-5 mg/L) was placed in the reactor and predetermined amounts of oxidant (10-100 mg/L H_2O_2) and the catalyst (0-30 mg/L Fe(II)) were injected to the reactor at the beginning of each experiment. The iron salt (catalyst) was mixed well with pesticide solution before the addition of hydrogen peroxide (oxidant). The experiments were started by addition of H_2O_2 to the reactor.

In peroxone oxidation treatments, the pH was manually adjusted to desired level (3-11) using dilute sulfuric acid or sodium hydroxide then, predetermined amounts of oxidant (0-100 mg/L H_2O_2) were injected to the reactor at the beginning of each experiment. The experiments were started by turning the the ozone generator on and when the oxidant added. Samples withdrawn from the reactor at certain time intervals were analyzed immediately to avoid further reaction. Samples (30 ml) of raw and treated pesticide solutions were analyzed for pesticide and organic content (total organic carbon) removals. pH level was also recorded. All experiments were carried out in batch mode.

4.2.3 Experimental Set-up

4.2.3.1 Configuration of UV Reactor

Figure 4.1 depicts a schematic diagram of the laboratory-scale photochemical reactor used in UV oxidations.

4.2.3.2 Configuration of Ozone reactor

A schematic diagram of the laboratory-scale ozone reactor is depicted in Figure 4.2.

4.2.4 Analytical Methods

Samples were removed from the jar tests, UV and ozone reactors at pre-determined time intervals for immediate analysis of pesticide, TOC. The temperature of the solution was kept constant at $25 \pm 2^{\circ}C$ throughout all experiments.

Simazine was analyzed using an HPLC (Agilent 1100 model), equipped with a UV-detector and a C18 column. The mobile phase composition was H_2O/acetonitrile with a ratio of 40/60. The UV-detection was operated at 214 nm. The flow rate was 1 mL min^{-1} and the injection volume was 20 μL. Under these conditions, the retention time for simazine was 4 min. Calibration curve for simazine was constructed using the peak areas of the standard samples under the same conditions as that of the experimental samples. Stock solution of simazine was prepared by dissolving the proper amount of the herbicide in 1 liter water and was stored in dark to protect from the light. Simazine calibration curve was prepared for concentrations between 0.0015 and 5 mg/L with a correlation coefficient of R^2= 0.9997. Higher concentrations of simazine could not be prepared due to low solubility of simazine

A Shimadzu TOC Analyzer was used to determine the total organic carbon (TOC) content of the samples. Samples were diluted properly before analysis. Potassium phthalate solutions with the concentrations between 0 and 5 mg/L were used as calibration standards for the TOC analyzer. A pH meter (WTW, Germany) was used to monitor pH during reaction period.

4.3 Pulp and Paper Wastewater Treatment by the AOPs

4.3.1 Chemicals

Ferrous sulphate ($FeSO_4.7H_2O$, Merck) was used as source of Fe(II) in the Fenton and photo-Fenton treatment. Fe(II) stock solution (1000 mg/L) was used for preparation of Fe(II) solutions of desired concentrations by dilution. Hydrogen peroxide solution (35%, w/w, Merck) was diluted with deionized water before treatment. The titanium dioxide (Degussa P-25) was composed of 80% anatase and 20% rutile with a BET surface area of 50 m^2 g^{-1} and average particle size of 30 nm. The pH of aqueous solutions was adjusted using dilute (1%) sodium hydroxide or sulfuric acid solutions. All solutions were prepared by using distilled water.

4.3.2 Reactor Configurations

A schematic diagram of the laboratory-scale ozone reactor is depicted in Figure 4.2. Figure 4.1 depicts a schematic diagram of the laboratory-scale photochemical reactor used in UV oxidations.

4.3.3 Experimental Procedure

Chemical oxidation with H_2O_2 was carried out by using 50 mM H_2O_2 at a pH of 11. The conventional jar tests were started by adding varying amounts of H_2O_2 to pH-adjusted wastewater samples. After pH adjustment and oxidant addition, wastewater was mixed rapidly for 30 min at 200 rpm. Samples were withdrawn for analysis at the end of the mixing period.

Fenton’s reagent experiments were carried out at room temperature using different hydrogen peroxide and ferrous ion concentrations at different pH values in order to determine the optimum conditions for the highest TOC and color removals. Desired amounts of hydrogen peroxide and Fe(II) were added to pH-adjusted wastewater samples. After fast mixing for five minutes at 200 rpm and slow mixing for 30 min at 25 rpm, one-hour sedimentation was applied. The supernatant was removed and pH was adjusted to 10 with the addition of 10% $Ca(OH)_2$ solution. The samples from the supernatant were analyzed for TOC, color and AOX contents after 4 hours of standing period.

In advanced oxidation treatments with UV and ozone, the pH was manually adjusted to desired level using dilute sulfuric acid or sodium hydroxide, then predetermined amounts of oxidants (H_2O_2 or/and Fe(II)) were injected to the reactor at the beginning of each experiment. For experiments using UV/H_2O_2 and peroxone treatment, desired amounts of hydrogen peroxide was injected into the reactor at the beginning of each experiment. In photo-Fenton treatment, the pH of the solution was adjusted to acidic conditions by the addition of dilute H_2SO_4 solution before startup, and then a desired amount of iron salt was added. The iron salt was mixed well with wastewater before the addition of hydrogen peroxide solution. The experiments were started by turning the UV lamp and the ozone generator on and when the oxidant added. All experiments were carried out in batch mode.

Chemical treatment with TiO_2 was carried out by using different TiO_2 doses at a pH of 11. The conventional jar tests were started by adding different amounts of TiO_2 to pH-adjusted wastewater samples. After pH adjustment and chemical addition, wastewater was mixed rapidly for 60 min at 45 rpm. Samples were withdrawn for analysis at the end of the mixing period.

TiO_2/H_2O_2 experiments were carried out at room temperature using different hydrogen peroxide and a constant titanium dioxide concentration of 0.75 g/L at a constant pH value of 7. Desired amounts of hydrogen peroxide and titanium dioxide were added to pH-adjusted wastewater samples. After pH adjustment and oxidant/catalyst addition, wastewater was mixed rapidly for 60 min at 45 rpm. Samples were withdrawn for analysis at the end of the mixing period.

In advanced oxidation treatments with UV, the pH was manually adjusted to a desired level using dilute sulfuric acid or sodium hydroxide, then predetermined amounts of chemicals (H_2O_2 or/and TiO_2) were injected to the reactor at the beginning of each experiment. For experiments, using UV/TiO_2 and UV/TiO_2/H_2O_2 treatment desired amounts of titanium dioxide was injected into the reactor after pH adjustments at the beginning of each experiment. Titanium dioxide was mixed well with wastewater before the addition of hydrogen peroxide solution. The experiments were started by turning the UV lamp on after the addition of the reagents. All experiments were carried out in batch mode.

4.3.4 Analytical Methods

Samples were removed from the jar test apparatus, UV and ozone reactors at pre-determined time intervals for immediate analysis of color, TOC, toxicity and AOX. The temperature of the solution was kept constant at 25 ± 2°C throughout all experiments. A spectrophotometer (Novaspec II, Pharmacia Biotech) was used for color measurements at 450 nm at which the absorbance was maximum. A bench scale pH meter (NEL pH meter 890) was used for pH measurements. TOC analyses were done using a DOHRMAN DC 190 TOC Analyzer. AOX contents were determined by an AOX MT 20 TOX analyzer after enrichment by activated carbon. A conductivity meter (YSI 33) was used for conductivity measurements. In order to decompose residual H_2O_2 to avoid interference with the color and toxicity measurement, the samples containing H_2O_2 were treated with MnO_2 powder and were centrifuged and filtered through 0.45μm milipore membranes to remove MnO_2.

Resazurin reduction method was used to determine the toxicity of the feed and effluent wastewater (Strotmann *et al.,* 1993; Brouwer, 1991). The test organisms (washed activated sludge) (The activated sludge culture obtained from PAK MAYA Bakers Yeast Company wastewater treatment plant in Izmir, Turkey was used as the seed culture) to be subjected to the toxic feed and effluent wastewater were cultivated on nutrient broth and were used for determination of the toxicity of wastewater samples. The test cultures were transferred every 2 days to fresh medium to keep the sludge age constant during the course of toxicity measurements. In the presence of active bacterial culture, because of dehydrogenase enzyme activity, resazurin changes color from blue to pink forming the reduced compound resorufin. Therefore, the color of the resazurin solution is an indicator of bacterial activity. A spectrometer (Novaspec II, Pharmacia Biotech) was used at 610 nm for determination of the color intensity of the resazurin added samples. Percent toxicity removal was calculated by using the following equation:

$$E = 1 - (TOX_e / TOX_o) \qquad \text{Eqn 4.1}$$

where TOX_e and TOX_o are the toxicities of the effluent and the feed wastewaters which were determined with respect to the test organisms dehydrogenase activity unexposed to pesticides.

4.4 Box-Behnken Statistical Experiment Design

Box Behnken statistical experiment design and the response surface methodology (Abbasi *et al.,* 1987; Charles *et al.,* 1999) were used to investigate the effects of the three independent variables on the response function and to determine the optimal conditions maximizing the percent removals of pesticide, TOC and AOX. The optimization procedure was described in section 3.3 .

CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 Advanced Oxidation of Pesticides

5.1.1 Diuron Removal by the AOPs

In this part of the thesis, Fenton, photo-Fenton and peroxone oxidations of diuron containing water was investigated by using Box-Behnken experimental design. Diuron, considered as a highly toxic, persistent priority substance by the EU (European Commission, 2001) and one of the most commonly used herbicides, belongs to the family of halogenophenylureas.

5.1.1.1 Fenton Oxidation

In the Box-Behnken design, the independent variables were the dose of pesticide (X_1=1-25 mg/L), hydrogen peroxide (X_2=1.5-340 mg/L), and ferrous ion (X_3=0.25-56 mg/L). The low, center and high levels of each variable are designated as -1, 0, and +1, respectively as shown in Table 5.1. The dependent variables (or objective functions) were the percent pesticide (Y_1) and TOC (Y_2) removals. The experimental conditions of the Box-Behnken experiment design are presented in Table 5.1. The center point (0,0,0) was repeated three times and almost the same results were obtained indicating the reproducibility of the data. Observed and predicted percent removals for diuron and TOC are compared in Table 5.2.

Table 5.1 The experimental conditions of the Box-Behnken experiment design for Fenton and photo-Fenton oxidation

Run No	**Actual Coded and Levels**		
	X_1 Diuron, (mg/L)	**X_2 H_2O_2, (mg/L)**	**X_3 Fe (II), (mg/L)**
1	25 (+1)	170.75 (0)	56 (+1)
2	25 (+1)	170.75 (0)	0.25 (-1)
3	13 (0)	1.5 (-1)	0.25 (-1)
4	13 (0)	170.75 (0)	28.125 (0)
5	13 (0)	340 (+1)	56 (+1)
6	13 (0)	170.75 (0)	28.125 (0)
7	13 (0)	170.75 (0)	28.125 (0)
8	13 (0)	1.5 (-1)	56 (+1)
9	13 (0)	340 (+1)	0.25 (-1)
10	1 (-1)	1.5 (-1)	28.125 (0)
11	25 (+1)	340 (+1)	28.125 (0)
12	25 (+1)	1.5 (-1)	28.125 (0)
13	1 (-1)	340 (+1)	28.125 (0)
14	1 (-1)	170.75 (0)	56 (+1)
15	1 (-1)	170.75 (0)	0.25 (-1)

Table 5.2 Observed and predicted percent removals for the response functions (Y) for Fenton Oxidation

Run No	**Predicted percent removals**		**Observed percent removals**	
	Y_1 Pesticide	**Y_2 TOC**	**Y_1 Pesticide**	**Y_2 TOC**
1	68.9	27.18	66.8	27.88
2	22.04	15.79	25.6	14.78
3	14.42	43.99	11.59	44.48
4	78	37.21	78	37.21
5	92.17	59.32	95	58.83
6	78	37.21	78	37.21
7	78	37.21	78	37.21
8	28.16	29.59	30.99	28.36
9	18.21	28.70	15.38	29.93
10	80.68	54.48	81.41	54.7
11	99.23	34.17	98.5	33.95
12	23.21	20.77	22.48	21.29
13	72.48	55.52	73.21	55
14	81.25	51.43	77.69	52.44
15	40.42	46.61	42.52	45.91

The coefficients of the response functions for different dependent variables were determined by correlating the experimental data with the response functions by using a Stat-Ease regression program. Different response functions with the determined coefficients are presented by Eqns 5.1 and 5.2. The model F-value of 102.66 implies the model is significant for pesticide removal. P value of < 0.05 for any factor in the analysis of variance (ANOVA) indicates a significant effect of the corresponding variable on the response. In this case X_1, X_2, X_3, X_1X_2, X_2X_3, X_2^2, X_3^2 are significant model terms. The ANOVA tests for the other response functions gave similar results. The results of analysis of variance (ANOVA) are also presented in Table A. 1 and Table A. 2 indicating the fact that that the predictability of the model is within the

95% confidence interval. The response functions for percent pesticide (Y_1) and percent TOC (Y_2) with the determined coefficients have the following forms:

$$Y_1 = 50.019 - 3.062\ X_1 + 0.019\ X_2 + 2.192\ X_3 + 0.010\ X_1X_2 - 0.0045\ X_1X_3 + 0.0032\ X_2X_3 + 0.0202\ X_1^2 - 0.00042\ X_2^2 - 0.0357\ X_3^2 \qquad \text{Eqn 5.1}$$

$$Y_2 = 63.613 - 1.444\ X_1 - 0.120\ X_2 - 0.225\ X_3 + 0.0015\ X_1X_2 + 0.0049\ X_1X_3 + 0.0024\ X_2X_3 - 0.0039\ X_1^2 + 0.00016\ X_2^2 - 1.797\ X_3^2 \qquad \text{Eqn 5.2}$$

5.1.1.1.1 Disappearance of Diuron. Response functions with determined coefficients were used to estimate variations of response functions with the independent variables under different conditions. Figure 5.1 shows the effect of initial H_2O_2 concentration on percent diuron removal at different diuron concentrations after 15 minutes of reaction time when Fe(II) was 15 mg/L. As expected, percent diuron degradation increased with increasing initial hydrogen peroxide concentration at high diuron concentrations above 10 mg/L where the H_2O_2 concentration was the limiting factor.

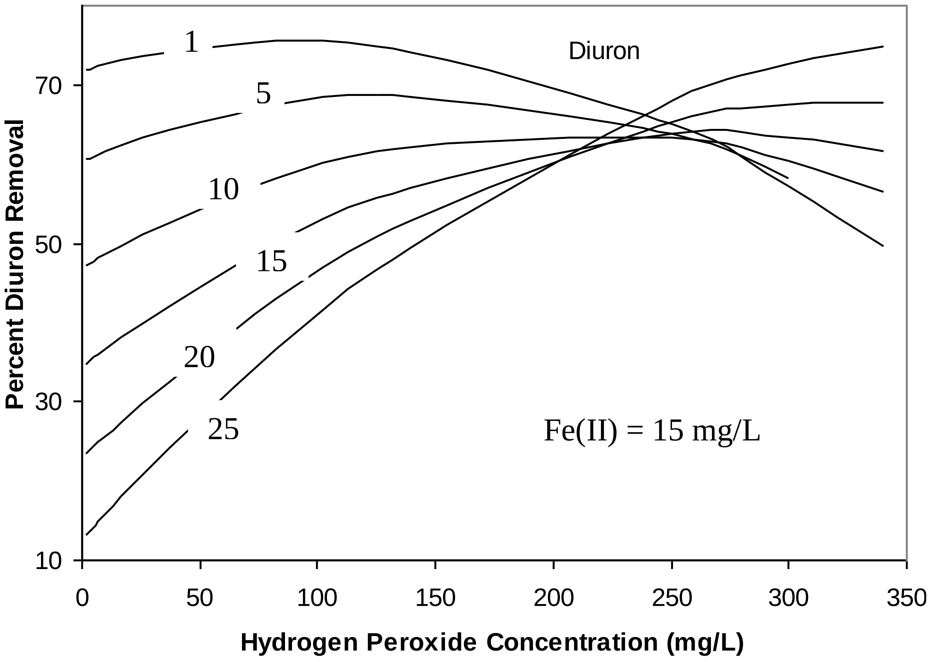

Figure 5.1 Variation of percent diuron removal with peroxide concentration at different initial diuron concentrations at the end of 15 min reaction time. Fe(II) = 15 mg/L.

However, at low diuron concentrations below 10 mg/L since H_2O_2 requirement was low, diuron removals decreased with increasing H_2O_2 concentrations above 150 mg/L peroxide dose due to inhibition caused by high concentrations of H_2O_2. At high hydrogen peroxide concentrations probably hydrogen peroxide served as a free-radical scavenger for itself reducing the hydroxyl radical concentration.

$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$ Eqn 5.3

$OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$ Eqn 5.4

In agreement with Glaze *et al.*, (1995) and Beltran *et al.*, (1996) a reduction in pesticide removal was observed at high H_2O_2 concentrations indicating the adverse effects of excess H_2O_2. At constant diuron and Fe(II) doses of 13 and 15 mg/L and variable H_2O_2 doses of 1.5, 170.75 and 340 mg/L percent pesticide removals were

40.7, 60.7 and 60.7%, respectively. At low diuron dose of 1 mg/L, the optimal H_2O_2/Fe(II)/diuron dose yielding the highest diuron removal was 50/15/1 mg/L, while at a high diuron concentration of 25 mg/L this ratio was 340/15/25 mg/L.

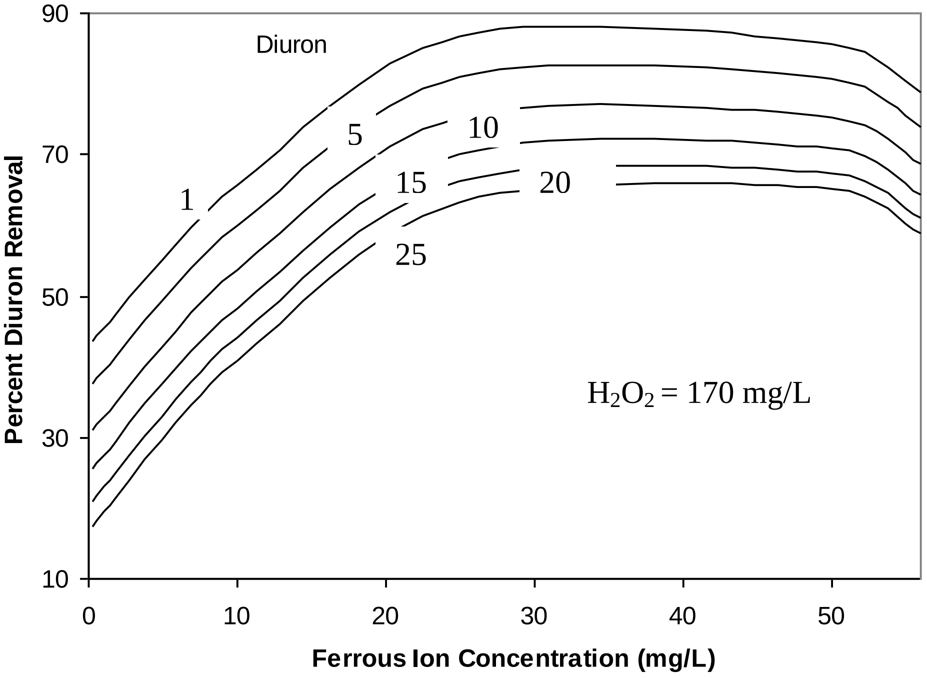

Figure 5.2 Variation of percent pesticide removals with Fe(II) dose at different initial diuron doses at the end of 15 min reaction time.

Effects of Fe(II) and diuron concentrations on percent diuron oxidation by the Fenton's reagent are depicted in Figure 5.2 at a H_2O_2 concentration of 170 mg/L. Percent pesticide removal increased with increasing Fe(II) concentrations for all initial pesticide levels up to 30 mg/L Fe(II) and leveled off for Fe(II) concentrations between 30 and 50 mg/L. Further increases in Fe(II) concentrations resulted in decreases in percent diuron removal probably due to adverse effects of high Fe(II) levels. Increases in pesticide concentrations yielded decreasing pesticide removals at all Fe(II) concentrations indicating limitations by pesticide concentration at high initial H_2O_2 concentrations. Percent pesticide removals were 60.7, 82 and 72% with an initial pesticide dose of 13 mg/L and Fe(II) doses of 15, 40 and 56 mg/L, respectively at a H_2O_2 dose of 170 mg/L. In this case, a Fe(II) dose of nearly 40 mg/L resulted in maximum degradation, decreasing very slightly above and below this value because of limitations or inhibitions by Fe(II). These results are in agreement with the literature reports, where a beneficial effect of increasing Fe(II) was observed in photo-degradation of pesticides (Krutzler *et al.,* 1999; Torrades *et al.,* 2003). Complete degradation of diuron was accomplished at hydrogen peroxide dose of 265 mg/L and Fe(II) concentrations above 40 mg/L after 15 minutes reaction time when diuron dose was 25 mg/L, while low concentrations of Fe(II) did not result in complete diuron degradation.

Apparently the use of high oxidant and catalyst doses inhibited the degradation of pesticides due to formation of radical scavengers. The ANOVA analysis (Table A. 1) indicated that all three variables pesticide, H_2O_2 and Fe(II) doses and their interactions (X_1, X_2, X_3, X_1X_2, X_2X_3, X_2^2, X_3^2) were significant and played important roles in diuron oxidation by the Fenton's reagent.

5.1.1.1.2 Total Organic Carbon Removal: Mineralization of Diuron. Overall mineralization of diuron using oxygen as oxidizing agent can be written as follows:

$$C_9H_{10}Cl_2N_2O + 13\ O_2 \rightarrow 2\ HNO_3 + 2\ HCl + 9\ CO_2 + 3\ H_2O \qquad \text{Eqn 5.5}$$

Complete mineralization of diuron was not achieved after 240 minutes of reaction time although diuron disappeared after 15 minutes. This difference indicated formation of intermediate products during the oxidation reaction, which were not degraded by hydroxyl radicals. Aniline and 3,4-dichloroaniline are the two major degradation intermediates reported in the literature (*Salvestrini et al.,* 2002; Simon *et al.,* 1998). Degradation of diuron by photo-induced Fe(III) in aqueous medium was reported earlier with the formation of 3,4-dichloroaniline as the main degradation product (Mazellier *et al.,* 1997). Formation of this product was also observed by Malato *et al.*, (2003) using solar photo-Fenton reaction and TiO_2 photo-catalysis.

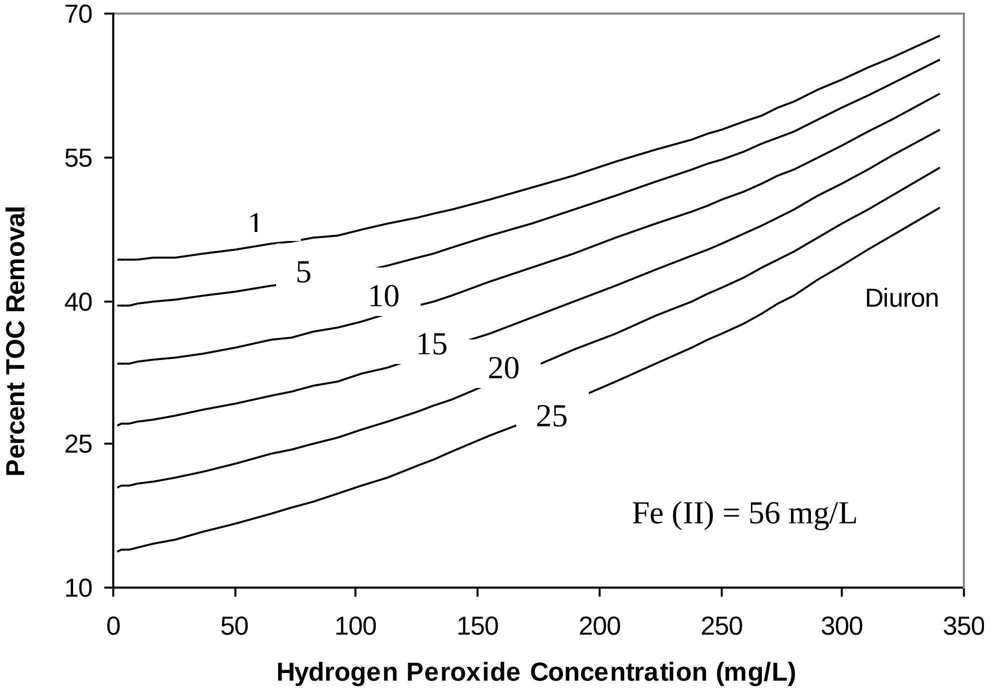

Figure 5.3 Variations of percent TOC removals with hydrogen peroxide concentration at different initial diuron doses at the end of 240 min reaction time.

As shown in Figure 5.3, percent mineralization of diuron or total organic carbon (TOC) removal increased with H_2O_2 concentration at all diuron concentrations. However, percent TOC removal decreased with increasing diuron concentration at all H_2O_2 concentrations yielding the highest diuron removal at the lowest diuron concentration due to limitations by Fe(II) and H_2O_2 concentrations. The highest percent TOC removal (68%) was obtained with 1 mg/L diuron at 350 mg/L H_2O_2 and 56 mg/L Fe(II) concentrations. High concentrations of H_2O_2 and Fe(II) were required for high degree of TOC removal at high pesticide concentrations.

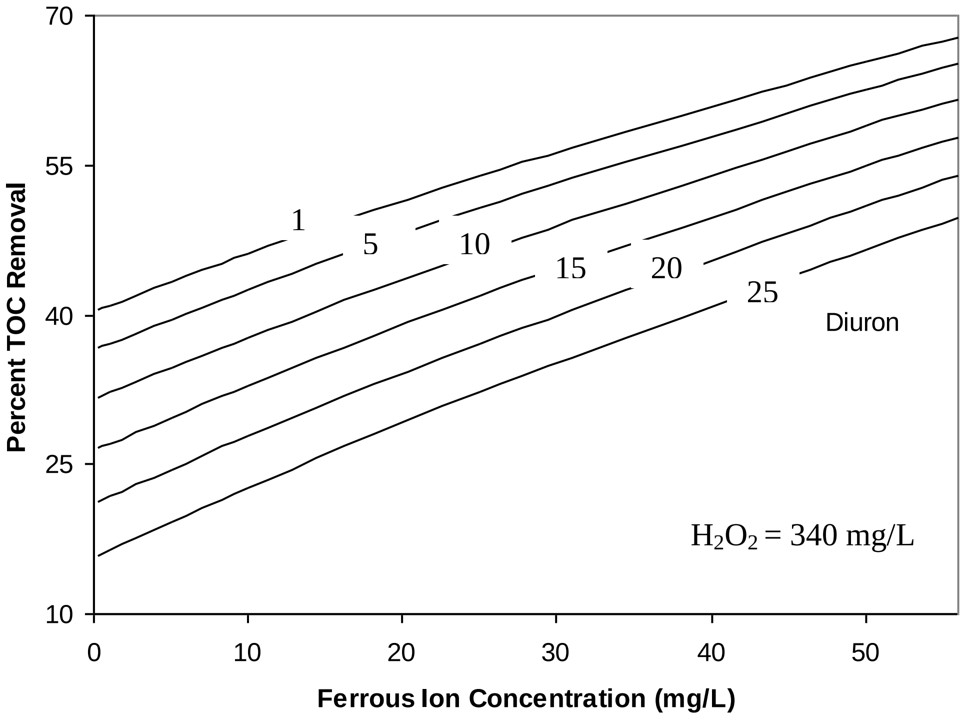

Figure 5.4 Variation of percent TOC removals with Fe(II) concentration at different diuron concentrations at the end of 240 min reaction time.

Initial pesticide concentration was the most important parameter affecting the efficiency of pesticide removal by the Fenton oxidation. Mineralization efficiencies obtained at low pesticide concentrations were higher than those obtained at high pesticide concentrations. Figure 5.4 depicts variations of percent TOC removal with Fe(II) concentration at different diuron concentrations. Percent TOC removal increased with increasing Fe(II) and decreasing diuron concentrations. When diuron concentration was 25 mg/L, percent TOC removals were 16, 34 and 49%, respectively, at Fe(II) doses of 1, 28 and 56 mg/L at a hydrogen peroxide dose of 340 mg/L. The ANOVA analysis (Table A. 2) indicated that all three variables pesticide, H_2O_2 and Fe(II) doses and their interactions (X_1, X_2, X_3, X_1X_2, X_1X_3, X_2X_3, X_2^2) played important roles for the mineralization of pesticide or TOC removal. In a literature study, diuron was degraded by photo-Fenton treatment with a limited TOC removal of 70% after 60 min of irradiation indicating the formation of recalcitrant intermediates supporting our findings (Salvestrini *et al.*, 2002).

5.1.1.2 Photo-Fenton Oxidation

In the Box-Behnken design, the independent variables were the dose of pesticide (X_1=1-25 mg/L), hydrogen peroxide (X_2=1.5-340 mg/L), and ferrous ion (X_3= 0.25-56 mg/L). The intensity of UV light was constant throughout the experiments. The low, center and high levels of each variable are designated as -1, 0, and +1, respectively, respectively as shown in Table 5.1. The dependent variables (or objective functions) were the pesticide (Y_1) and TOC (Y_2) removals. The experimental conditions of the Box-Behnken experiment design are presented in Table 5.1. The center point (0, 0, 0) was repeated three times and the nearly same results were obtained indicating the reproducibility of the data. Observed and predicted percent removals for diuron and TOC are compared in Table 5.3.

Table 5.3 Observed and predicted percent removals for the response functions (Y) for photo-Fenton oxidation

Run No	**Predicted percent removals**		**Observed percent removals**	
	Y_1 Pesticide	**Y_2 TOC**	**Y_1 Pesticide**	**Y_2 TOC**
1	98.12	77.41	98.81	74.94
2	47.73	52.20	48.98	53.40
3	34.80	23.94	32.94	21.02
4	96.72	52.24	97.08	51.64
5	95.74	43.85	97.60	46.77
6	96.72	52.24	96.08	52.57
7	96.72	52.24	97.00	52.50
8	68.42	10.91	67.12	11.33
9	85.66	3.59	86.96	39.17
10	65.84	12.84	68.38	13.30
11	100.00	81.06	98.68	80.60
12	34.07	31.84	34.68	33.89
13	76.68	12.21	76.25	10.16
14	73.29	4.22	72.04	3.34
15	79.98	37.87	79.29	40.34

The coefficients of the response functions for different dependent variables were determined correlating the experimental data with the response functions by using a Stat-Ease regression program. Different response functions with the determined coefficients are presented by Eqns 5.7 and 5.8. The model F-value of 142.06 implies the model is significant for pesticide removal. P value of < 0.05 for any factor in analysis of variance (ANOVA) indicates a significant effect of the corresponding variable on the response. In this case X_2, X_3, X_1X_2, X_2X_3, X_1X_3, X_1^2, X_2^2, X_3^2 are significant model terms. The ANOVA tests for the other response functions gave similar results. The results of analysis of variance (ANOVA) are also presented in Table A. 3 and Table A. 4 indicating the fact that that the predictability of the model is at 95% confidence interval. The response functions for percent pesticide (Y_1) and percent TOC (Y_2) removals with the determined coefficients have the following forms:

The response functions for percent pesticide (Y_1) and percent TOC (Y_2) removals with the determined coefficients have the following forms:

$$Y_1 = 53.057 - 0.403\, X_1 + 0.244\, X_2 + 0.784\, X_3 + 0.007\, X_1X_2 + 0.043 X_1X_3 - 0.0012\, X_2X_3 - 0.082\, X_1^2 - 0.00054\, X_2^2 - 0.013\, X_3^2 \qquad \text{Eqn 5.6}$$

$$Y_2 = 26.820 - 0.054\, X_1 + 0.152\, X_2 - 0.290 X_3 + 0.006\, X_1X_2 + 0.044\, X_1X_3 + 0.0009\, X_2X_3 - 0.015\, X_1^2 - 0.00054\, X_2^2 - 0.009\, X_3^2 \qquad \text{Eqn 5.7}$$

5.1.1.2.1 Disappearance of Diuron. Response functions with determined coefficients were used to estimate variations of response functions with the independent variables under different conditions. Figure 5.5 depicts the effects of initial H_2O_2 concentration on percent diuron removal at different diuron concentrations after 15 minutes of reaction time when Fe(II) was 40 mg/L.

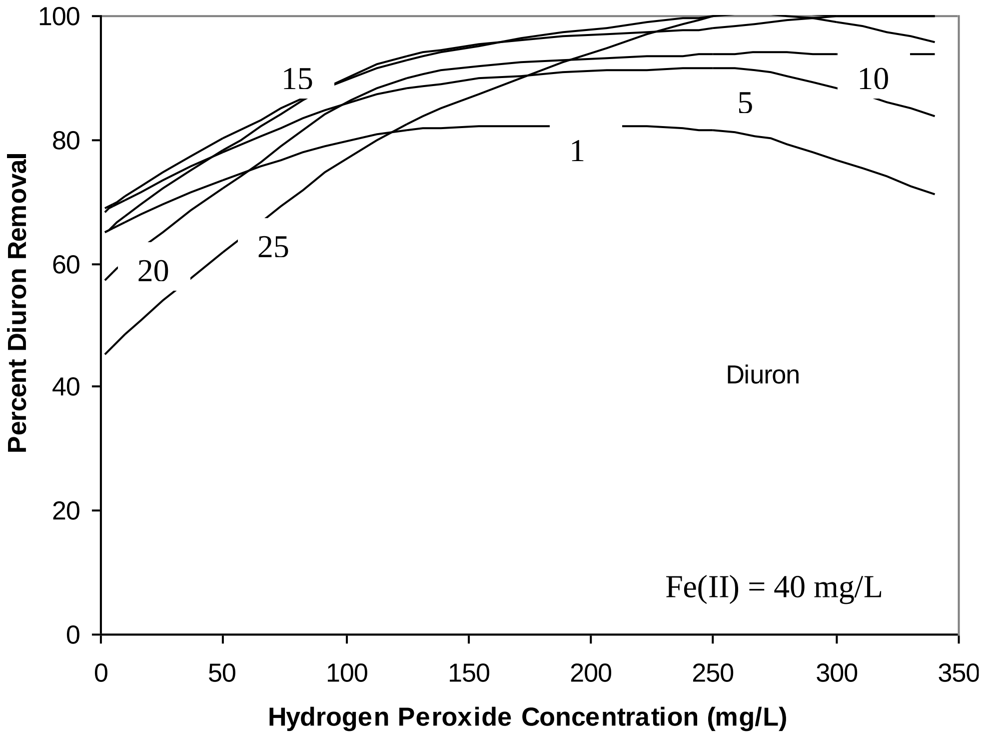

Figure 5.5 Variation of percent pesticide removal with H_2O_2 concentration at different diuron doses by the Photo-Fenton oxidation. Reaction time 15 min, Fe(II) = 40 mg/L.

As expected, percent diuron degradation increased with increasing initial hydrogen peroxide concentration for diuron concentrations above 15 mg/L. However, below this concentration, since H_2O_2 requirement was low, diuron removals decreased with increasing H_2O_2 concentrations above 150 mg/L due to inhibition caused by high concentrations of H_2O_2. Previous studies have reported that the increase of the H_2O_2 concentration improves the degradation of organic compounds in photo-Fenton reactions up to a certain limit due to additional production of $HO^{\bullet}$ radicals (Nogueira & Guimaraes 2000; Emilio *et al.,* 2002). However, adverse effects were also observed when excess concentrations of H_2O_2 are present (Ghaly *et al.,* 2001; Torrades *et al.,* 2003). This is due to the scavenging of $HO^{\bullet}$ by H_2O_2 and consequent formation of the less reactive radical $HO_2^{\bullet}$, as shown in Eqn 5.4 and Eqn 5.5. At constant diuron and Fe(II) doses of 13 and 38 mg/L and variable H_2O_2 doses of 1.5, 170.75 and 340 mg/L percent pesticide removals were 66.4, 99.3 and 100%, respectively. At low diuron dose of 1 mg/L, the optimal H_2O_2/Fe(II)/diuron dose yielding the highest diuron removal (87.7%) was

202/23/1 mg/L, while at a high diuron concentration of 25 mg/L this ratio was 230/38/25 mg/L yielding 100% pesticide removal.

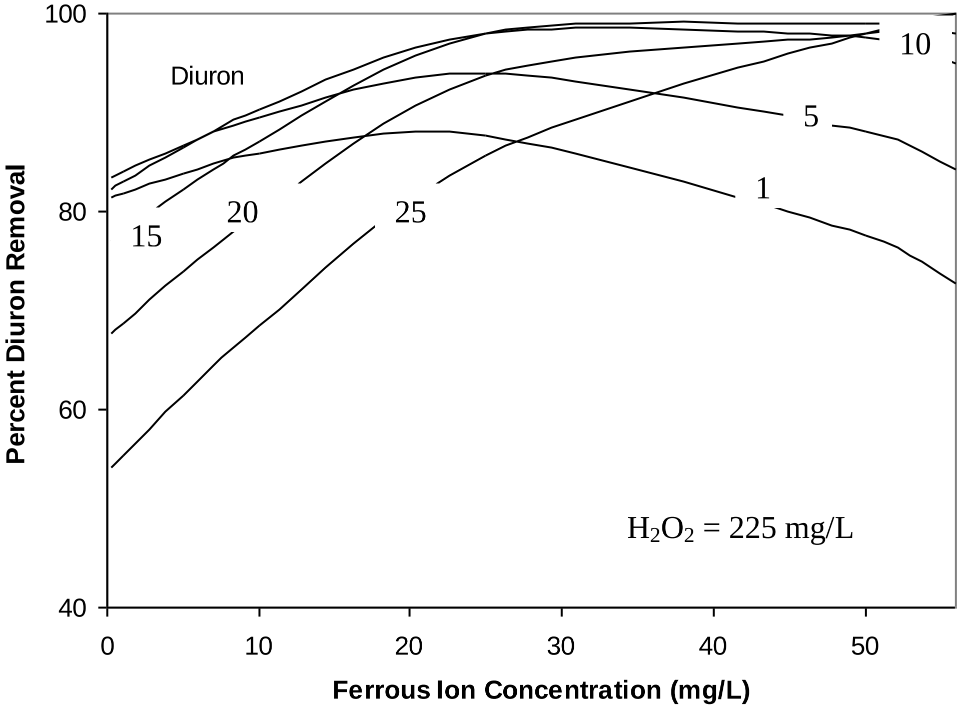

Figure 5.6 Variation of percent pesticide removals with Fe(II) dose at different initial diuron doses by the photo-Fenton oxidation. Reaction time 15 min, H_2O_2 = 225 mg/L

Effects of Fe(II) and diuron concentrations on percent diuron oxidation by photo-Fenton treatment are depicted in Figure 5.6 at a H_2O_2 concentration of 200 mg/L. Percent pesticide removal increased with increasing Fe(II) concentrations for diuron concentrations above 15 mg/L up to 45 mg/L Fe(II) and leveled off for Fe(II) concentrations between 45 ad 56 mg/L. For diuron concentrations below 10 mg/L, pesticide removal increased with increasing Fe(II) concentration up to 20 mg/L and then decreased with further increases in Fe(II) dose due to adverse effects of high Fe(II) doses such as inhibition effect on UV light. Optimal Fe(II) concentration was nearly 20 mg/L for diuron concentrations below 10 mg/L. Percent pesticide removals were 86.9, 100 and 100% with an initial pesticide dose of 13 mg/L and Fe(II) doses of 5, 28 and 56 mg/L, respectively at a H_2O_2 dose of 225 mg/L.

These results are in agreement with the literature reports, where a beneficial effect of increasing Fe(II) was observed in photo-degradation of pesticides (Krutzler *et al.,* 1999; Torrades *et al.,* 2003). However, high iron concentrations can also scavenge $OH^{\bullet}$ radicals, requiring a strict pH control to avoid precipitation of iron hydroxides. Moreover, penetration of light can be limited due to high absorption capacity of the solution hindering the generation of Fe(II) and consequently the degradation reaction. Complete degradation of diuron was accomplished at a hydrogen peroxide dose of 230 mg/L and Fe(II) concentrations above 38 mg/L after 15 minutes reaction time when diuron dose was 25 mg/L. At low concentrations of Fe(II), diuron degradation was low due to limitations by the Fe(II).

Apparently the use of high oxidant and catalyst doses inhibited the degradation of diuron at low diuron concentrations due to formation of radical scavengers. The ANOVA analysis (Table A. 3) indicated that all three variables pesticide, Fe(II) and H_2O_2 doses and independent variable interactions (X_1, X_2, X_1X_2, X_1X_3, X_2X_3, X_2^2, X_3^2) were significant and played important roles in diuron oxidation by the photo-Fenton treatment.

5.1.1.2.2 Total Organic Carbon Removal: Mineralization of Diuron. Overall mineralization of diuron using oxygen as oxidizing agent can be written in Eqn 5.6. Complete mineralization of diuron was not achieved after 240 minutes of reaction time although diuron disappeared after 15 minutes. This difference indicated formation of intermediate products during the oxidation reaction, which were not degraded by hydroxyl radicals. Aniline and 3, 4-dichloroaniline are the two major degradation intermediates reported in the literature (Salvestrini *et al.,* 2002; *Simon et al.,* 1998). Moreover, 3,4-dichloroaniline and 3,4-dichlorophenyl isocyanate were also proposed as the main degradation intermediates by Salvestrini *et al.,* (2002), but not observed in our studies.

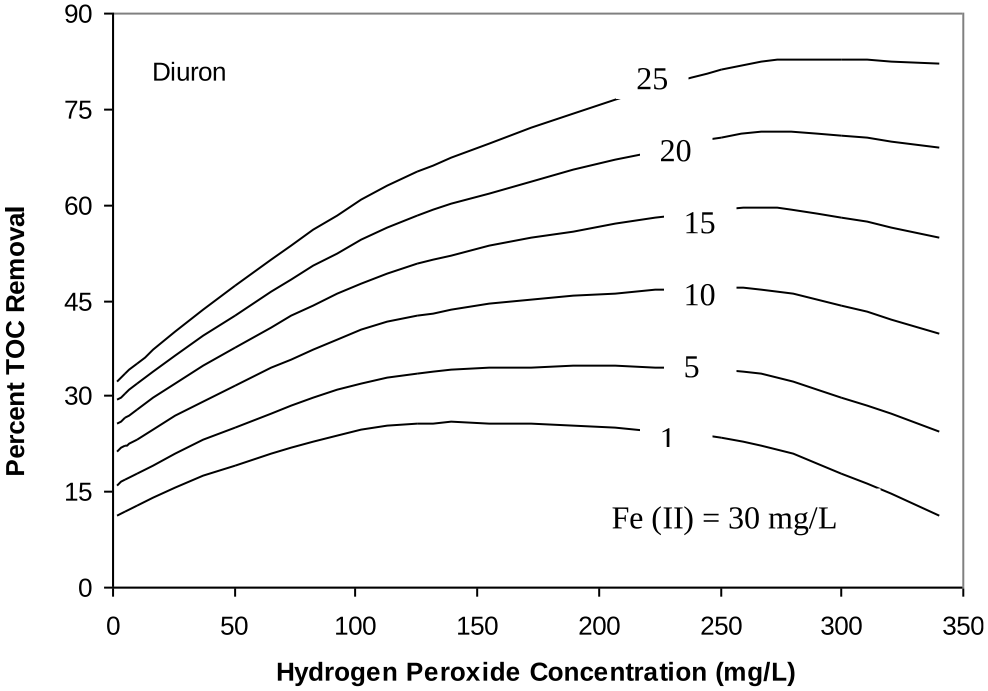

Figure 5.7 Variations of percent TOC removals with hydrogen peroxide concentration at different initial diuron doses by the photo-Fenton oxidation. Reaction time =240 min, Fe(II) = 30 mg/L.

As shown in Figure 5.7, percent mineralization of diuron or total organic carbon (TOC) removal increased with H_2O_2 concentrations up to 200 mg/L and then decreased with increasing H_2O_2 for low diuron concentrations below 15 mg/L. H_2O_2 concentrations above 250 mg/L resulted in decreases in percent TOC removal indicating adverse effects of high H_2O_2 concentrations. Percent TOC removal steadily increased with increasing diuron concentrations when Fe(II) was 30 mg/L indicating the fact that 30 mg/L Fe(II) was sufficient for degradation of diuron.

As expected, percent mineralization increased with increasing initial hydrogen peroxide concentration at high diuron concentrations above 15 mg/L. However, below this concentration, TOC removals decreased with increasing H_2O_2 concentrations above 200 mg/L. At high hydrogen peroxide concentrations, hydrogen peroxide served as a free-radical scavenger reducing the hydroxyl radical concentration. At constant diuron and Fe(II) doses of 25 and 56 mg/L and variable

H_2O_2 doses of 1.50, 170.75 and 340 mg/L percent pesticide removals were 32.9, 77.4 and 90.8%, respectively.

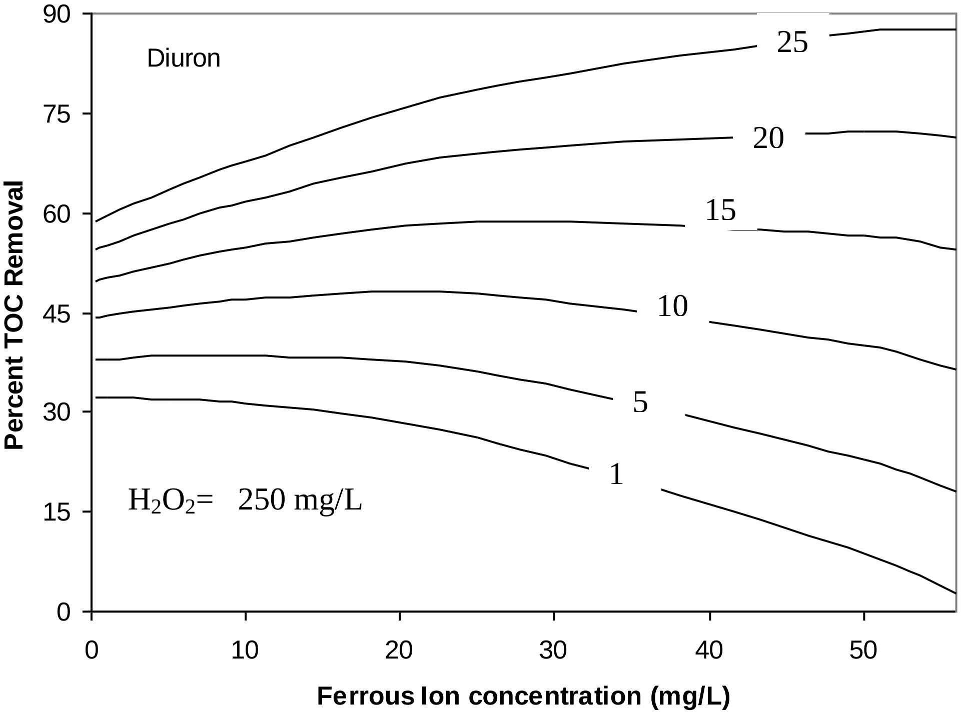

Figure 5.8 Variation of percent TOC removals with Fe(II) concentration at different diuron doses by the photo-Fenton oxidation. Reaction time =240 min.

Figure 5.8 depicts variations of percent TOC removal with Fe(II) concentration at different diuron concentrations. Initial pesticide concentration was the most important parameter affecting the percentage of pesticide removal by the photo-Fenton oxidation. Mineralization efficiencies obtained at high pesticide concentrations were higher than those obtained at low pesticide concentrations due to adverse effects of high oxidant and catalyst doses at low pesticide concentrations. The TOC removal was mainly influenced by Fe(II) concentration according to Eqn.5.12, because of the high coefficient for the Fe(II) effects. Percent TOC removal increased with increasing diuron concentrations at all Fe(II) doses. However, excess ferrous ions in the system yielded lower mineralization at low concentrations of diuron as shown in Figure 5.8.

When diuron concentration was 25 mg/L, percent TOC removals were 58, 81 and 91%, respectively, at Fe(II) doses of 1, 28 and 56 mg/L at a hydrogen peroxide dose of 340 mg/L. For diuron dose of 1 mg/L, the optimal H_2O_2/Fe(II)/diuron dose yielding the highest TOC removal (38%) was 145/0.8/1 mg/L, while at a high diuron concentration of 25 mg/L this ratio was 340/56/25 mg/L yielding 90.76% TOC removal. High concentrations of H_2O_2 and Fe(II) were required for high degree of TOC removal at high pesticide concentrations.

The ANOVA analysis indicated (Table A. 4) that all three variables pesticide, Fe(II) and H_2O_2 doses and independent variable interactions (X_1, X_2, X_1X_2, X_1X_3, X_1^2, X_2^2, X_3^2) played important roles for the mineralization of pesticide or TOC removal. In a literature study, diuron was degraded by photo-Fenton treatment with a limited TOC removal of 70% after 60 min of irradiation indicating the formation of recalcitrant intermediates supporting our findings (Mazellier *et al.*, 1997). In another literature study, different reactant dose combinations were evaluated, each one corresponding to the minimum quantities of Fe(II) and hydrogen peroxide needed to achieve a desired mineralization percentage. For the treatment of 42 mg/L diuron dose with the 46% TOC removal efficiency, the selected oxidant and catalyst doses were H_2O_2= 250 mg/L and Fe(II)= 20 mg/L, respectively (Farre *et al.,* 2006).

Independent variables and their interactions were found to be effective in pesticide and TOC removals by the photo-Fenton treatment. Maximum pesticide removal (100%), percent mineralization or TOC removal (85%) were obtained with a H_2O_2/Fe(II)/diuron ratio of 267/37/25 (mg/L). As compared to treatment by the Fenton reagent alone, photo-Fenton treatment resulted in higher TOC removals indicating beneficial effects of UV light.

5.1.1.3 Peroxone (O_3/H_2O_2) Process

In the Box-Behnken design, the independent variables were the dose of pesticide (X_1=1-25 mg/L), hydrogen peroxide (X_2=1.5-340 mg/L), and ferrous ion (X_3= 3-11). The low, center and high levels of each variable are designated as -1, 0, and +1, respectively. The dependent variables (or objective functions) were the percent pesticide (Y_1) and TOC (Y_2) removals. Ozone feeding rate was kept constant at

45 mg/h. The experimental conditions of the Box-Behnken experiment design are presented in Table 5.4. The center point (0, 0, 0) was repeated three times and the nearly same results were obtained indicating the reproducibility of the data. Observed and predicted percent removals for diuron and TOC are compared in Table 5.5.

Table 5.4 The experimental conditions of the Box-Behnken experiment design for Peroxone oxidation

Run No	**X_1 Diuron, (mg/L)**	**X_2 H_2O_2, (mg/L)**	**X_3 pH**
1	1 (-1)	0 (-1)	7 (-1)
2	25 (-1)	0 (-1)	7 (-1)
3	1 (-1)	340 (-1)	7 (-1)
4	25 (+1)	340 (+1)	7 (0)
5	1 (-1)	170 (0)	3 (-1)
6	25 (+1)	170 (0)	3 (-1)
7	1 (-1)	170 (0)	11 (+1)
8	25 (+1)	170 (0)	11 (+1)
9	13 (0)	0 (-1)	3 (-1)
10	13 (0)	340 (+1)	3 (-1)
11	13 (0)	0 (-1)	11 (+1)
12	13 (0)	340 (+1)	11 (+1)
13	13 (0)	170 (0)	7 (0)
14	13 (0)	170 (0)	7 (0)
15	13 (0)	170 (0)	7 (0)

Table 5.5 Observed and predicted percent removals for the response functions (Y) for Peroxone oxidation

Run No	**Predicted percent removals**		**Observed percent removals**	
	Y_1 Pesticide	**Y_2 TOC**	**Y_1 Pesticide**	**Y_2 TOC**
1	99.9	58.83	100	59.78
2	96.74	27.69	96	25
3	93.26	77.31	94	80
4	97.5	61.15	97.4	60.2
5	83.06	57.01	82	55
6	96.97	41.37	96.75	43
7	99.78	100	100	100
8	86.94	69.99	88	72
9	97.54	23.47	98.5	24.53
10	94.03	72.43	94.35	71.75
11	100	83.8	100	83.76
12	97.96	86.06	97	85
13	100	75	100	75
14	100	75	100	75
15	100	75	100	75

The coefficients of the response functions for different dependent variables were determined by correlating the experimental data with the response functions using a Stat-Ease regression program. Different response functions with the determined coefficients are presented by Eqns 5.10 and 5.11. The model F-value of 37.19 implies the model is significant for pesticide removal. P value of < 0.05 for any factor in analysis of variance (ANOVA) indicates a significant effect of the corresponding variable on the response. In this case X_2, X_3, X_1X_2, X_1X_3, X_1^2, X_3^2 are significant model terms. The ANOVA tests for the other response functions gave similar results. The results of analysis of variance (ANOVA) are also presented in Table A. 5 and Table A. 6 indicating the fact that that the predictability of the model is at 95% confidence interval. The response functions for percent pesticide (Y_1) and percent TOC (Y_2) with the determined coefficients have the following forms:

The response functions for percent pesticide (Y_1) and percent TOC (Y_2) removals with the determined coefficients have the following forms:

$$Y_1 = 72.36 + 1.65\ X_1 - 0.039\ X_2 + 5.53\ X_3 + 9.07*10^{-4}\ X_1X_2 - 0.139\ X_1X_3 + 4.23*10^{-4}\ X_2X_3 - 0.031\ X_1^2 + 4.54*10^{-5} X_2^2 - 0.241\ X_3^2 \qquad \text{Eqn 5.8}$$

$$Y_2 = 2.713 + 0.867\ X_1 + 0.288\ X_2 + 7.43\ X_3 + 1.84*10^{-3}\ X_1X_2 - 0.083\ X_1X_3 - 1.69*10^{-2}\ X_2X_3 - 0.06\ X_1^2 - 3.46*10^{-4}\ X_2^2 + 0.079\ X_3^2 \qquad \text{Eqn 5.9}$$

5.1.1.3.1 Disappearance of Diuron. Figure 5.9 depicts the effect of initial pH and pesticide dose on percent diuron removal at the initial peroxide dose of 150 mg/L. Both pesticide dose and initial pH affected percent diuron removal considerably. At low diuron doses below 15 mg/L, percent diuron removal increased with increasing pH and reached the highest percent removal (nearly 100%) around pH=11 indicating indirect ozonation at alkaline pHs (Eqn 3.6 and Eqn 3.7). With the increase in diuron dose above 15 mg/L, pH optimum for diuron removal shifted towards lower pHs. For a diuron dose of 15 mg/L the optimum pH was around 7. However, for higher diuron doses pH optimum was around pH=4. Probably peroxide and ozone oxidations took place at the same time (Eqn 3.8) at high diuron doses favoring low pHs for high degree of diuron removal. Probably indirect ozon oxidation (no peroxide requirement) was effective at low diuron doses, which did not suffice at high diuron doses requiring contribution of peroxide. At low pHs (pH < 7) diuron removal increased with increasing diuron dose and reached the highest removal (97%) at a diuron dose of 20 mg/L. Apparently, the peroxide and ozon doses were in excess and diuron dose was the rate limiting reactant at low pHs where peroxone oxidation was effective. However, at high pHs (pH > 7), diuron removal decreased with increasing diuron dose with the highest removal at a diuron dose of 5 mg/L. The limiting factor at alkaline pH was ozon dose which was not sufficient at high diuron doses yielding lower rates. Percent diuron removal decreased from 97% to 87% when the pH was increased from 3 to 11 at a pesticide dose of 25 mg/L. pH and diuron doses affected diuron removal due to a shift in degradation mechanisms depending on pH and also oxidant limitations depending on diuron dose.

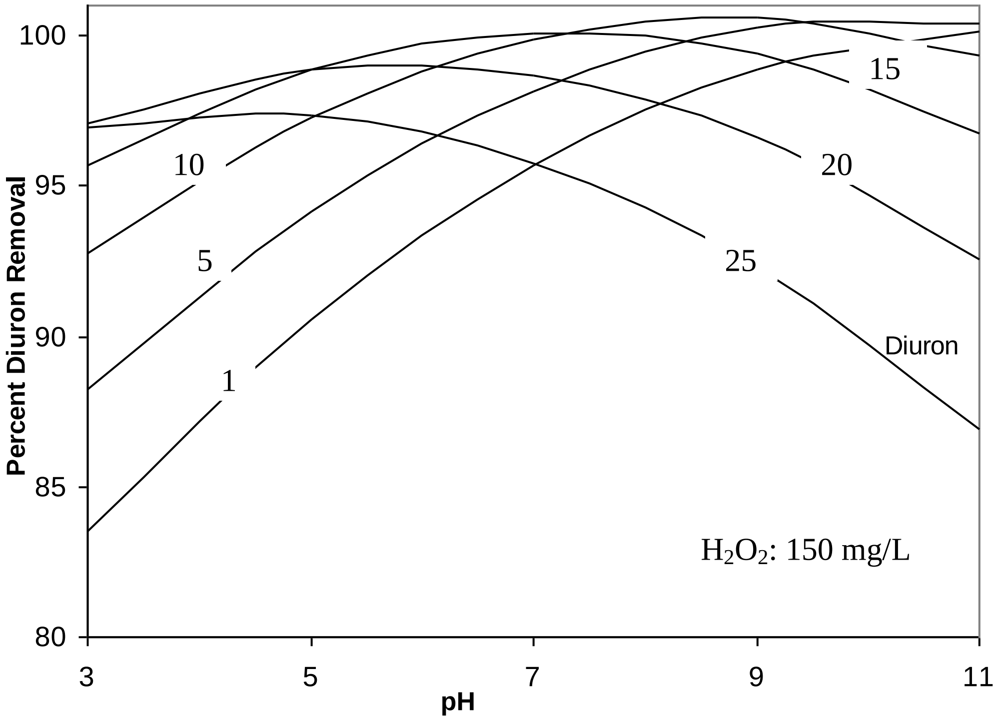

Figure 5.9 Variation of percent diuron removal with pH and diuron dose in peroxone treatment (reaction time: 5 min, H_2O_2: 150 mg/L, ozone dose: 45 mg/min).

Effects of pH and hydrogen peroxide dose on percent diuron removal in peroxone treatment at a high diuron dose of 25 mg/L is depicted in Figure 5.10. Diuron removal was not affected from peroxide doses up to 150 mg/L due to oxidation by ozone at low peroxide doses. Further increases in peroxide dose above 150 mg/L resulted in increases in diuron removal due to involvement of peroxide in ozone oxidations at high concentrations (peroxone treatment). Diuron removal was also affected from changes in pH. Oxidation at low pHs resulted in higher diuron removal as compared to high pHs. Apparently acidic pHs were favored for effective removal of diuron at high concentrations indicating requirement for peroxide since peroxide oxidations favor low pHs. In order to obtain more than 95% diuron removal pH must be lower than 7 and peroxide dose can be between 0 and 150 mg/L at high diuron doses of 25 mg/L. Diuron dose is the determining factor for the optimum pH and peroxide dose. Low diuron doses require alkaline pHs and high diuron requires acidic pHs for effective degradation. Similarly, low peroxide doses are required at low diuron doses (0 mg/L).

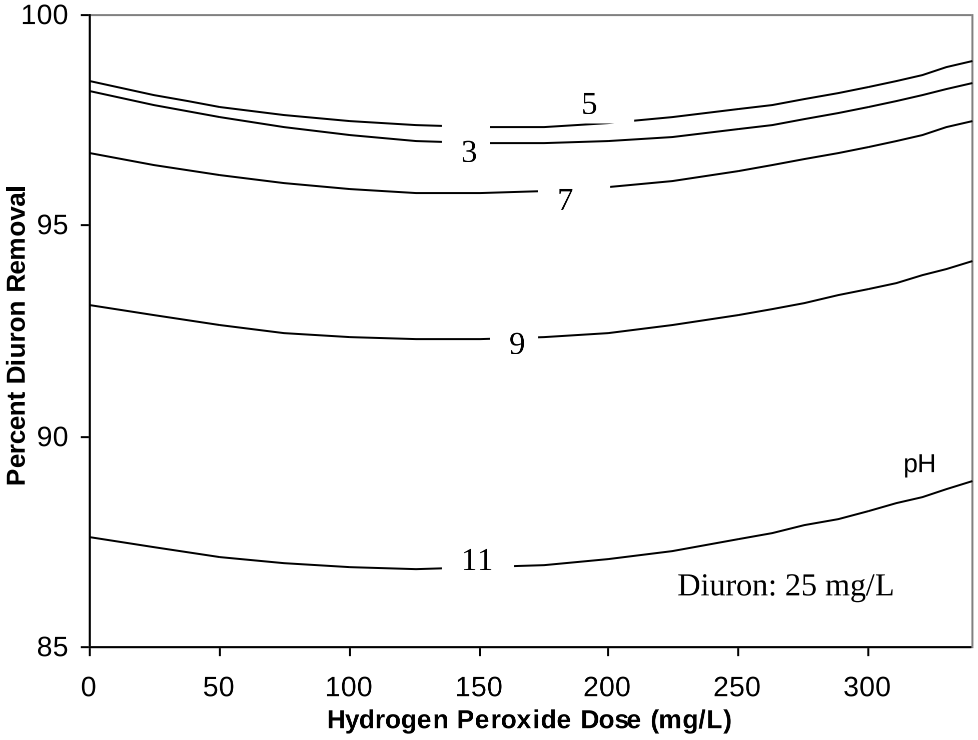

Figure 5.10 Variation of percent diuron removal with hydrogen peroxide dose and pH in peroxone treatment (reaction time: 5 min, diuron dose: 25 mg/L, ozone dose: 45 mg/min).

Oxidation of four phenyl-urea herbicides (isoproturon, chlortoluron, diuron, and linuron) in ground water and lake water by ozone (1-3*10^{-5} M) and by a combination of O_3/H_2O_2 (1*10^{-5} M H_2O_2) was investigated by Benitez *et al.*, (2007) at different ozone and peroxide doses. Partial contributions of direct ozonation and radical pathways were evaluated, and the results showed that oxidation with OH radicals were the major mechanism. Pesticide removal was 87.4% with peroxone treatment, while 82.9% removal was obtained by ozone oxidation alone at pH=7. Unlike our study, mineralization (TOC removal) and dehalogenation (AOX removal) were not considered by Benitez *et al.*, (2007) study. Higher diuron removals were obtained in our study as compared to Benitez *et al.*, (2007) along with considerable TOC and AOX removals.

The ANOVA analysis indicated that diuron dose and pH played important roles for degradation of the diuron (Table A. 5). Peroxide effect was not that significant. Low ‘p’ value for X_1X_3 indicated significance of interactions between the pesticide dose and pH affecting the diuron removal.

5.1.1.3.2 Total Organic Carbon Removal: Mineralization of Diuron. Degradation of diuron can be expressed by the following reaction

$$\text{Diuron} \rightarrow \text{Intermediates} + HCl \rightarrow CO_2 + H_2O + HNO_3 \qquad \text{Eqn 5.10}$$

The first reaction is diuron degradation to intermediates and dehalogenation (AOX removal) and is relatively fast. The second reaction is mineralization (TOC removal) and is slow. The mechanisms of oxidations are also different. Diuron and AOX removals follow the same path, but TOC removal involves complete oxidation to CO_2, H_2O and NO_3^-. The complete oxidation reaction can be expressed in Eqn 5.6. Mineralization of diuron required more than 60 minutes although diuron degradation or dehalogenation took place within 5 minutes. This difference indicated formation of intermediate products during the oxidation reaction. Aniline and 3, 4-dichloroaniline were the two major degradation intermediates reported in the literature (Salvestrini *et al.,* 2002; Simon *et al.*, 1998). Moreover, 3,4-dichloroaniline and 3,4-dichlorophenyl isocyanate were also proposed as the main degradation intermediates by Salvestrini *et al*., but not observed in our studies.

Variation of percent TOC removal (mineralization) with the peroxide dose and pH at a constant diuron dose of 25 mg/L is depicted in Figure 5.11. Percent mineralization of diuron or total organic carbon (TOC) removal steadily increased with increasing pH at all peroxide doses indicating TOC removal by indirect ozone oxidation. For a pesticide dose of 25 mg/L percent TOC removal increased from 46% to 70.6% when pH was increased from 3 to11 at a peroxide dose of 200 mg/L due to enhanced hydroxyl radical formation at alkaline pHs. TOC removal also increased with increasing peroxide concentrations due to more hydroxyl radical formation at high peroxide concentrations. Ozonation favors alkaline pHs while peroxide oxidation was favoring acidic pHs. Since TOC removal increased by both increasing pH and peroxide dose, both ozone and peroxide oxidations were effective mechanisms (peroxone). The highest percent TOC removal (70%) was lower than the highest diuron removal (100%) indicating formation of unoxidized intermediates at high diuron doses. Complete mineralization was possible at low diuron doses such as 1 mg/L.

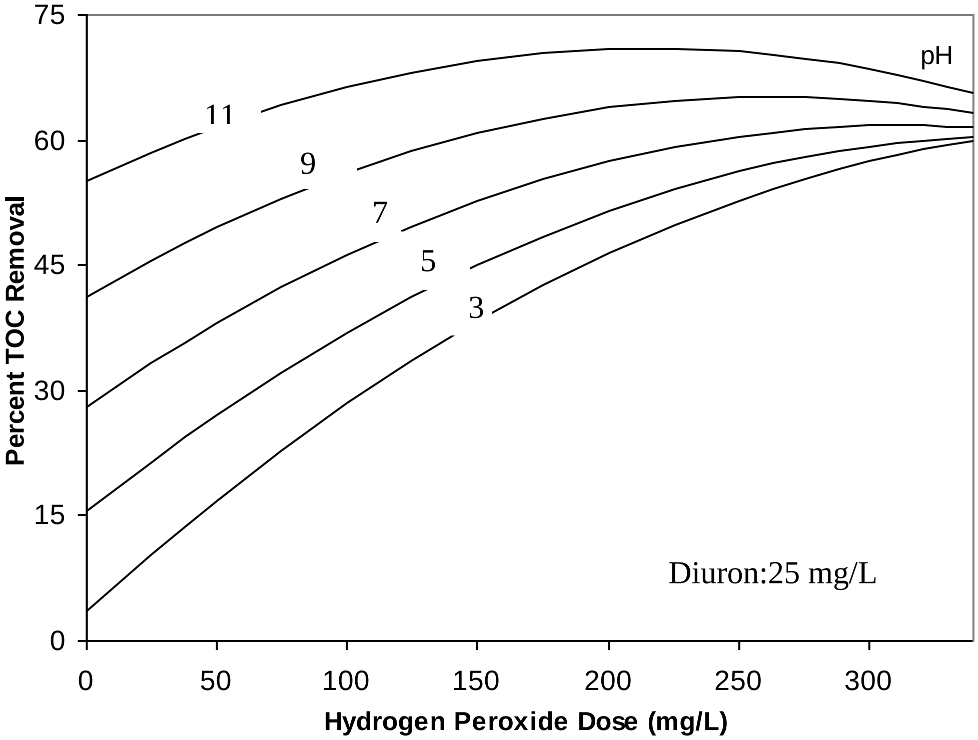

Figure 5.11 Variation of percent TOC removal with hydrogen peroxide dose and pH in peroxone treatment (Reaction time: 5 min, Diuron dose: 25 mg/L, Ozone dose:45 mg/min).

Figure 5.12 depicts variation of percent TOC removal with peroxide and pesticide doses at a constant pH of 11. More than 90% TOC removals were obtained at low diuron doses below 5 mg/L with peroxide dose of 150 mg/L. Percent TOC removal decreased with increasing diuron dose indicating limitations by the oxidants (ozone and peroxide) and formation of intermediates at high pesticide doses. At a diuron dose of 25 mg/L, percent mineralization was lower than 70%. Increases in peroxide dose resulted in increasing TOC removals up to 150 or 200 mg/L peroxide concentrations indicating effectiveness of peroxide in hydroxyl radical formation in peroxone treatment. However, further increases in peroxide dose yielded lower TOC removals due to hydroxyl ion scavenging effect of high peroxide doses. Hydroxyl ion scavenging at high peroxide concentrations can be described in Eqn 5.4 and Eqn 5.5.

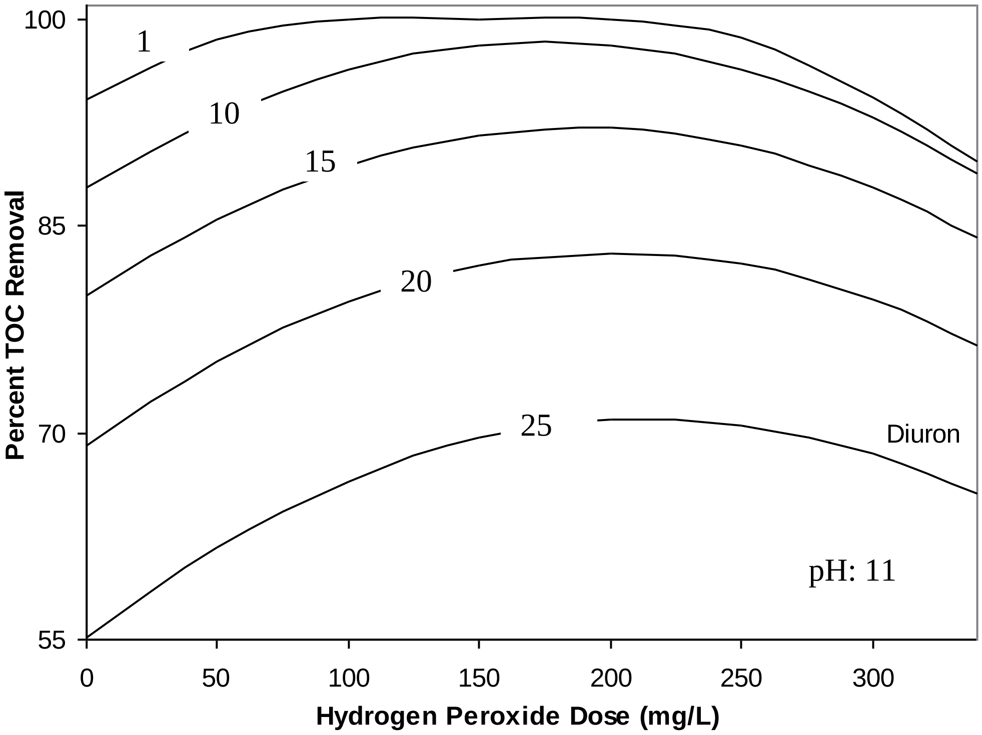

Figure 5.12 Variation of percent TOC removal with hydrogen peroxide and pesticide doses in peroxone treatment (Reaction time: 5 min, pH:11, Ozone dose: 45 mg/min).

The ANOVA analysis (Table A. 6) indicated that all independent variables, pH, pesticide and H_2O_2 doses affected TOC removal (mineralization). An optimization program was used to determine the optimum dose of peroxide and pH maximizing TOC removal. At a low diuron dose of 1 mg/L, the optimal H_2O_2/pH/diuron dose yielding the highest TOC removal (100%) was 50/11/1 mg/L. At a diuron dose of 25 mg/L the optimum ratio was 200/11/25 mg/L yielding 70.6% TOC removal. Alkaline pHs were favored and high diuron doses required high peroxide doses for effective mineralization of diuron.

Both diuron and TOC removals were profoundly affected from the pH, peroxide and diuron doses. Optimum operating conditions varied depending on diuron dose. Nearly complete diuron removals were obtained. Neutral pHs was recommended for high degradation and mineralization at the same time. However, TOC removal was always lower than diuron removal indicating formation of intermediates due to incomplete mineralization.

5.1.1.4 Comparision of Advanced Oxidation Processes for Diuron Removal

The optimal pesticide, H_2O_2 and Fe(II) doses resulting in the highest pesticide (diuron) and TOC removals were determined by using an optimization program and the results are presented in Table 5.6. In photo-Fenton treatment, the highest pesticide removal (100%) and mineralization (85%) were obtained with a H_2O_2/Fe(II)/diuron ratio of 267/37/25 (mg/L). However, at the same reaction conditions, 100% pesticide removal, 26.7% mineralization (TOC removal) were obtained by using the Fenton treatment in the absence of UV light. Maximum removal efficiencies in the Fenton's reagent treatment were 95.4% for pesticide, 53.5% for TOC (mineralization) with a H_2O_2/Fe(II)/diuron ratio of 340/44/13 (mg/L). Apparently, the use of UV light along with the Fenton's reagent improved the TOC removals considerably.

Table 5.6 Optimum levels of the variables maximizing the diuron and TOC removals by the Fenton, photo-Fenton and peroxone treatments

Response	**Pesticide (X_1)**	**H_2O_2 (X_2)**	**Fe (II) (X_3)**	**Photo-Fenton**	**Fenton**	**Peroxone**
	Dose (mg/L)			**Efficiency (Y) %**		
Degradation	25.0	230.0	38.6	100.0	91.9	97.2
Mineralization	25.0	340.0	56.6	90.8	49.7	59.6

However, diuron and TOC removals with the ozone/H_2O_2 treatment at peroxide dose of 250 mg/L and pH of 3 (pH value of Fenton and photo-Fenton treatment) were 100% and 52.5%, respectively. Apparently, application of ozone in direct ozone oxidation did not improve degree of mineralization of diuron. Optimum TOC removal (70.6%) was obtained with the optimum ratio of 200/11/25 mg/L at a diuron dose of 25 mg/L. Although, O_3/H_2O_2 combination gives a good yield of •OH radicals, photo-Fenton treatment resulted in higher TOC removals indicating beneficial effects of UV light. Photo-Fenton treatment is preferred as compared to the Fenton and peroxone treatments.

5.1.2 Simazine Removal by AOPs

In this part of the thesis, Fenton, photo-Fenton and peroxone oxidations were used for treatment of simazine containing water by using Box-Behnken experimental design. Simazine, considered as a highly toxic, persistent priority substance by the EU (European Commission, 2001) and one of the most commonly used herbicides, belongs to the family of triazine herbicides.

5.1.2.1 Fenton Oxidation

In the Box-Behnken design, the independent variables were the dose of pesticide (X_1=0.5-5 mg/L), hydrogen peroxide (X_2=10-100 mg/L), and ferrous ion (X_3=0-30 mg/L). The low, center and high levels of each variable are designated as -1, 0, and +1, respectively as shown in Table 5.7. The dependent variables (or objective functions) were the percent pesticide (Y_1) and TOC (Y_2) removals. The experimental conditions of the Box-Behnken experiment design are presented in Table 5.7. The center point (0,0,0) was repeated three times and the same results were obtained indicating the reproducibility of the data. The observed and predicted percent removals for simazine and TOC are compared in Table 5.8.

Table 5.7 The experimental conditions of the Box-Behnken experiment design for Fenton and photo-Fenton oxidation.

Run No	**Actual Coded and Levels**		
	X_1 Simazine, (mg/L)	**X_2 H_2O_2, (mg/L)**	**X_3 Fe (II), (mg/L)**
1	0.5 (-1)	10 (-1)	15 (0)
2	5 (+1)	10 (-1)	15 (0)
3	0.5 (-1)	100 (+1)	15 (0)
4	5 (+1)	100 (+1)	15 (0)
5	0.5 (-1)	55 (0)	0 (-1)
6	5(+1)	55 (0)	0 (-1)
7	0.5 (-1)	55 (0)	30 (+1)
8	5 (+1)	55 (0)	30 (+1)
9	2.75 (0)	10 (-1)	0 (-1)
10	2.75 (0)	100 (+1)	0 (-1)
11	2.75 (0)	10 (-1)	30 (+1)
12	2.75 (0)	100 (+1)	30 (+1)
13	2.75 (0)	55 (0)	15 (0)
14	2.75 (0)	55 (0)	15 (0)
15	2.75 (0)	55 (0)	15 (0)

Table 5.8 Observed and predicted percent removals for the response functions (Y)

Run No	**Predicted percent removals**		**Observed percent removals**	
	Y_1 **Pesticide**	**Y_2** **TOC**	**Y_1** **Pesticide**	**Y_2** **TOC**
1	100	11.93	99.36	12.05
2	99.79	15.93	99.17	16.18
3	98.50	11.74	99.11	11.49
4	97.16	14.69	97.80	14.57
5	5.62	8.72	5.17	8.31
6	4.17	8.15	3.70	7.61
7	100	5.95	100	6.49
8	100	14.00	100	14.41
9	2.60	3.19	3.69	3.48
10	3.49	4.20	3.32	4.86
11	100	9.10	100.17	8.44
12	100	5.19	98.91	4.90
13	99.05	31.97	99.58	31.80
14	99.68	31.80	99.58	31.80
15	100	31.64	99.58	31.80

The coefficients of the response functions for different dependent variables were determined correlating the experimental data with the response functions by using the Stat-Ease regression program. Different response functions with the determined coefficients are presented by Eqn 5.14 and Eqn 5.15. The model F-value of 2789.45 implies the model is significant for pesticide removal. P value of < 0.05 for any factor in analysis of variance (ANOVA) indicates a significant effect of the corresponding variable on the response. In this case, X_3, X_3^2 are significant model terms. The ANOVA tests for the other response functions gave similar results. The results of analysis of variance (ANOVA) are also presented in Table A. 7 and Table

A. 8 indicating the fact that that the predictability of the model is at 95% confidence level. The response functions for percent pesticide (Y_1) and percent TOC (Y_2) removals with the determined coefficients have the following forms:

$$Y_1 = 3.96 - 0.289\ X_1 + 4.81\ 10^{-2}\ X_2 + 9.487\ X_3 - 2.790\ 10^{-3}\ X_1X_2 + 1.074\ 10^{-2}\ X_1X_3 - 3.296\ 10^{-4}\ X_2X_3 + 2.082\ 10^{-2}\ X_1^2 - 4.047\ 10^{-4}\ X_2^2 - 0.210\ X_3^2 \qquad \text{Eqn 5.11}$$

$$Y_2 = -12.858 + 7.833\ X_1 + 0.620\ X_2 + 2.058\ X_3 - 2.592\ 10^{-3}\ X_1X_2 + 6.385\ 10^{-2}\ X_1X_3 - 1.822\ 10^{-3}\ X_2X_3 - 1.426\ X_1^2 - 5.436\ 10^{-3}\ X_2^2 - 6.833\ 10^{-2}\ X_3^2 \qquad \text{Eqn 5.12}$$

5.1.2.1.1 Disappearance of Simazine. Response functions with determined coefficients were used to estimate variations of percent simazine and TOC removals as function of the reagent concentrations. Figure 5.13 depicts the effect of initial H_2O_2 concentration on percent simazine removal at different Fe(II) concentrations after 6 minutes of reaction time when the initial simazine dose was 5 mg/L. Simazine removal was not affected from hydrogen peroxide doses above 10 mg/L since simazine dose was high (5 mg/L) and peroxide doses were relatively high. However, Fe(II) dose significantly affected percent simazine removal which increased with increasing Fe(II) dose up to Fe(II)=15 mg/L. Further increases in Fe(II) doses did not yield higher simazine removals.

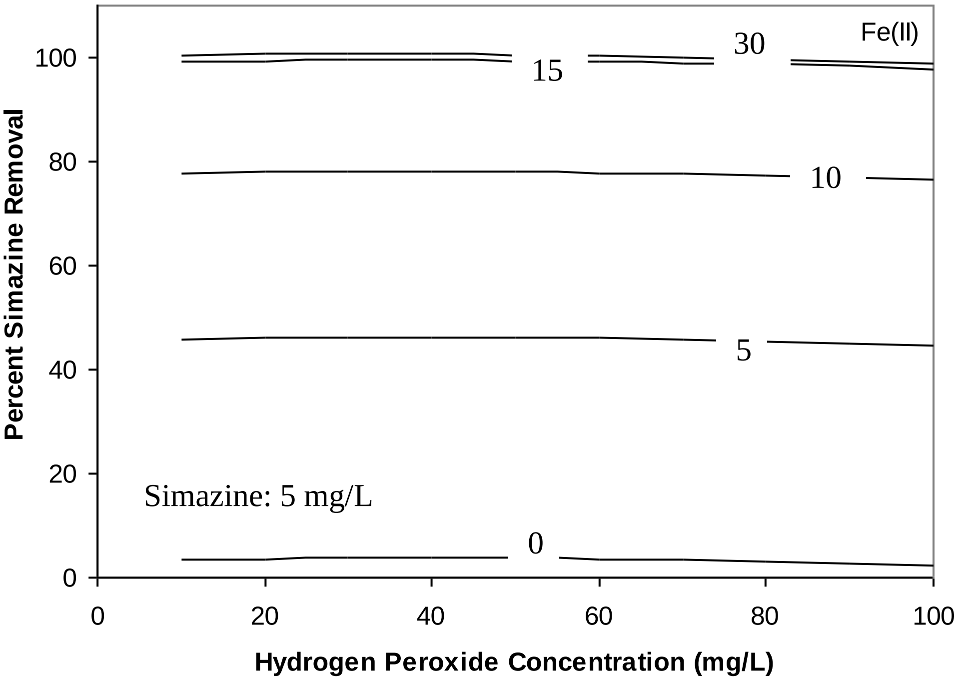

Figure 5.13 Variation of percent simazine removal with H_2O_2 concentration at different Fe(II) doses by the Fenton reagent treatment after 6 min reaction time. Simazine = 5 mg/L.

The optimum Fe(II) concentration for complete removal of simazine was 15 mg/L. Percent pesticide removals were 3.5, 99.4 and 100% for an initial pesticide dose of 5 mg/L and at Fe(II) doses of 0, 15 and 30 mg/L, respectively when H_2O_2 dose was 20 mg/L. High Fe(II) doses above 30 mg/L had adverse effects on pesticide removal due to hydroxyl ion scavenging effect of Fe(II). The results are in agreement with the literature reports, where a beneficial effect of increasing Fe(II) was observed in photo-degradation of pesticides (Torrades *et al.*, 2003; Krutzler *et al.*, 1999). Complete degradation of simazine (5 mg/L) was accomplished at a hydrogen peroxide dose of 20 mg/L and Fe(II) concentration of 15 mg/L after 6 minutes reaction time. Lower concentrations of Fe(II) did not result in complete simazine removal.

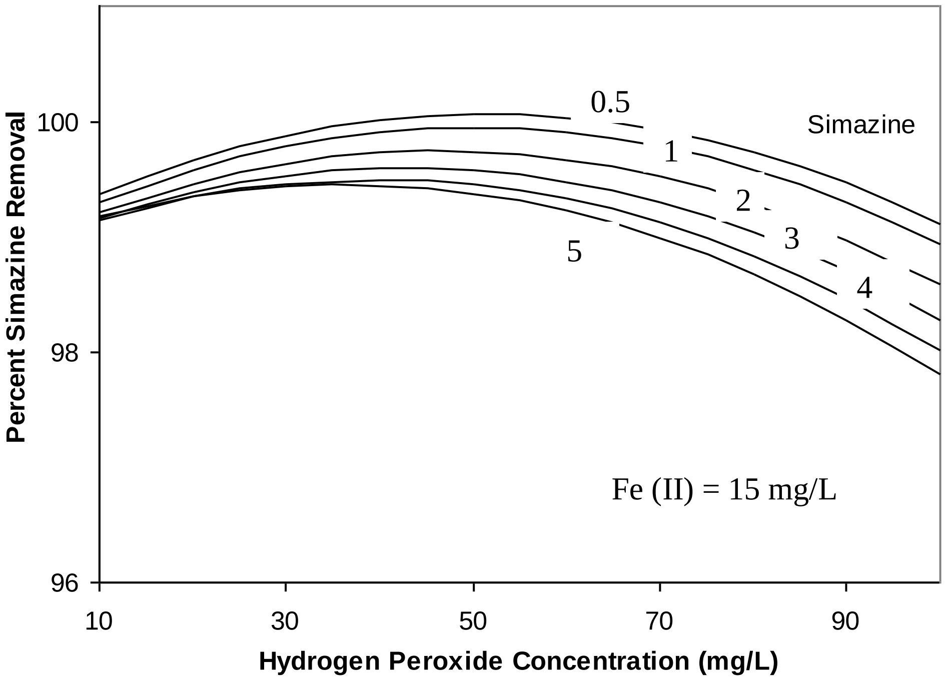

Figure 5.14 Variation of percent simazine removal with H_2O_2 concentration at different simazine doses by the Fenton reagent oxidation at the end of 6 min reaction time. Fe(II) = 15 mg/L.

Effects of simazine and H_2O_2 concentrations on percent simazine oxidation by the Fenton treatment are depicted in Figure 5.14 at a Fe(II) dose of 15 mg/L. Percent simazine removal decreased with increasing initial simazine concentrations. However, simazine removals were between 98 and 100% indicating rather slight changes in percent removals with simazine concentration since the initial simazine doses were low (0.5-5 mg/L). Simazine removals increased with H_2O_2 concentration up to 50 mg/L, due to H_2O_2 limitations at low peroxide doses. Further increases in peroxide dose resulted in decreases in percent simazine removals probably due to hydroxyl radical scavenging effects of high peroxide doses. At constant simazine and Fe(II) doses of 5 and 15 mg/L and variable H_2O_2 doses of 10, 50 and 100 mg/L percent pesticide removals were 99.0, 99.5 and 98.2%, respectively. Therefore, peroxide dose of 50 mg/L was optimal maximizing the pesticide removal.

Rivas *et al.,* (2004) investigated the effects of pH, temperature and Fe(II) concentration on simazine removal at a constant peroxide dose. Peroxide dose was considered as a variable in this study and the effects of peroxide on both simazine and TOC removals were investigated. Fe(II) dose was found to have more profound effect on simazine removal as compared to peroxide dose. Furthermore, both Fe(II) and peroxide doses had adverse effects on simazine removal above certain concentrations due to hydroxyl ion scavenging effects of those reagents. The ANOVA analysis (Table A. 7) indicated that only Fe(II) doses (X_3, X_3^2) played important roles in simazine oxidation by the Fenton's reagent treatment. This is due to low simazine doses used.

5.1.2.1.2 Total Organic Carbon Removal: Mineralization of Simazine. Overall mineralization of simazine using oxygen as oxidizing agent can be written as follows:

$$C_7H_{12}ClN_5 + 16\,O_2 \rightarrow 5\,HNO_3 + HCl + 7\,CO_2 + 3\,H_2O \qquad \text{Eqn 5.13}$$

Complete mineralization of simazine was not achieved after 60 minutes of oxidation although simazine disappeared within 6 to 12 minutes. This difference indicated formation of intermediate products during simazine oxidation which were not completely degraded to CO_2 and H_2O. 2-hydroxy-4,6-bis(ethylamino)-s-triazine,2-chloro-4-amino-6-ethylamino)-s-triazine (deisopropylatrazine), and 2-chloro-4,6-diamino-s-triazine (diamino chlorotriazine) were reported to be the main photochemical degradation intermediates under alkaline conditions (Spurlock *et al.,* 2000; Evgenidou *et al.,* 2002).

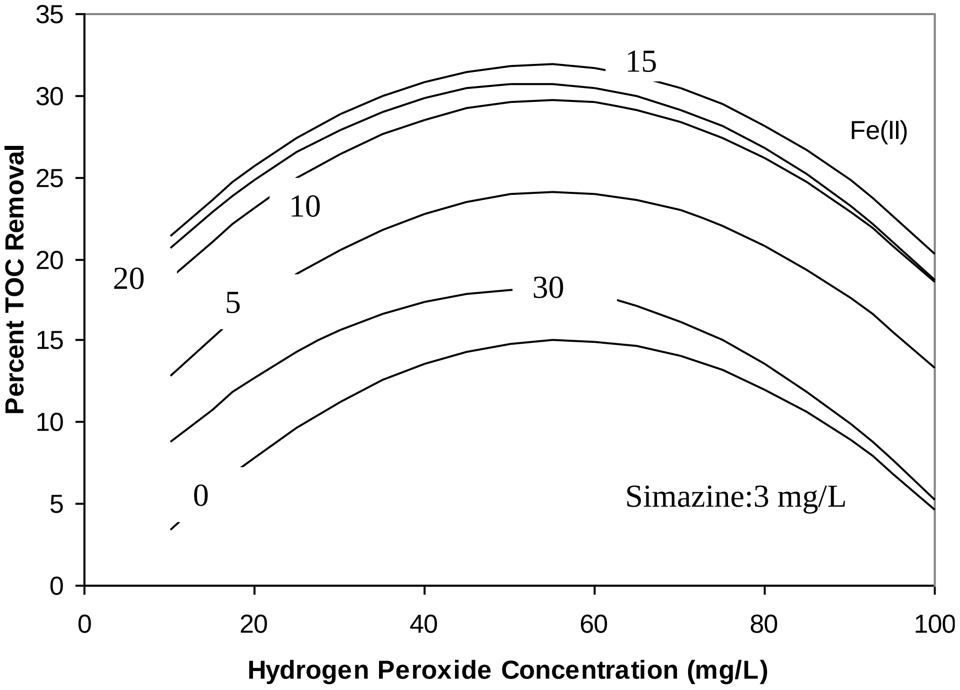

Figure 5.15 Variation of percent TOC removals with H_2O_2 concentration at different Fe(II) doses by the Fenton oxidation at the end of 15 min reaction time. Simazine = 3 mg/L.

As depicted in Figure 5.15, percent mineralization or TOC removal increased with peroxide dose up to 50 mg/L at all Fe(II) doses indicating peroxide limitations at low peroxide concentrations. Peroxide concentrations above 50 mg/L resulted in decreases in percent TOC removal indicating adverse effects of high H_2O_2 concentrations. Therefore, the optimum peroxide dose was 50 mg/L under the experimental conditions used. In agreement with Glaze *et al.*, (1995) and Beltran *et al.*, (1996), a reduction in TOC removal was observed at high peroxide concentrations indicating the adverse effects of excess peroxide doses. This is due to hydroxyl ion ($HO^{\bullet}$) scavenging by excess H_2O_2 and consequent formation of the less reactive radical $HO_2\bullet$ as presented in Eqn 5.4 and Eq 5.5. At constant simazine and Fe(II) doses of 3 and 15 mg/L and variable H_2O_2 doses of 10, 50 and 100 mg/L, percent TOC removals were 21.5, 31.8 and 20.4%, respectively, indicating the optimum peroxide dose of 50 mg/L. Percent TOC removals were much lower than simazine removals indicating incomplete degradation of simazine and formation of some intermediate products.

Percent TOC removals also increased with Fe(II) doses up to 15 mg/L due to Fe(II) limitations at low Fe doses (Figure 5.15). Further increases in Fe(II) dose above 15 mg/L resulted in decreases in simazine removal probably due to hydroxyl ion scavenging effects of high Fe(II) doses. Therefore, the optimum Fe(II) dose was 15 mg/L. The highest TOC removal was 32.5% obtained at peroxide and Fe(II) doses of 50 and 15 mg/L when simazine was 3 mg/L. At a simazine concentration of 5 mg/L (not shown in Figure 5.15), percent TOC removals were 7.4, 26.4 and 14.5%, respectively, at Fe(II) doses of 0, 15 and 30 mg/L at a hydrogen peroxide dose of 50 mg/L indicating the same optimum doses of peroxide (50 mg/L) and Fe (15 mg/L).

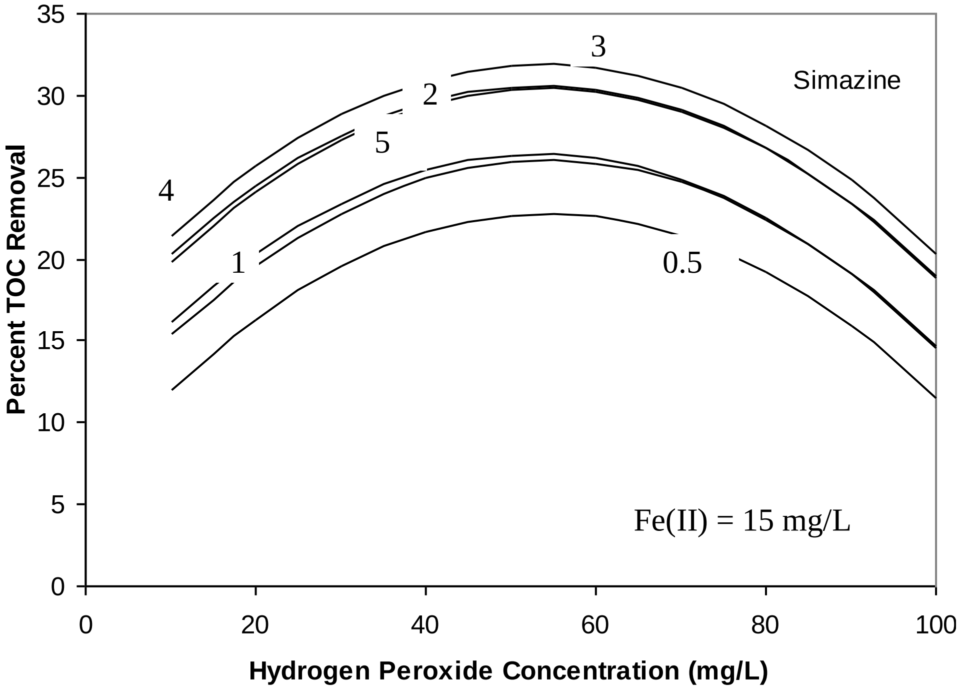

Figure 5.16 Variation of percent TOC removals with H_2O_2 concentration at different initial simazine doses by the Fenton oxidation at the end of 15 min reaction time. Fe(II) = 15 mg/L.

Variation of percent TOC removal (mineralization) with the peroxide dose at different simazine concentrations is depicted in Figure 5.16 at a constant Fe(II) dose of 15 mg/L. Percent TOC removal steadily increased when simazine concentration increased from 0.5 to 3 mg/L due to pesticide limitation at low pesticide doses.

Further increases in simazine dose above 3 mg/L resulted in decreases in TOC removal yielding an optimum simazine dose of 3 mg/L under the specified experimental conditions. Similarly, percent TOC removal increased with increasing peroxide dose up to 50 mg/L due to the oxidant (peroxide) limitations at low concentrations. TOC removals decreased when peroxide dose increased above 50 mg/L due to adverse effects of high peroxide concentrations by scavenging hydroxyl ions. Therefore, the optimum doses of peroxide and Fe(II) was found to be 50 and 15 mg/L, respectively.

Initial simazine concentration was the most important parameter affecting percent simazine removal by the Fenton oxidation. At a low simazine dose of 0.5 mg/L, the optimal H_2O_2/Fe(II)/simazine dose yielding the highest TOC removal (22.1%) was 45/13/0.5 mg/L, while at a simazine concentration of 3 mg/L this ratio was 55/15/3 mg/L yielding 31.9% TOC removal.

The ANOVA analysis (Table A. 8) indicated that all three variables pesticide, H_2O_2 and Fe(II) doses and their interactions (X_1, X_3, X_1X_3, X_2X_3, X_1^2, X_2^2, X_3^2) played important roles for the mineralization of pesticide.

5.1.2.2 Photo-Fenton Oxidation

In the Box-Behnken design, the independent variables were the dose of pesticide (X_1=0.5-5 mg/L), hydrogen peroxide (X_2=10-100 mg/L), and ferrous ion (X_3=0-30 mg/L). The low, center and high levels of each variable are designated as -1, 0, and +1, respectively as shown in Table 5.7. The dependent variables (or objective functions) were percent pesticide (Y_1) and TOC (Y_2) removals. The dependent and independent variable values and the observed results are presented in Table 5.7. The center point (0,0,0) was repeated three times and the same results were obtained indicating the reproducibility of the data. Observed and predicted percent removals for simazine and TOC are compared in Table 5.9.

Table 5.9 Observed and predicted percent removals for the response functions (Y) for photo-Fenton oxidation

Run No	**Predicted percent removals**		**Observed percent removals**	
	Y_1 Pesticide	**Y_2 TOC**	**Y_1 Pesticide**	**Y_2 TOC**
1	99.58	79.84	100.0	82.29
2	91.37	20.59	91.32	21.55
3	99.95	67.97	100.0	67.01
4	100.23	46.13	99.81	43.68
5	97.46	78.33	97.47	76.48
6	89.98	61.19	90.46	60.83
7	100.0	99.25	100.0	99.61
8	100.0	35.29	100.0	37.14
9	88.43	41.44	88.0	40.84
10	97.06	41.55	97.0	44.36
11	98.98	32.24	99.04	29.43
12	99.57	45.77	100.00	46.37
13	97.23	58.80	96.90	58.80
14	97.23	58.80	96.90	58.80
15	97.23	58.80	96.90	58.80

The coefficients of the response functions for different dependent variables were determined by correlating the experimental data with the response functions using the Stat-Ease regression program. Different response functions with the determined coefficients are presented by Eqn 5.17 and Eqn 5.18. The model F-value of 63.6 implies the model is significant for pesticide removal. The P value of < 0.05 for any factor in analysis of variance (ANOVA) indicates a significant effect of the corresponding variable on the response. In this case X_1, X_2, X_3, X_1X_2, X_1X_3, X_2X_3, X_3^2 are significant model terms. The ANOVA tests for the other response functions gave similar results. The results of analysis of variance (ANOVA) are also presented in Table A. 9 and Table A. 10 indicating the fact that that the predictability of the model is at 95% confidence level. The response functions for percent pesticide (Y_1) and percent TOC (Y_2) removals with the determined coefficients have the following forms:

$$Y_1 = 96.244 - 3.64\ X_1 + 0.0497\ X_2 + 0.373\ X_3 + 0.0209\ X_1X_2 + 0.0519\ X_1X_3 - 2.978\ 10^{-3}\ X_2X_3 + 0.150\ X_1^2 - 1.045\ 10^{-4}\ X_2^2 - 4.496\ 10^{-3}\ X_3^2 \qquad \text{Eqn 5.14}$$

$$Y_2 = 74.864 - 21.435\ X_1 + 0.655\ X_2 + 0.842\ X_3 + 0.092\ X_1X_2 - 0.347\ X_1X_3 + 4.97\ 10^{-3}\ X_2X_3 + 2.281\ X_1^2 - 8.255\ 10^{-3}\ X_2^2 - 8.15\ 10^{-3}\ X_3^2 \qquad \text{Eqn 5.15}$$

5.1.2.2.1 Disappearance of Simazine. Response functions with determined coefficients were used to estimate variations of percent simazine and TOC removals as function of the reagent concentrations. Figure 5.17 depicts the effect of initial Fe(II) concentration on percent simazine removal at different H_2O_2 concentrations after 6 minutes of reaction time when the initial simazine dose was 3 mg/L.

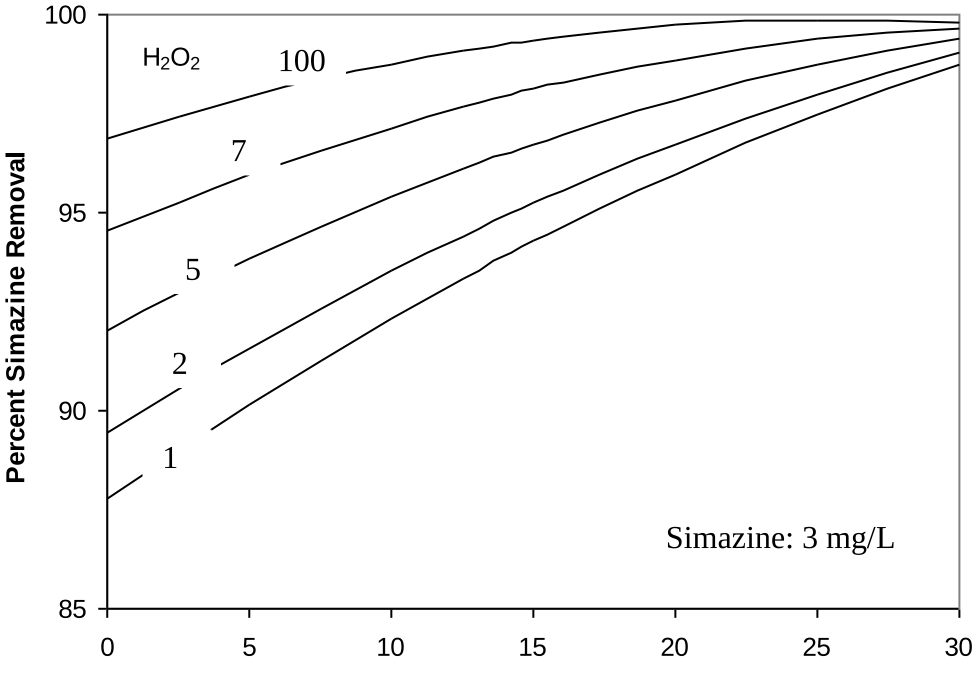

Figure 5.17 Variation of percent simazine removal with Fe(II) concentration at different H_2O_2 doses by the Photo-Fenton treatment. Reaction time = 6 min. Simazine = 3 mg/L.

Both peroxide and Fe(II) doses affected percent simazine removal considerably. At low peroxide concentrations such as 10 mg/L, Fe(II) concentration affected percent simazine removal more profoundly indicating limitations by the catalyst dose. However, at high peroxide doses such as 100 mg/L, simazine removal was less affected from increases in Fe(II) doses. At a constant Fe(II) dose of 10 mg/L, percent simazine removal increased with increasing peroxide dose indicating limitations by the peroxide concentration. Simazine removal was above 95% for peroxide and Fe(II) doses above 50 mg/L and 15 mg/L, respectively. At a Fe(II) dose of 30 mg/L, percent simazine removal was 97% even with a peroxide dose of 10 mg/L. Fe(II) dose had a more profound effect on simazine removal as compared to the peroxide. Simazine removal by the Fenton oxidation was investigated by Rivas *et al.*, (2004) at different pH, temperature and Fe(II) concentration at a constant peroxide dose. Unlike Rivas study, peroxide dose was considered as a variable in this study and the effects of peroxide on both simazine and TOC removals were investigated.

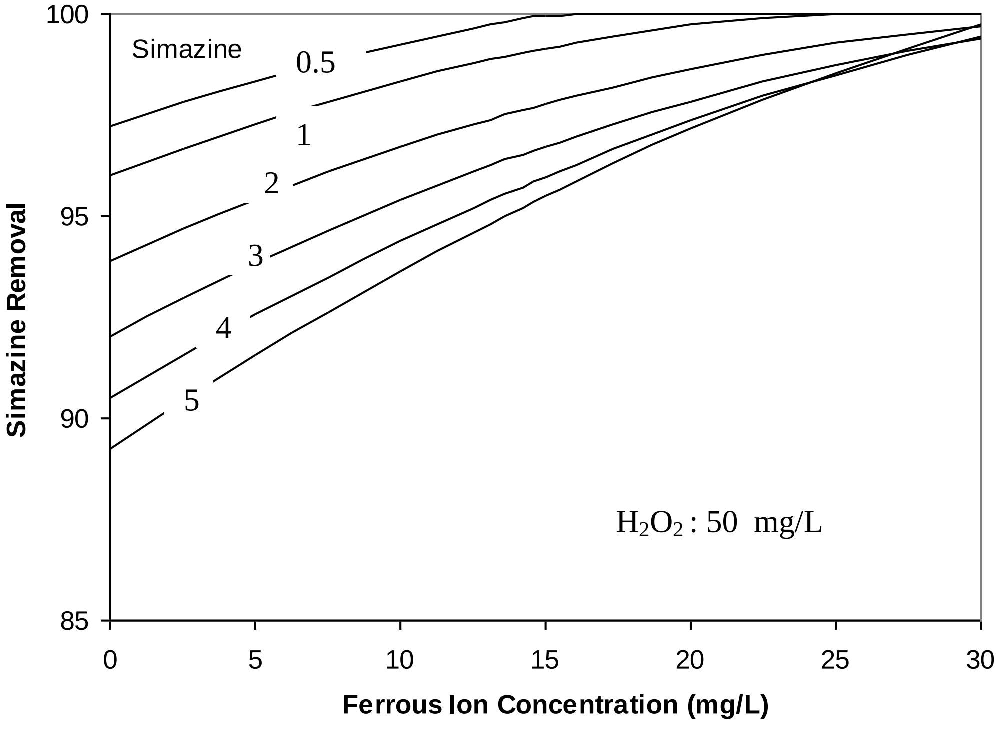

Figure 5.18 Variation of percent simazine removal with Fe(II) concentration at different simazine doses by Photo-Fenton treatment. Reaction time = 6 min. Peroxide = 50 mg/L.

Effects of simazine and ferrous ion concentrations on percent simazine oxidation by the photo-Fenton treatment are depicted in Figure 5.18 at a H_2O_2 dose of 50 mg/L. Percent simazine removal increased with decreasing initial simazine and increasing Fe(II) concentrations indicating adverse effects of simazine and positive effects of Fe(II). At low simazine doses such as 0.5 mg/L, complete removal was achieved with a Fe(II) dose of 15 mg/L. However, at high simazine doses such as 5 mg/L, 30 mg/L Fe(II) was required for complete simazine removal. At a constant Fe(II) dose of 10 mg/L, simazine removal increased from 92% to 99% when simazine dose was decreased from 5 to 0.5 mg/L. In order to obtain more than 95% simazine removal at a constant peroxide dose of 50 mg/L, simazine must be below 2 mg/L and Fe(II) should be above 15 mg/L. Peroxide and Fe(II) requirements increased with increasing simazine dose for complete simazine removal. However, Fe(II) doses above 30 mg/L was not beneficial for the simazine doses tested. High Fe(II) doses may have adverse effects on simazine removal due to hydroxyl ion scavenging effect as presented in the literature (Torrades *et al.,* 2003; Krutzler *et al.,* 1999).

The ANOVA analysis indicated that peroxide and Fe(II) doses played important roles for degradation of the pesticide (Table A. 9). High ‘F’ and low ‘p’ values for the varaible X_3 indicated significant effect of Fe(II) dose on percent simazine removal.

5.1.2.2.2 Total Organic Carbon Removal: Mineralization of Simazine. Overall mineralization of simazine using oxygen as the oxidizing agent is presented in Eqn 5.16. Mineralization of simazine required more than 60 minutes although simazine degradation took place within 6 to 12 minutes. This difference indicated formation of intermediate products during the oxidation reaction, which were mentioned in section 2.2 .

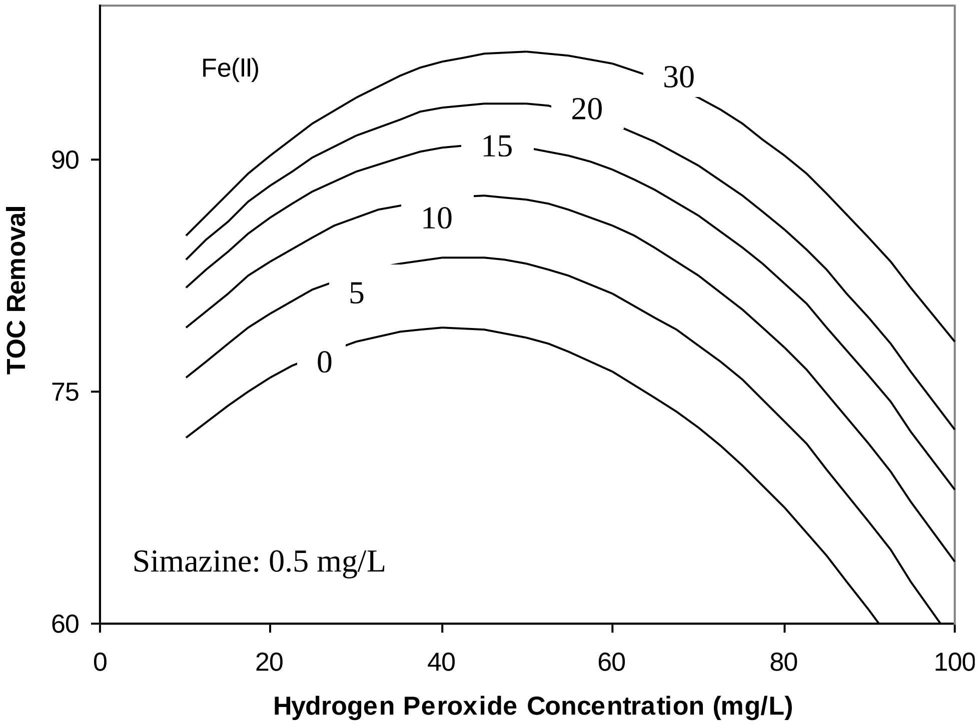

Figure 5.19 Variation of percent TOC removal with H_2O_2 concentration at different Fe(II) doses by the Photo-Fenton treatment. Reaction time = 60 min. Simazine = 0.5 mg/L.

Figure 5.19 depicts variation of percent TOC removal (mineralization) with the peroxide and Fe(II) doses at a constant simazine dose of 0.5 mg/L. Percent TOC removal increased with the peroxide dose up to 50 mg/L at all Fe(II) doses indicating peroxide limitations at low peroxide doses. Peroxide concentrations above 50 mg/L resulted in decreases in percent TOC removal due to hydroxyl ion scavenging effects of excess peroxide. Therefore, the optimum peroxide dose was 50 mg/L under the experimental conditions used. Our results are in agreement with Glaze *et al.*, (1995) and Beltran *et al.*, (1996), where a reduction in TOC removal was observed at high peroxide concentrations indicating the adverse effects of excess peroxide doses. This is due to hydroxyl ion ($HO^\bullet$) scavenging by excess H_2O_2 and consequent formation of the less reactive radical $HO_2^\bullet$ as presentedin Eqn 5.4 and Eqn 5.5.

Therefore, high peroxide doses above 50 mg/L should be avoided for low simazine concentrations. However, at high simazine doses such as 3 mg/L, peroxide doses up to 100 mg/L can be used for complete pesticide removal. At a constant peroxide dose of 50 mg/L, percent TOC removal increased with increasing Fe(II) dose up to 30 mg/L. At high simazine doses, percent TOC removals were lower than simazine removals indicating incomplete degradation of simazine and formation of some intermediate products. Almost complete TOC removal was obtained with 50 mg/L peroxide and 30 mg/L Fe(II) doses when the pesticide concentration was 0.5 mg/L.

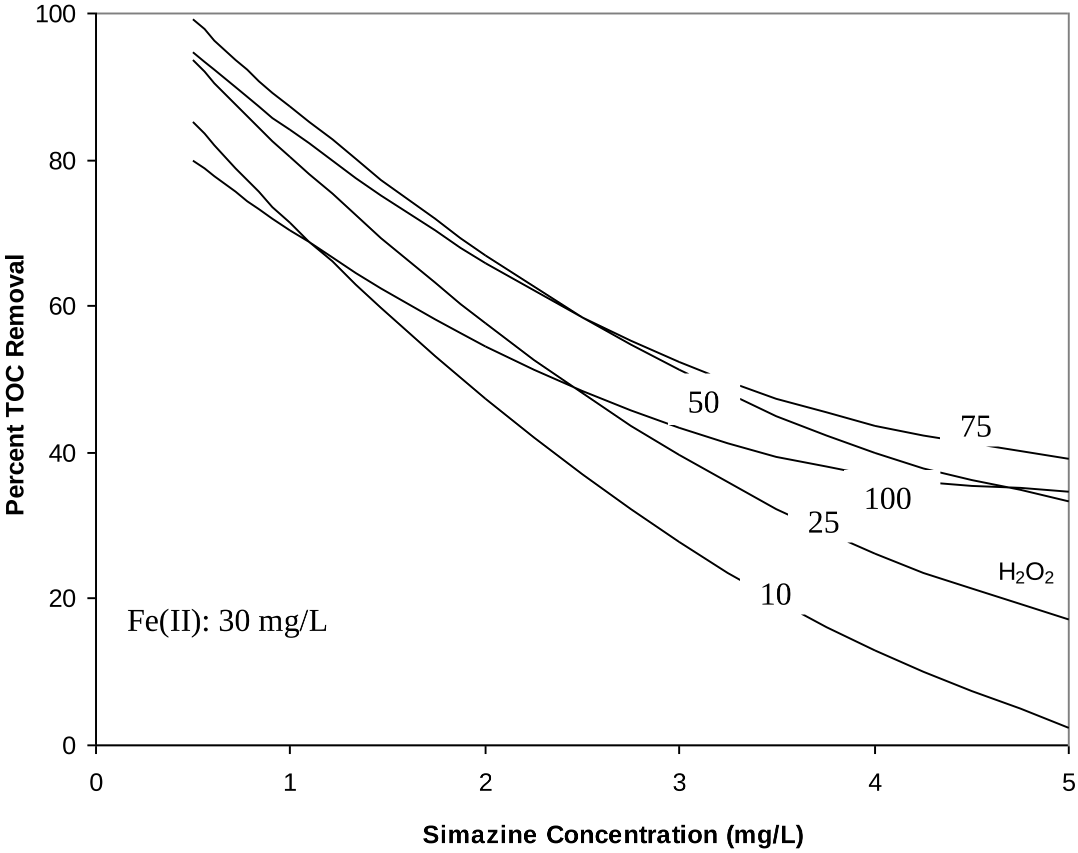

Figure 5.20 Variation of percent TOC removal with simazine concentration at different peroxide doses at a constant Fe(II) dose of 30 mg/L. Reaction time = 60 min. Fe(II) = 30 mg/L.

Figure 5.20 depicts variation of percent TOC removal with simazine concentration at different peroxide doses and at a constant Fe(II) dose of 30 mg/L. Percent TOC removal decreased with increasing simazine concentration at all peroxide doses due to limitations by the oxidant (peroxide) and catalyst (Fe) doses at high simazine concentrations. At low simazine doses below 1 mg/L, TOC removal was above 80% for all peroxide concentrations. Similarly, TOC removal increased with increasing peroxide dose up to 75 mg/L indicating limitations by low peroxide doses. Further increases in the peroxide dose above 75 mg/L resulted in decreases in percent TOC removal (mineralization) due to hydroxyl ion scavenging effect of excess peroxide doses.

An optimization program was used to determine the optimum doses of peroxide and Fe(II) maximizing the pesticide and TOC removal. At a low simazine dose of 0.5 mg/L, the optimal H_2O_2/Fe(II)/simazine dose yielding the highest TOC removal (100%) was 50/30/0.5 mg/L, while at a simazine concentration of 3 mg/L this ratio was 50/30/3 mg/L yielding 51.2% TOC removal. At high pesticide doses, simazine mineralization was incomplete yielding formation of intermediates, which were not completely mineralized to CO_2 and H_2O. Initial pesticide concentration was the most important parameter affecting the mineralization (TOC removal) by the photo-Fenton oxidation. The ANOVA analysis indicated (Table A. 9) that pesticide and Fe(II) doses were the two major factors affecting the TOC removal due to high ‘F’ ratios and low ‘p’ values.

5.1.2.3 Peroxone Treatment

In the Box-Behnken design, the independent variables were the dose of pesticide (X_1=0.5-5 mg/L), hydrogen peroxide (X_2=10-100 mg/L), and pH (X_3=3-11). The low, center and high levels of each variable are designated as -1, 0 and +1, respectively as shown in Table 5.10. The dependent variables (or objective functions) were the percent pesticide (Y_1) and TOC (Y_2) removals. Ozone feeding rate was kept constant at 45 mg/h. The dependent and independent variable values and the observed results are presented in Table 5.10. The center point (0,0,0) was repeated three times and the same results were obtained indicating the reproducibility of the data. Observed and predicted percent removals for simazine, TOC and AOX are compared in Table 5.11.

Table 5.10 The experimental conditions of the Box-Behnken experiment design for peroxone oxidation

Run No	**Actual Coded and Levels**		
	X_1 Simazine, (mg/L)	**X_2 H_2O_2, (mg/L)**	**X_3 Fe (II), (mg/L)**
1	0.5 (-1)	0 (-1)	7 (0)
2	5 (+1)	0 (-1)	7 (0)
3	0.5 (-1)	100 (+1)	7 (0)
4	5 (+1)	100 (+1)	7 (0)
5	0.5 (-1)	50 (0)	3 (-1)
6	5(+1)	50 (0)	3 (-1)
7	0.5 (-1)	50 (0)	11 (+1)
8	5 (+1)	50 (0)	11 (+1)
9	2.75 (0)	0 (-1)	3 (-1)
10	2.75 (0)	100 (+1)	3 (-1)
11	2.75 (0)	0 (-1)	11 (+1)
12	2.75 (0)	100 (+1)	11 (+1)
13	2.75 (0)	50 (0)	7 (0)
14	2.75 (0)	50 (0)	7 (0)
15	2.75 (0)	50 (0)	7 (0)

Table 5.11 Observed and predicted percent removals for the response functions (Y) for peroxone oxidation

Run No	**Predicted percent removals**		**Observed percent removals**	
	Y_1 Pesticide	**Y_2 TOC**	**Y_1 Pesticide**	**Y_2 TOC**
1	94.72	54.33	95.00	53.00
2	90.39	22.43	90.00	22.03
3	95.46	63.26	95.85	63.66
4	95.28	41.67	95.00	43.00
5	89.92	52.19	90.00	51.85
6	89.00	53.28	89.75	52.00
7	95.92	78.40	95.17	79.68
8	92.33	23.82	92.25	24.16
9	85.36	53.72	85.00	55.40
10	95.77	49.66	95.30	49.60
11	97.63	33.95	98.10	34.00
12	92.84	66.18	93.20	64.50
13	99.00	70.40	99.00	70.40
14	99.00	70.40	99.00	70.40
15	99.00	70.40	99.00	70.40

The coefficients of the response functions for different dependent variables were determined by correlating the experimental data with the response functions using the Stat-Ease regression program. Different response functions with the determined coefficients are presented by Eqn 5.19 and Eqn 5.20. The model F-value of 55.95 implies the model is significant for pesticide removal. The P value of < 0.05 for any factor in analysis of variance (ANOVA) indicates a significant effect of the corresponding variable on the response. In this case, X_1, X_2, X_3, X_1X_2, X_2X_3, X_1^2, X_2^2, X_3^2 are significant model terms. The ANOVA tests for the other response functions gave similar results. The results of analysis of variance (ANOVA) are also presented in Table A. 11 and Table A. 12 indicating the fact that that the predictability of the model is at 95% confidence interval. The response functions for percent pesticide (Y_1) and percent TOC (Y_2) removals with the determined coefficients have the following forms:

$$Y_1 = 68.86 + 2.90\ X_1 + 0.21\ X_2 + 5.36\ X_3 + 9.23*10^{-3}\ X_1X_2 - 7.42*\ 10^{-2}\ X_1X_3 - 1.9*10^{-2}\ X_2X_3 - 0.61\ X_1^2 - 7.86*10^{-4}\ X_2^2 - 0.26\ X_3^2 \qquad \text{Eqn 5.16}$$

$$Y_2 = 19.56 + 16.73\ X_1 + 0.28\ X_2 + 7.47\ X_3 - 2.29*10^{-2}\ X_1X_2 - 1.55\ X_1X_3 + 4.54*10^{-2}\ X_2X_3 - 2.36\ X_1^2 - 5.2*10^{-3}\ X_2^2 - 0.41\ X_3^2 \qquad \text{Eqn 5.17}$$

5.1.2.3.1 Disappearance of Simazine. Response functions with determined coefficients were used to estimate variations of percent simazine and TOC removals as function of the reagent concentrations. Figure 5.21 depicts the effect of initial pH value on percent simazine removal at different H_2O_2 concentrations after 5 minutes of reaction time when the initial simazine dose was 0.5 mg/L. Ozone feeding rate was constant at 45 mg/min. Both peroxide dose and pH affected percent simazine removal considerably. At a constant pH of 3, percent simazine removal increased with increasing peroxide dose indicating peroxide limitations at low peroxide concentrations.

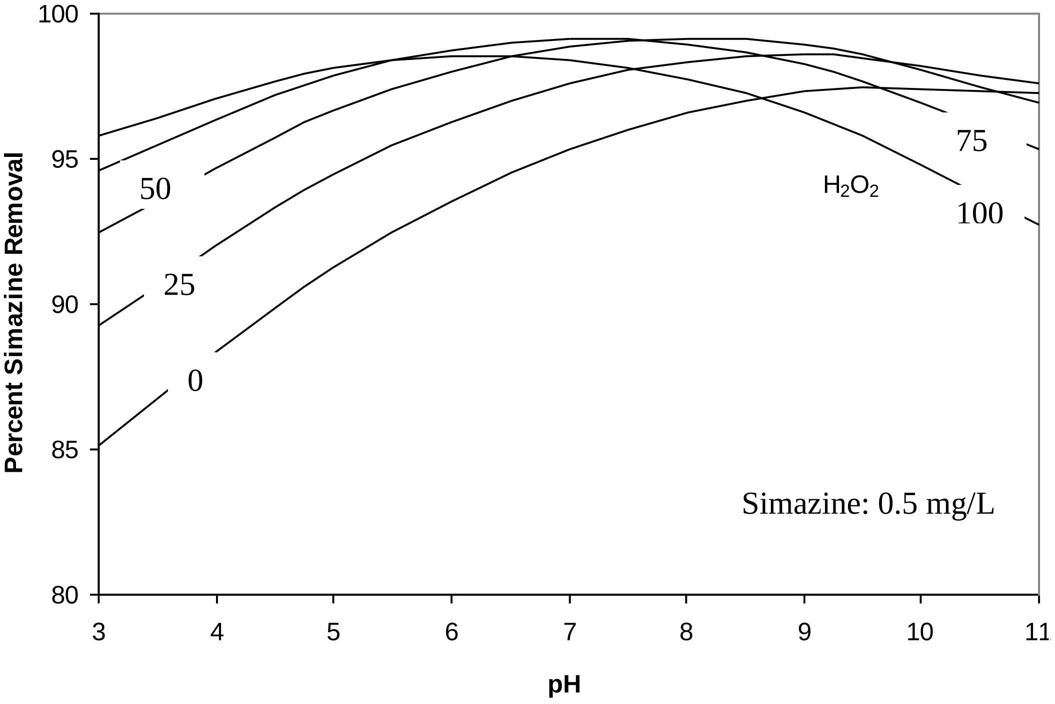

Figure 5.21 Variation of percent simazine removal with pH at different H_2O_2 doses by the Ozone/H_2O_2 treatment (Reaction time: 5 min, Simazine: 0.5 mg/L, Ozone Dose: 45 mg/min).

Addition of hydrogen peroxide to the reaction media resulted in a faster simazine decomposition due to generation of radicals with high oxidation power. However, at high pH values (pH>9), simazine removal was less affected from increases in peroxide doses because of indirect oxidation by ozone and adverse effects of excess hydrogen peroxide. In the absence of peroxide, simazine removal by only ozonation increased with increasing pH and became maximum (97%) at pH=11. The optimum pH shifted towards neutral pHs upon addition of peroxide to ozone. At peroxide doses above 50 mg/L, the optimum pH maximizing simazine removal was around pH = 7. Apparently, pH had a more profound effect on simazine removal as compared to the peroxide, since degradation pathways as well as kinetics vary with pH. Peroxide addition improved simazine removal considerably especially for acidic pHs (pH<7). The highest simazine removal (98%) was obtained with simazine and peroxide doses of 0.5 and 50 mg/L, respectively at pH = 7.5. Low pH (pH < 7) operations required higher doses of peroxide for high simazine removals.

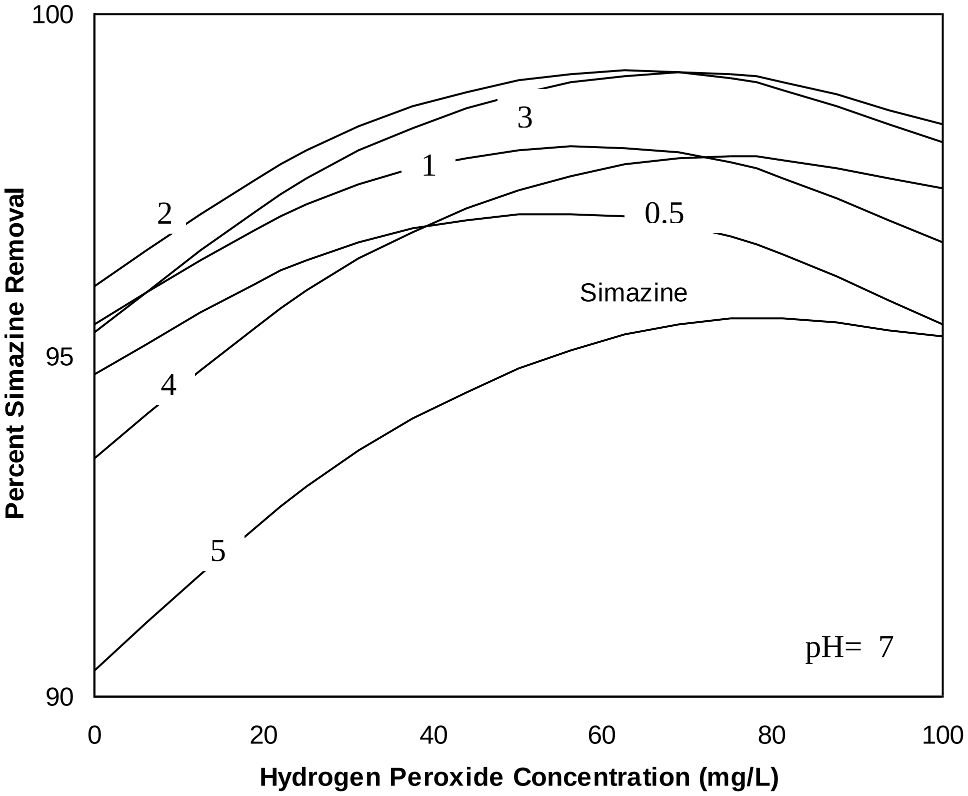

Figure 5.22 Variation of percent simazine removal with H_2O_2 concentration at different simazine doses by the Ozone/H_2O_2 treatment (Reaction time: 5 min, pH: 7, Ozone Dose: 45 mg/min).

Effects of simazine and hydrogen peroxide concentrations on percent simazine oxidation by ozon/hydrogen peroxide treatment are depicted in Figure 5.22 at pH= 7. At high simazine doses above 4 mg/L, percent simazine removal increased with increasing peroxide dose and reached a maximum level at a peroxide dose of 70 mg/L. However, at low simazine doses below 3 mg/L, simazine removal increased with increasing peroxide dose up to 60 mg/L due to peroxide limitations at low concentrations. Further increases in peroxide dose resulted in reductions in simazine removal due to hydroxyl ion scavenging effects of excess peroxide doses. Hydroxyl ion scavenging effect of high peroxide doses are also reported in literature (Torrades *et al.,* 2003; Krutzler *et al.,* 1999).

At a constant hydrogen peroxide dose of 60 mg/L, simazine removal increased with increasing simazine dose up to 2 mg/L and reached the maximum removal (98%) due to limitations at low simazine doses. However, at high simazine doses above 3 mg/L simazine removal decreased with increasing simazine doses due to limitations by peroxide or ozone. At peroxide dose of 60 mg/L, simazine removal decreased from 99% to 93.5% when simazine dose was increased from 2 to 5 mg/L. In order to obtain more than 95% simazine removal at pH =7 and at a constant peroxide dose of 60 mg/L, simazine must be below 5 mg/L.

Simazine removal in drinking water by the ozone oxidation was investigated by Ormad *et al.,* (2008) along with other pesticides at different ozone and coagulant doses. Unlike Ormad’s study, simazine and peroxide doses and pH effects on both simazine and TOC removals were investigated in our study by using a statistical experiment design method.

The ANOVA analysis (Table A. 11) indicated that pesticide, peroxide doses and pH played important roles for degradation of the pesticide ($f < 0.005$ for all variables). However, pH (X_3) and X_2X_3 (peroxide x pH) had more profound effects ($f < 0.0001$) on simazine removal as compared to the other variables.

5.1.2.3.2 Total Organic Carbon Removal: Mineralization of Simazine. Overall mineralization of simazine using oxygen as the oxidizing agent is presented in Eqn 5.16. Mineralization of simazine required more than 60 minutes although simazine degradation took place within 5 minutes. This difference indicated formation of intermediate products during the oxidation reaction, which were not completely degraded to CO_2 and H_2O within 5 minutes. The main photochemical degradation intermediates of simazine were reported under alkaline conditions (Spurlock *et al.*, 2000; Evgenidou & Fytianos, 2002).

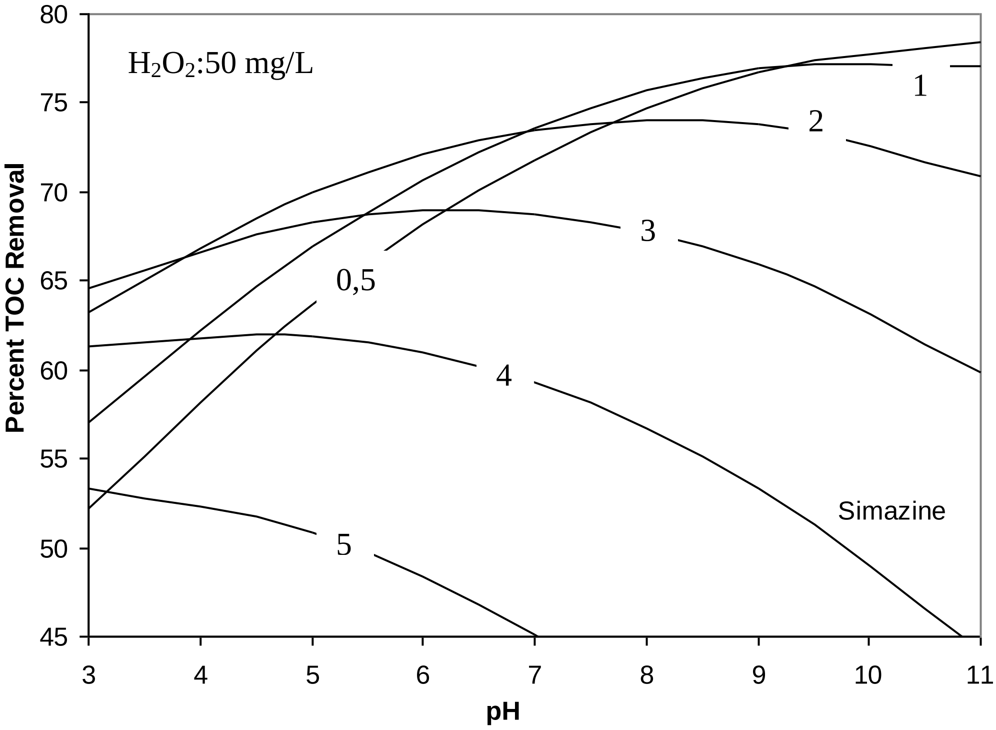

Figure 5.23 Variation of percent TOC removal with pH at different H_2O_2 doses by the Ozone/H_2O_2 treatment (Reaction time: 60 min, H_2O_2 dose:50 mg/L, Ozone Dose: 45 mg/min).

Figure 5.23 depicts variation of percent TOC removal (mineralization) with the pesticide dose and pH at a constant peroxide dose of 50 mg/L. Both pH and simazine dose had profound effects on TOC removal. pH effects varied depending on simazine dose. At low simazine doses below 2 mg/L, TOC removal increased with increasing pH and became maximum at pH=10 by the indirect ozone oxidation at alkaline pHs. Due to high solubility of ozone at low pHs (highly acidic conditions), low simazine doses require low ozone doses or high pH levels. However at high simazine doses above 2 mg/L, pH optimum varied with the simazine dose. For example, the optimum pHs yielding maximum TOC removals at simazine doses of 2, 3, 4 and 5 mg/L were 9, 7, 5, 3, respectively. Apparently, low pHs (high H^+ concentrations) are required for effective TOC removal at high simazine doses by direct oxidation of ozone. Percent TOC removals (mineralization) were always lower than simazine removals indicating incomplete degradation of simazine and formation of some intermediate products.

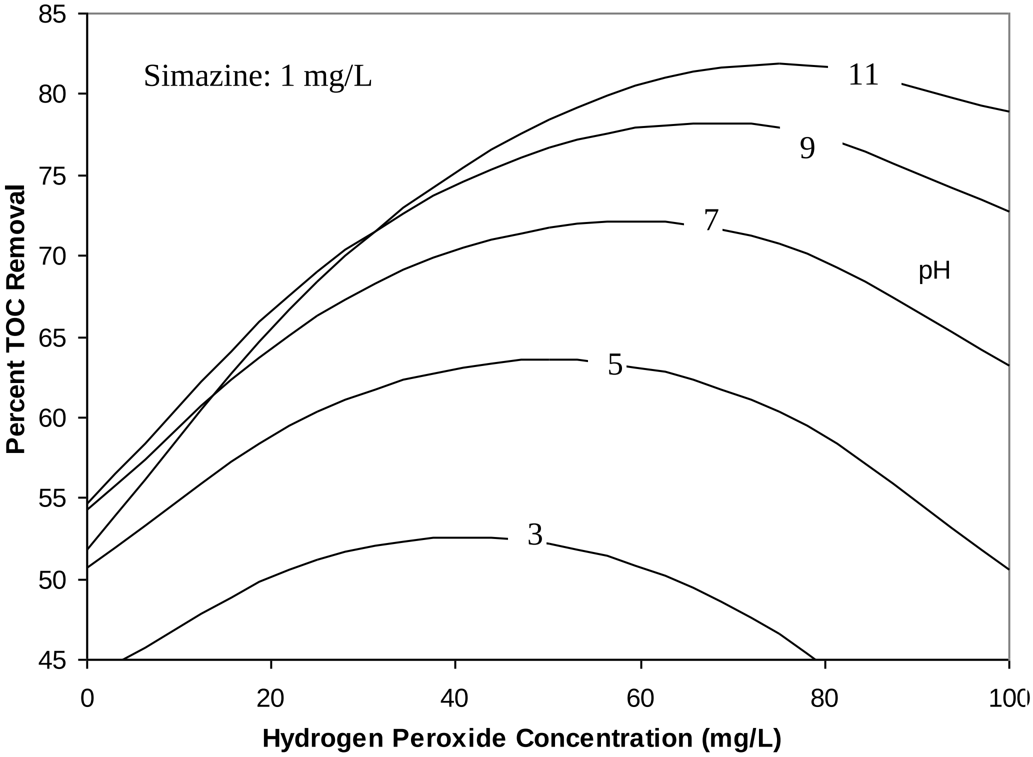

Figure 5.24 Variation of percent TOC removal with H_2O_2concentration at different initial pHs by the Ozone/H_2O_2 treatment (Reaction time: 60 min, Simazine: 1 mg/L, Ozone Dose: 45 mg/min).

Figure 5.24 depicts variation of percent TOC removal with peroxide doses and pH at a constant simazine dose of 1 mg/L. Percent TOC removal increased with increasing pH at all peroxide doses since simazine concentration was low (1 mg/L). The highest TOC removal (82%) was obtained at pH=11 with a peroxide dose of 70 mg/L due to indirect ozone oxidation at alkaline pHs. TOC removals increased with increasing peroxide dose up to a certain peroxide dose and then decreased with increasing peroxide concentrations. At low peroxide doses simazine mineralization was limited by the insufficient peroxide. At high peroxide doses, simazine mineralization was low due to hydroxyl ion scavenging effect of high peroxide doses. The optimum peroxide dose varied depending on the pH. At high pHs (alkaline conditions) the optimum peroxide dose yielding the highest percent TOC removal was 70 mg/L which decreased to 60, 50 and 40 mg/L at pHs 7, 5 and 3. At low pH levels soluble ozone concentration was high and the removal was by direct ozone oxidation requiring low peroxide concentrations. However, at alkaline pHs since the soluble ozon was low, TOC removal required higher concentrations of peroxide for oxidation by indirect mechanism. The ANOVA analysis (Table A. 12) indicated that pesticide and H_2O_2 doses (X_1, X_2, X_1X_2, X_1X_3, X_2X_3, X_1^2, X_2^2, X_3^2) were the two major factors affecting the TOC removal due to high ‘F’ ratios and low ‘p’ values. According to the ANOVA analysis, the initial pesticide concentration was the most important parameter affecting the mineralization (TOC removal) by the peroxone method. High initial simazine concentrations yielded low TOC removals.

An optimization program was used to determine the optimum doses of peroxide and pH maximizing the pesticide and TOC removals. At a low simazine dose of 0.5 mg/L, the optimal H_2O_2/pH/simazine dose yielding the highest TOC removal (82%) was 75/11/0.5 mg/L. At a simazine dose of 5 mg/L the optimum ratio was 50/3/5 mg/L yielding 53.3% TOC removal. High simazine doses yielded low TOC removals due to intermediate formation.

5.1.2.4 Comparision of Advanced Oxidation Processes for Simazine Removal

The optimal pesticide, H_2O_2 and Fe(II) doses resulting in the highest pesticide (simazine) and TOC removals were determined by using an optimization program and the results are presented in Table 5.12. In photo-Fenton treatment, the highest percent pesticide removal (100%) and mineralization (51%) were obtained with a H_2O_2/Fe(II)/diuron ratio of 50/30/3 (mg/L). However, at the same reaction conditions, 100% pesticide removal and 17% mineralization (TOC removal) were obtained by using the Fenton treatment in the absence of UV light. Maximum removal efficiencies in the Fenton’s reagent treatment were 100% for pesticide and 32% for TOC (mineralization) with a H_2O_2/Fe(II)/diuron ratio of 50/15/3 (mg/L). Apparently, the use of UV light along with the Fenton’s reagent improved the TOC removals considerably.

Table 5.12 Optimum levels of the variables maximizing the simazine and TOC removals by the Fenton, Photo-Fenton and peroxone treatments

Response	**Pesticide (X_1)**	**H_2O_2 (X_2)**	**Fe (II) (X_3)**	**Photo-Fenton**	**Fenton**	**Peroxone**
	Dose (mg/L)			**Efficiency (Y) %**		
Degradation	3	50	30	100.0	100	100
Mineralization	3	50	30	51	17	69

As compared to the experimental results obtained with the Fenton and photo-Fenton treatment, ozone/peroxide treatment yielded higher mineralization yields although there were no differences in simazine removals. This is due to use of ozone along with hydrogen peroxide. Simazine and TOC removals with the ozone/H_2O_2 treatment at peroxide dose of 50 mg/L and pH of 7 were 100% and 69%, respectively. Apparently, combined ozone and hydrogen peroxide treatment improved degree of mineralization of simazine. The optimal H_2O_2/pH/Simazine ratio resulting in the maximum pesticide (94%) and TOC removal (82%) was found to be 75/11/0.5 (mg/L). At high pesticide doses, simazine mineralization was incomplete yielding formation of intermediates, which were not completely mineralized to CO_2 and H_2O.

5.2 Kinetics of Pesticide Degradation

Time course of variations of pesticide concentrations for different experiments of the Box-Behnken design were drawn. Pesticide degradation by Fenton/photo-Fenton oxidation can be described by the following reaction,

$$\text{Pesticide} + H_2O_2 + \text{Fe(II)} \xrightarrow{h\nu} \text{Products} + H_2O + CO_2 \qquad \text{Eqn 5.18}$$

The initial reaction rates of pesticide degradation can be expressed in terms of initial pesticide, H_2O_2 and Fe(II) concentrations as follows,

$$R_o = (-dP/dt)_o = k\, P_o^{\alpha}\; HP_o^{\,\beta}\; Fe_o^{\,\gamma} \qquad \text{Eqn 5.19}$$

where, R_o is the initial rate of pesticide degradation (mg P L^{-1} min^{-1}); k is the rate constant; P_o, HP_o and Fe_o are the initial simazine, peroxide and Fe(II) concentrations, respectively (mg/L)

In linearized form, the rate equation can be written as follows

$$\text{Ln } R_o = \text{Ln } k + \alpha \text{ Ln } P_o + \beta \text{ Ln } HP_o + \gamma \text{ Ln } Fe_o \qquad \text{Eqn 5.20}$$

The coefficients of eqn 3.17 were determined by correlation with the experimental data.

5.2.1 Kinetic Studies on Pesticide Degradation by AOPs

5.2.1.1 Kinetics of Diuron Degradation by Fenton Reagent Treatment

Time course of variations of diuron concentrations for different experiments of the Box-Behnken design are depicted in Figure 5.25. Diuron concentration decreased steadily with time and the reaction was completed nearly in 5 minutes.

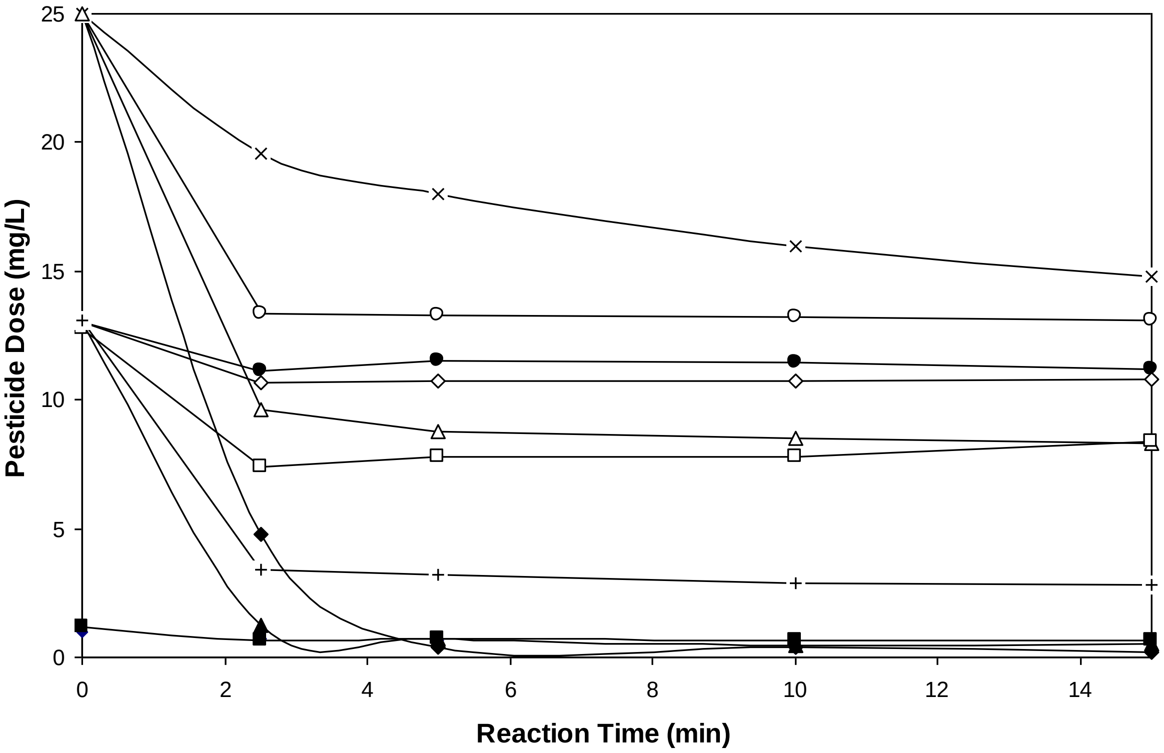

Figure 5.25 Time course of variations of diuron concentration for different experiments ■A$_1$, ○ A$_2$, ■A$_3$, ♦A$_4$, ■A$_5$, x A$_6$, ■A$_7$, Δ A$_8$, ◊ A$_9$, ● A$_{10}$, □ A$_{11}$, ▲A$_{12}$, + A$_{13}$

Table 5.13 Initial rates of diuron degradation by the Fenton treatment at different experimental conditions

Run No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
R_o (mg/L min^{-1})	0.071	2.348	0.164	4.917	0.1	1.4	0.202	3.24	0.448	0.3	1.005	2.452	1.968
R_o (calculated)	0.096	1.899	0.182	3.581	0.061	1.202	0.194	3.828	0.377	0.711	1.201	2.265	1.803
Diuron $_o$ (mg/L)	1	25	1	25	1	25	1	25	13	13	13	13	13
$(H_2O_2)_o$ (mg/L)	1.5	1.5	340	340	170.75	170.75	170.75	170.75	1.5	340	1.5	340	170.75
Fe(II)$_o$ (mg/L)	28.125	28.125	28.125	28.125	0.25	0.25	56	56	0.25	0.25	56	56	28.125

The initial rates obtained within the first five minutes are presented in Table 5.14 for every experiment of the Box-Behnken design. The experimental data was used for calculation of the initial rates for every experiment by using the equation Ro= - ΔD/Δt where Δt = 5 min. The initial rates were correlated with the initial diuron, peroxide and Fe(II) concentrations by using the Statistica 5.0 computer program to determine the exponents and the coefficient of the rate expression. The following constants were determined from the regression analysis.

$k = 0.045, \alpha = 0.926, \beta = 0.117, \gamma = 0.214 \qquad (R^2 = 0.97)$

Therefore, the rate equation takes the following form,

$$R_o = (-dD/dt)_o = 0.045 D_o^{0.926}\ HP_o^{0.117}\ Fe_o^{0.214} \qquad \text{Eqn 5.21}$$

The rate of diuron degradation is almost first-order (0.926) with respect to diuron concentration; almost zeroth-order with respect to peroxide and 0.21th order with respect to Fe(II) concentration. In agreement with our previous findings, the rate of diuron degradation is more affected from the diuron dose as compared to the Fe(II) and peroxide doses.

5.2.1.2 Kinetics of Diuron Degradation by Photo-Fenton Treatment

Time course of variations of diuron concentrations for different experiments of the Box-Behnken design are depicted in Figure 5.26. Diuron concentration decreased steadily with time and the reaction was completed nearly in 10 minutes.

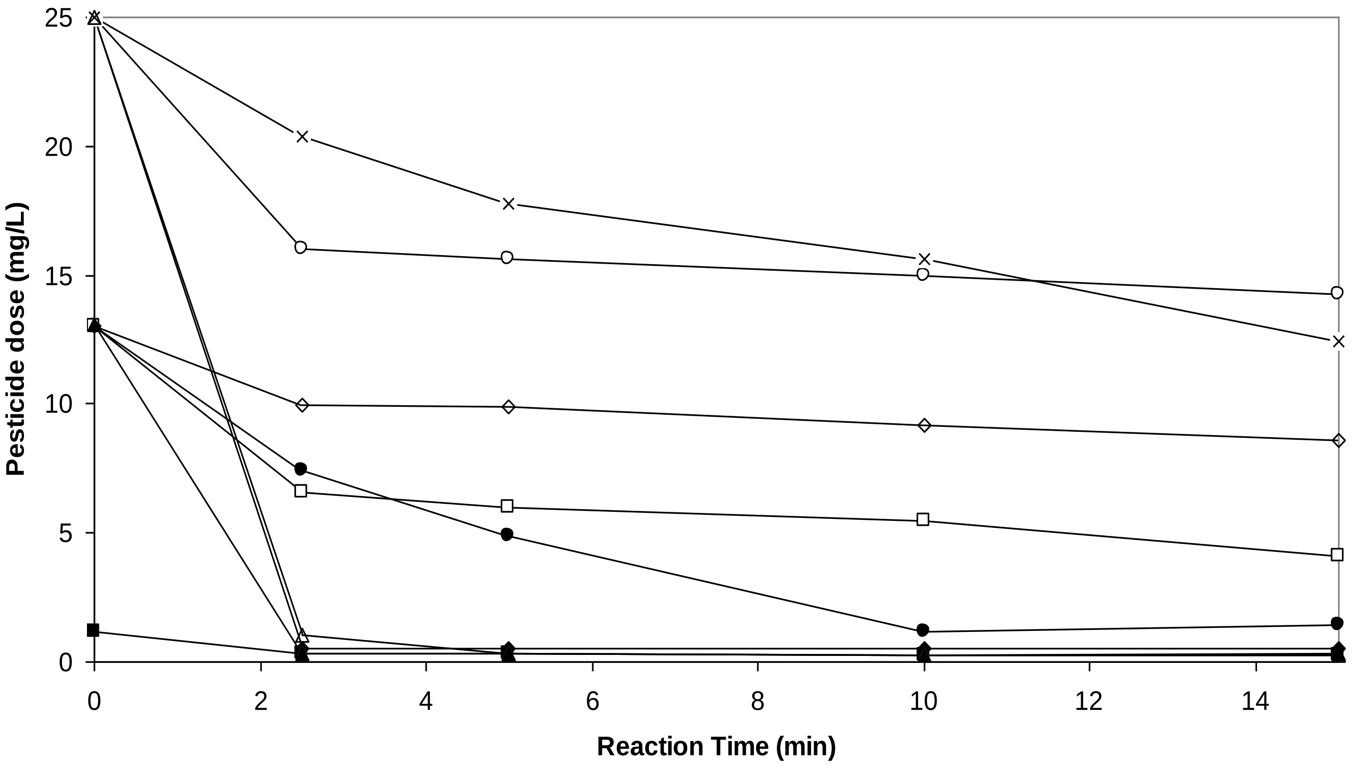

Figure 5.26 Time course of variations of diuron concentration for different experiments ■A$_1$, ○ A$_2$, ■A$_3$, ♦A$_4$, ■A$_5$, x A$_6$, ■A$_7$, Δ A$_8$, ◊ A$_9$, ● A$_{10}$, □ A$_{11}$, ▲A$_{12}$, ▲ A$_{13}$

Table 5.14 Initial rates of diuron degradation by the Photo-Fenton treatment at different experimental conditions

Run No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
R_o (mg/L min^{-1})	0.0535	1	0.0915	2.446	0.098	0.94	0.083	2.471	0.38	1.181	0.75	1.265	1.278
R_o (calculated)	0.052	1.082	0.109	2.274	0.072	1.490	0.104	2.171	0.421	0.884	0.613	1.288	1.117
Diuron $_o$ (mg/L)	1	25	1	25	1	25	1	25	13	13	13	13	13
$(H_2O_2)_o$ (mg/L)	1.5	1.5	340	340	170.75	170.75	170.75	170.75	1.5	340	1.5	340	170.75
$Fe(II)_o$ (mg/L)	28.125	28.125	28.125	28.125	0.25	0.25	56	56	0.25	0.25	56	56	28.125

The initial rates obtained within the first ten minutes are presented in Table 5.14 for every experiment of the Box-Behnken design. The experimental data were used for calculation of the initial rates for every experiment by using the equation $Ro=-\Delta D/\Delta t$ where $\Delta t = 10$ min. The initial rates were correlated with the initial simazine, peroxide and Fe(II) concentrations by using the Statistica 5.0 computer program to determine the exponents and the coefficient of the rate expression. The following constants were determined from the regression analysis.

$k = 0.039$, $\alpha = 0.943$, $\beta = 0.137$, $\gamma = 0.0695$ ($R^2 = 0.987$)

Therefore, the rate equation takes the following form,

$$R_o = (-dD/dt)_o = 0.039\ D_o^{0.943}\ HP_o^{0.137}\ Fe_o^{0.0695} \qquad \text{Eqn 5.22}$$

The rate of diuron degradation is almost first-order (0.943) with respect to simazine concentration. In agreement with our previous findings, the rate of diuron degradation is more affected from the pesticide dose as compared to the Fe(II) and peroxide doses.

5.2.1.3 Kinetics of Simazine Degradation by Fenton Reagent Ttreatment

Time course of variations of simazine concentrations for different experiments of the Box-Behnken design are depicted Figure 5.27. Simazine concentration decreased steadily with time and the reaction was completed in nearly 3 minutes.

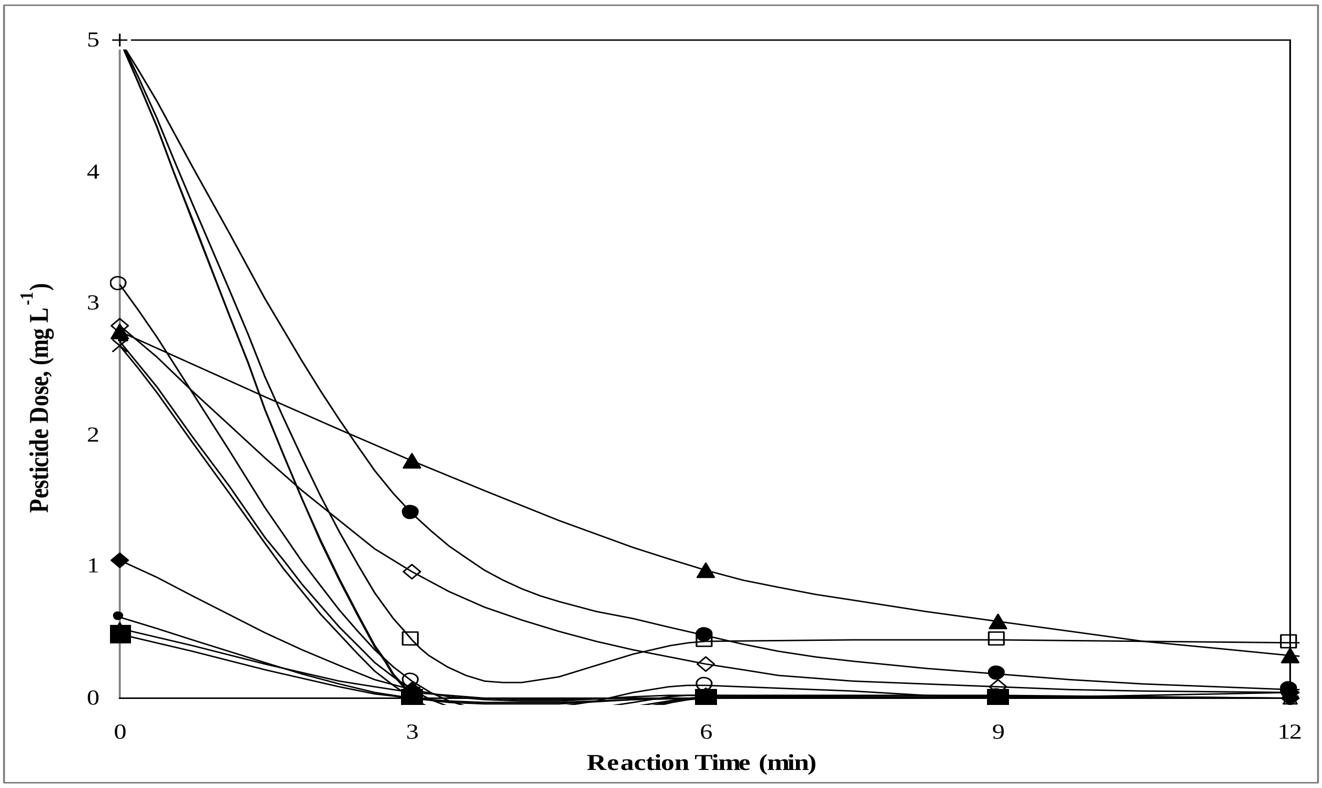

Figure 5.27 Time course of variations of simazine concentration for different experiments • A_1, □ A_2, Δ A_3, ♦A_4, ♦ A_5, ● A_6, ■ A_7, + A_8, ▲A_9, ◊ A_{10}, - A_{11}, x A_{12}, ○ A_{13}

Table 5.15 Initial rates of simazine degradation by the Fenton treatment at different experimental conditions

Run No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
R_o (mg/L min^{-1})	0.32	1.66	0.31	1.48	0.00	0.07	0.32	1.68	0.02	0.03	0.96	0.96	0.95
R_o (calculated)	0.146	1.323	0.136	1.237	0.000	0.000	0.341	3.095	0.000	0.000	1.834	1.716	0.710
Simazine$_o$ (mg/L)	0.5	5	0.5	5	0.5	5	0.5	5	2.75	2.75	2.75	2.75	2.75
$(H_2O_2)_o$ (mg/L)	10	10	100	100	55	55	55	55	10	100	10	100	55
Fe(II)$_o$ (mg/L)	15	15	15	15	0	0	30	30	0	0	30	30	15

The initial rates obtained within the first three minutes are presented in Table 5.15 for every experiment of the Box-Behnken design. The experimental data was used for calculation of the initial rates for every experiment by using the equation $Ro = - \Delta S/\Delta t$ where $\Delta t = 3$ min. The initial rates were correlated with the initial simazine, peroxide and Fe(II) concentrations by using the Statistica 5.0 computer program to determine the exponents and the coefficient of the rate expression. The following constants were determined from the regression analysis.

$k = 0.009$, $\alpha = 0.957$, $\beta = -0.03$, $\gamma = 1.297$ ($R^2 = 0.96$)

Therefore, the rate equation takes the following form,

$$R_o = (-dS/dt)_o = 0.009\ S_o^{0.957}\ HP_o^{-0.03}\ Fe_o^{1.297} \qquad \text{Eqn 5.23}$$

The rate of diuron degradation is almost first-order (0.957) with respect to simazine concentration; almost zeroth-order with respect to peroxide and 1.3rd order with respect to Fe(II) concentration. Excess peroxide concentrations were used due to low simazine concentrations yielding almost zero order kinetics with respect to peroxide concentration. In agreement with our previous findings, the rate of simazine degradation is more affected from the Fe(II) and simazine doses as compared to the peroxide dose.

5.2.1.4 Kinetics of Simazine Degradation by Photo-Fenton Treatment

Time course of variations of simazine concentrations for different experiments of the Box-Behnken design are depicted in Figure 5.28. Simazine concentration decreased steadily with time and the reaction was completed in nearly 3 minutes.

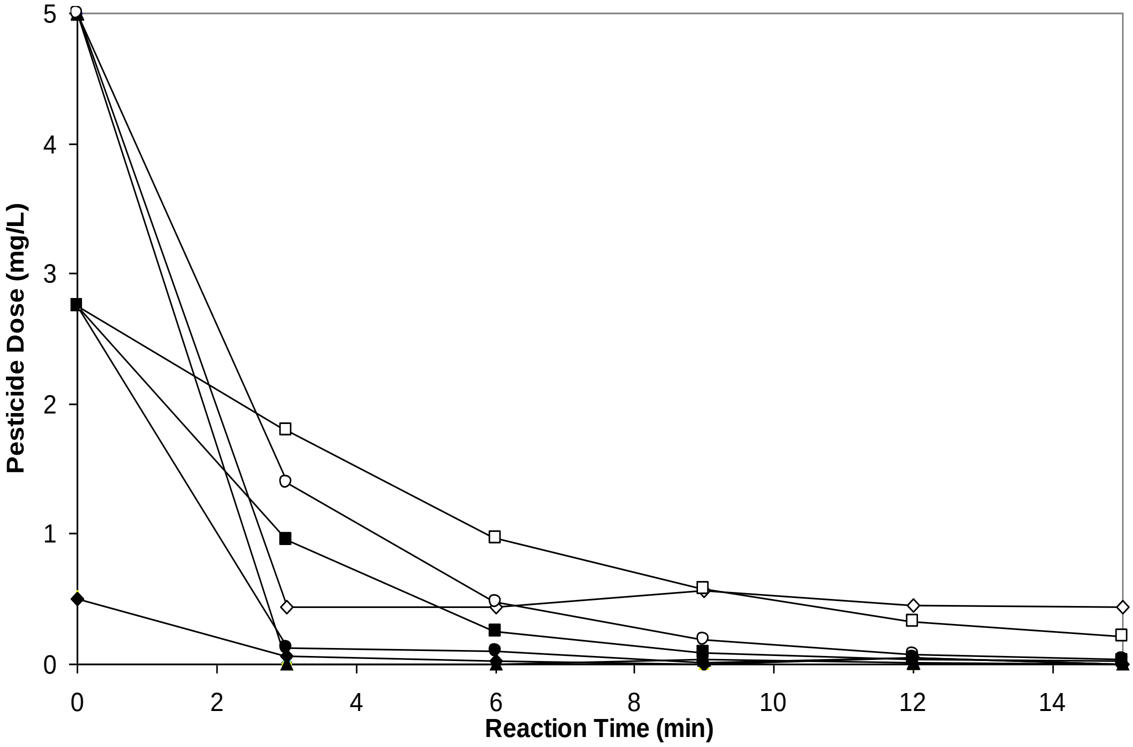

Figure 5.28 Time course of variations of simazine concentration for different experiments ▲A$_1$, ◊ A$_2$, ♦ A$_3$, ♦A$_4$, ▲ A$_5$, ○ A$_6$, ♦ A$_7$, ♦ A$_8$, ●A$_9$, ■ A$_{10}$, ● A$_{11}$, □ A$_{12}$, ● A$_{13}$

Table 5.16 Initial rates of simazine degradation by photo-Fenton treatment at different experimental conditions

Run No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
R_o (mg/L min^{-1})	0.21	1.52	0.16	1.66	0.33	1.51	0.16	1.67	0.61	0.62	0.895	0.89	0.64
R_o (calculated)	0.200	1.417	0.206	1.462	0.161	1.139	0.210	1.484	0.670	0.691	0.872	0.900	0.872
Simazine $_o$ (mg/L)	0.5	5	0.5	5	0.5	5	0.5	5	2.75	2.75	2.75	2.75	2.75
$(H_2O_2)_o$ (mg/L)	10	10	100	100	55	55	55	55	10	100	10	100	55
Fe(II)$_o$ (mg/L)	15	15	15	15	0	0	30	30	0	0	30	30	15

The initial rates obtained within the first three minutes are presented in for every experiment of the Box-Behnken design. The experimental data was used for calculation of the initial rates for every experiment by using the equation $Ro = -\Delta S/\Delta t$ where $\Delta t = 3$ min. The initial rates were correlated with the initial simazine, peroxide and Fe(II) concentrations by using the Statistica 5.0 computer program to determine the exponents and the coefficient of the rate expression. The following constants were determined from the regression analysis.

$k = 0.32, \quad \alpha = 0.85, \quad \beta = 0.0134, \quad \gamma = 0.033 \qquad (R^2 = 0.97)$

Therefore, the rate equation takes the following form,

$$R_o = (-dS/dt)_o = 0.32\, S_o^{0.85}\ HP_o^{0.0134}\ Fe_o^{\,0.033} \qquad \text{Eqn 5.24}$$

The rate of simazine degradation by the photo-Fenton treatment was strongly dependent on the simazine concentration. Fe(II) dose had a more pronunced effect on simazine degradation as compared to peroxide dose.

5.3 Pulp and Paper Wastewater Treatment by Advanced Oxidation Processes

5.3.1 Characterization of Pulp Mill Effluents

The treatability of pulp mill effluents by different advanced oxidation technologies under different conditions was investigated. Pulp mill effluent used in the experimental studies was obtained from the effluent of biological treatment unit of paper and pulp industry in Dalaman and Izmir. Composition of the wastewater as presented in Table 5.17 and Table 5.18 were determined using the standard methods of analysis (APHA, 1992).

Table 5.17 Characterization of pulp mill effluent I obtained from the pulp and paper industry located in Dalaman

Parameters	**Value**	**Parameters**	**Value**
pH	7.3	Phenol (mg/L)	3.2
COD (mg/L)	400	Chloride (mg/L)	1.6
BOD (mg/L)	240	ZSF	2
TOC (mg/L)	110	Tot. P. (mg/L)	0.9
SS (mg/L)	50	Tot. N. (mg/L)	12
Oil and grease (mg/L)	50	Detergents (mg/L)	1

Table 5.18 Characterization of pulp mill effluent II obtained from the pulp and paper industry located in İzmir

Parameters	**Value**	**Parameters**	**Value**
pH	7.08	Phenol (mg/L)	0.755
COD (mg/L)	592	AOX (mg/L)	1.936
BOD (mg/L)	240	Conductivity (μmhos/cm)	979
TOC (mg/L)	171	UV_{254} (m^{-1})	0.479

5.3.2 Treatment of Pulp and Paper Mill Effluent I using Fenton and Photo-Fenton Processes

5.3.2.1 Treatment by Fenton's Reagent

A number of experiments were carried out with the Fenton's reagent to determine the effects of initial hydrogen peroxide and Fe(II) concentrations, and pH on color, TOC and AOX removals from the pulp mill effluent.

5.3.2.1.1 Effects of Initial pH. pH of the treatment solution is an important factor for effective oxidation by the Fenton's reagent (Lin &.Peng, 1995). Batch oxidation experiments with the Fenton's reagent were carried out under acidic pH levels (pH 3-4-5) since higher pH values were reported to be unsatisfactory for oxidations of organic compounds by the Fenton's reagent (Hassan & Hawkyard, 2002; Hsueh *et al.*, 2005; Kim *et al.*, 2004). Fe(II) and H_2O_2 concentrations were constant at 5 mM and 50 mM, respectively and the reaction time was 30 minutes throughout the variable pH experiments. Table 5.19 shows variation of percent color and TOC removals from the wastewater with pH of the solution. Percent color and TOC removals increased with pH yielding 88.1% color and 84.6% TOC removals at pH 5, which was selected as the most suitable pH for the Fenton oxidation.

Table 5.19 Effects of initial pH on percent color and TOC removals from the pulp mill effluent by Fenton treatment. (H_2O_2 = 50 mM, Fe(II) = 5 mM, reaction time = 30 min)

pH	Color removal (%)	TOC removal (%)
3	66.6	63.4
4	71.1	78.8
5	88.1	84.6

5.3.2.1.2 Effects of Initial Fe(II) Concentration. Both the color and TOC removals from the wastewater were significantly improved with the addition of ferrous salt to H_2O_2 in our preliminary studies even at very low Fe(II) concentrations. Percent color and TOC removals increased to 81.3% and 85.6%, respectively when 1 mM Fe(II) was added to the H_2O_2 solution, while the color and TOC removals were around 24% and 5.1%, respectively with oxidation by H_2O_2 solution alone. Figure 5.29 depicts variations of percent color and TOC removals with the Fe(II) concentration at an initial pH of 5 and H_2O_2 concentration of 50 mM at the end of 30 min reaction time. Percent TOC removals varied between 85 and 89% depending on Fe(II) concentrations with a maximum at 5 mM Fe(II) concentration. However, percent color removal decreased from 83% to 73% when Fe(II) concentration increased from 2.5 mM to 10 mM due to inhibition effect of iron (Yang *et al.,* 1998; Bali & Karagözoglu, 2006). Therefore, an initial ferrous concentration of 2.5 mM was selected as the most suitable Fe(II) concentration yielding 83% color and 87% TOC removal and used in further experiments.

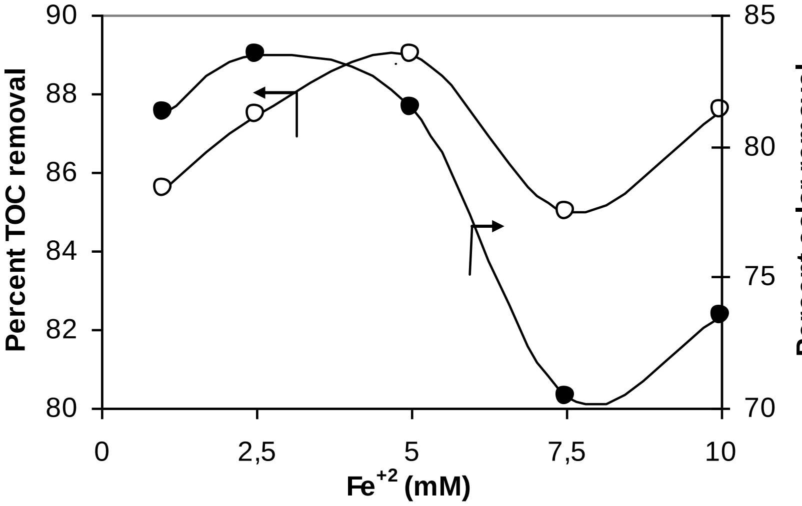

Figure 5.29 Variations of percent color and TOC removals with the Fe(II) concentration in Fenton treatment. (●) percent color removal and (○) percent TOC removal (pH 5, H_2O_2 50 mM, reaction time 30 min).

5.3.2.1.3 Effects of Initial H_2O_2 Concentration. H_2O_2 concentration was varied between 5 and 100 mM in this set of experiments while the Fe(II) concentration was constant at 2.5 mM. Variations of percent color and TOC removals from the pulp mill effluent with H_2O_2 concentrations are depicted in Figure 5.30. Percent TOC removals increased up to H_2O_2 concentration of 50 mM and then decreased with further increases. The highest percent color, TOC and AOX removals were 84.7%, 87.5% and 89%, respectively after 30 min of oxidation with a H_2O_2/Fe(II) molar ratio of 20. In another study, optimum molar ratio in Fenton oxidation was found as

20-40 (Solozhenko *et al.,* 1995; Casero *et al.,* 1997). Percent color and TOC removals decreased to 84.7% and 75.6%, respectively at a H_2O_2/Fe(II) molar ratio of 40. Therefore, the optimal molar ratio for H_2O_2/Fe(II) yielding the highest color and TOC removals was found to be 20 corresponding to 2.5 mM Fe(II) and 50 mM H_2O_2 concentrations.

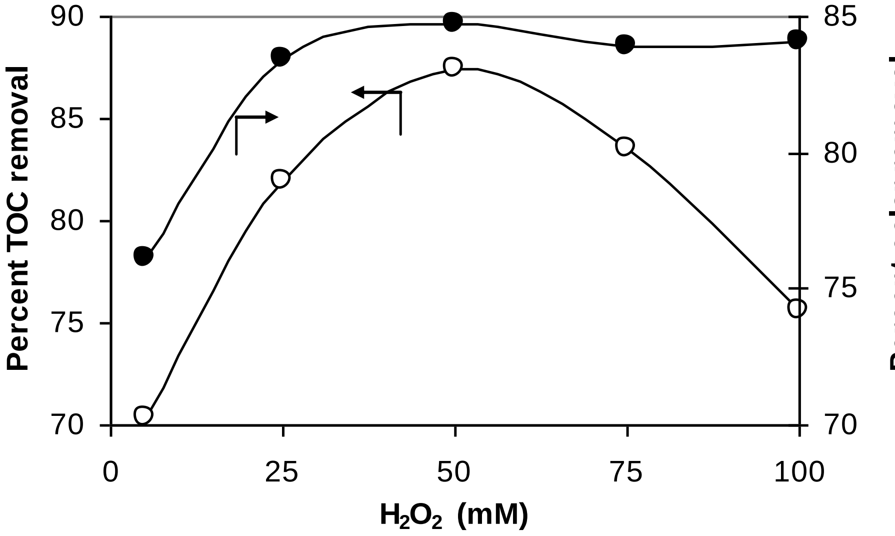

Figure 5.30 Variations of percent color and TOC removals with initial H_2O_2 concentration in Fenton treatment. (●) percent color removal and (○) percent TOC removal (pH 5, Fe(II) 2.5 mM, reaction time 30 min).

5.3.2.2 Photolysis by UV Irradiation

A number of experiments were carried out with the direct UV photolysis of pulp mill effluent to determine the effects of pH on color and TOC removals. These experiments were used as the reference for UV radiation combinations with hydrogen peroxide or Fenton's reagent used to improve the oxidation performance.

5.3.2.2.1 Effect of Initial pH. Acidic (pH 3), neutral (pH 7) and alkaline (pH 11) pH levels were used in order to determine the most suitable pH for direct UV photolysis in terms of percent color and TOC removals from the pulp mill effluent. Percent color removal from the wastewater decreased with increasing pH yielding 6.6% removal at initial pH of 3 and 0.8 % at pH values of 7 and 11. TOC and AOX removals also decreased with increasing pH. Maximum TOC (4.1%) and AOX

(17%) removals were also obtained at pH 3. Apparently, direct UV photolysis alone was not effective and suitable for color and TOC removals from the pulp mill effluent. Direct UV photolysis alone is known to decompose some organic molecules with very slow rates. However, UV radiation may be more effective when combined with H_2O_2, salts of particular metals (Fe(II)) or ozone. Therefore, a number of experiments with UV/H_2O_2 and UV/H_2O_2/Fe(II) were carried out to investigate the effects of hydrogen peroxide and Fe(II) on color and TOC removals from the pulp mill effluent.

5.3.2.3 UV/H_2O_2 Treatment

Ultraviolet photolysis combined with hydrogen peroxide (UV/H_2O_2) is one of the most widely used AOP technologies for degradation of toxic organics since this process may occur in nature itself.

5.3.2.3.1 Effects of Initial pH. Experiments were carried out at acidic (pH 3), neutral (pH 7) and basic (pH 11) pH levels at a constant initial a hydrogen peroxide concentration of 50 mM. Table 5.20 shows variation of percent color and TOC removals with the initial pH at constant hydrogen peroxide concentration of 50 mM and reaction time of 30 min. Percent color removal increased with pH resulting in 41% color removal at pH 11. However, percent TOC removals were not affected from pH changes yielding 8 to 11% TOC removals. Since the maximum color and TOC removals were obtained at pH 11, further experiments with UV/H_2O_2 were carried out at pH=11. In another UV/H_2O_2 oxidation study, pH 11 was also found to be the optimum pH for the treatment of phenol containing wastewater (Catalkaya *et al.*, 2003).

Table 5.20 Effects of initial pH on percent color and TOC removals from the pulp mill effluent by UV/H_2O_2 treatment. (H_2O_2 50 mM, reaction time 30 min)

pH	Color removal (%)	TOC removal (%)
3	12.3	8
7	22.3	10
11	41	11.1

5.3.2.3.2 Effects of Initial H_2O_2 Concentration. A set of experiments with UV/H_2O_2 were carried out with variable H_2O_2 concentration at pH of 11. Figure 5.31 depicts variation of percent color and TOC removals with the H_2O_2 concentration at constant initial pH of 11, reaction time of 30 min and hydrogen peroxide doses of between 5 and 100 mM. Addition of H_2O_2 to the UV irradiation improved both color and TOC removals considerably as compared to UV treatment alone even at low H_2O_2 concentrations. Percent color removal increased with increasing H_2O_2 concentration. Percent TOC removal slightly increased with H_2O_2 concentration up to 50 mM and then decreased with further increases in H_2O_2. The optimal H_2O_2 concentration was found to be 50 mM yielding 41% color and nearly 11% TOC removals. At high concentrations, hydrogen peroxide probably served as a free-radical scavenger (Buxton *et al.,* 1988; Alnaizy & Akgerman, 2000; Ashraf *et al.,* 2006).

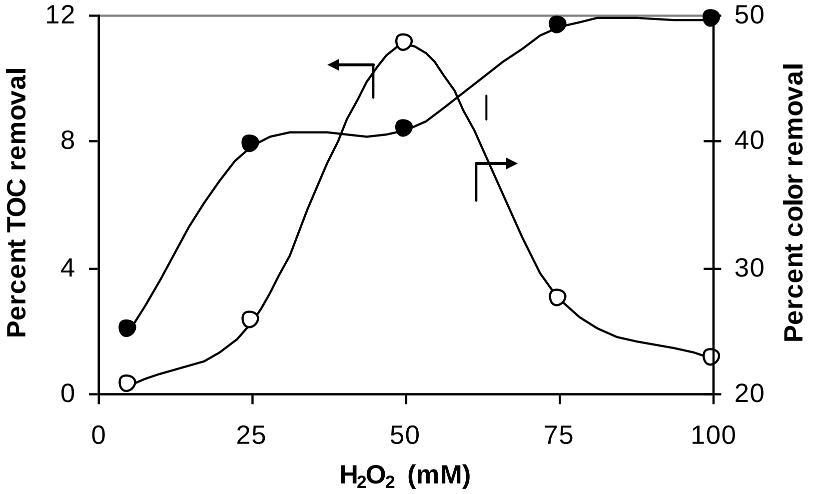

Figure 5.31 Variations of percent color and TOC removals with initial H_2O_2 concentration in UV/H_2O_2 treatment. (●) percent color removal and (○) percent TOC removal (pH 11, reaction time 30 min).

5.3.2.4 Photo-Fenton Treatment

According to literature reports on photo-Fenton oxidation, higher concentrations of $OH^{\bullet}$ radicals and Fe(II) can be attained with the UV/H_2O_2/Fe(II) treatment as compared to the conventional Fenton's reagent treatment. The reaction time needed for the photo-Fenton process is extremely low and depends on the operating pH and the concentrations of H_2O_2 and Fe (II). In UV/H_2O_2 treatment, maximum color removal was 41% at the optimal hydrogen peroxide concentration (50 mM) at the end of 30 min oxidation period. Besides, the maximum TOC and AOX removal efficiencies were only around 11% and 18.5%, respectively. Therefore, in order to shorten the required irradiation time and enhance the TOC and AOX removals, a number of experiments were carried out using the photo-Fenton treatment.

5.3.2.4.1 Effects of Initial pH. Experiments were carried out at three different pH levels of 3, 4 and 5 at constant initial hydrogen peroxide and Fe(II) concentrations of 50 mM and 5 mM, respectively for 30 min since higher pH levels were proven to be ineffective for the Fenton treatment (Hassan & Hawkyard, 2002; Hsueh *et al.,* 2005; Kim *et al.,* 2005). Table 5.21 summarizes the experimental results. Color removal was not affected from pH changes (66-67%). However, percent TOC removals increased with pH yielding 79% TOC removal at pH 5. Therefore, pH 5 was considered to be the optimal and further photo-Fenton experiments were carried out at pH 5.

Table 5.21 Effects of initial pH on percent color and TOC removals from the pulp mill effluent by the photo-Fenton treatment. (H_2O_2 50 mM, Fe(II) 5 mM, reaction time 30 min)

pH	**Color removal (%)**	**TOC removal (%)**
3	66	56.8
4	67.4	77.7
5	66.8	79.2

5.3.2.4.2 Effects of Initial Fe(II) Concentration. In order to investigate the effect of ferrous ions on the performance of the photo-Fenton treatment, experiments were carried out at a constant H_2O_2 concentration of 50 mM, pH of 5, reaction time of 30 min and temperature of 25 ± 2°C at different Fe(II) concentrations between 1 and 10 mM.

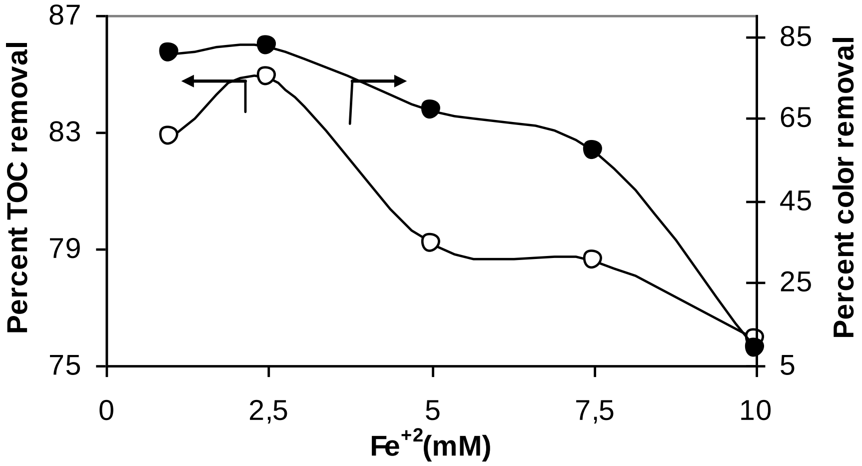

Figure 5.32 Variations of percent color and TOC removals with initial Fe(II) concentration in the photo-Fenton treatment. (●) percent color removal and (○) percent TOC removal (pH 5, H_2O_2 50 mM, reaction time 30 min).

Variations of color and TOC removals with the Fe(II) concentration in the photo-Fenton treatment are depicted in Figure 5.32. Addition of Fe(II) to UV/H_2O_2 considerably enhanced color and TOC removals even at very low Fe(II) concentrations. Percent color and TOC removals after 30 min reaction time were around 41% and 11%, respectively with UV/H_2O_2 treatment which increased up to 80.6% and 82.8% when 1 mM Fe(II) was added to the reaction medium. When Fe(II) concentration was increased to the optimum concentration of 2.5 mM, 85% TOC removal was achieved even after 5 min of irradiation. Therefore, photo-Fenton method improved both the extent and the rate of TOC and color removals as compared to the UV/H_2O_2 treatment. Both percent TOC and color removals were maximum at Fe(II) concentration of 2.5 mM and decreased with increasing Fe(II) at higher concentrations. At high Fe(II) concentrations such as 10 mM, the initial hydroxyl radicals originated from the decomposition of H_2O_2 were probably scavenged yielding low TOC removals (Yang *et al.*, 1998; Bali & Karagözoglu, 2006).

5.3.2.4.2 Effects of Initial H_2O_2 Concentration. Figure 5.33 depicts variation of percent color and TOC removals with the H_2O_2 concentration at a constant Fe(II) concentration of 2.5 mM, pH 5 at the end of 30 min reaction time. Hydrogen peroxide concentration was varied between 5 and 100 mM.

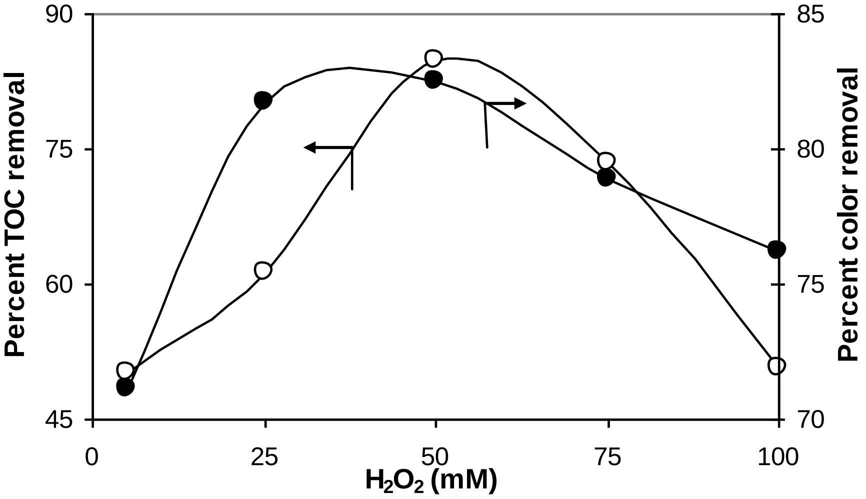

Figure 5.33 Variations of percent color and TOC removals with initial H_2O_2 concentration in the photo-Fenton treatment. (●) percent color removal and (○) percent TOC removal. (pH 5, Fe(II) 2.5 mM, reaction time 30 min)

The highest percent color and TOC removals were obtained at H_2O_2 concentration of 50 mM which decreased with further increases in H_2O_2 dose. Percent color and TOC removals with UV/H_2O_2 treatment were around 41% and 11% after 30 min of irradiation which increased up to 82.3 % and 85 %, respectively at 50 mM H_2O_2 and 2.5 mM Fe(II) or at a H_2O_2/Fe(II) molar ratio of 20 after 5 min of irradiation. At a H_2O_2 dose of 100 mM or H_2O_2/Fe(II) molar ratio of 40, hydrogen peroxide adversely affected the UV treatment because of high rates of free-radical production. Color and TOC removals obtained at a H_2O_2/Fe(II) ratio of 40 after 30 min of irradiation was approximately 76.2% and 50.7%, which were much less than those obtained with a peroxide /Fe ratio of 20. The highest color, TOC and AOX removals of 82.3%, 85% and 93.5% were obtained at H_2O_2 concentration of 50 mM and Fe(II) concentration of 2.5 mM or at a H_2O_2/Fe(II) ratio of 20.

5.3.2.5 Ozone Treatment

Ozone is a strong oxidizing agent with oxidation mechanism either by direct reaction with dissolved compounds or by the generated radicals depending on the pH of solution (Perez *et al.,* 2002b). The ozone dosage applied to the pulp mill effluent depends on total color and TOC content (Ince *et al.,* 1997) and also on the presence of toxic metabolites (Gahr *et al.,* 1994). For effective ozone treatment, continuous ozonation is required due to short half-life (20 min) of ozone. For this reason, the cost of continuous ozone production is one of the major drawbacks in ozone treatment. Stability of ozone is also affected by the presence of salts, pH and temperature. Alkaline solutions accelerate ozone decomposition (Xu & Lebrun, 1999). Ozone treatment was proven to be rather inefficient for the reduction of chemical oxygen demand (COD) or total organic carbon (TOC), usually not exceeding 50% and 40% removals, respectively (Arslan & Balcioglu, 2000). Therefore, ozone treatment alone can only be used for partial oxidation of organic compounds, while it is expected to be effective for color removal.

5.3.2.5.1 Effects of Initial pH. To investigate the effects of pH on color and TOC removals, the pH of the pulp mill effluent was adjusted to 3, 7 and 11 with an ozone feeding rate of 4.7 g/h. Variations of percent color, TOC removals with time by ozone treatment are depicted in Figure 5.34, for different initial pH values. Almost complete color removals were observed for all tested pHs. Percent TOC removal at pH 7 was much higher than those obtained at pH 3 and 11. Percent color removal at pH 11 was 81% which increased to 91% at pH 7, while color removal at pH 3 was 95% at the end of 30 minutes. The highest percent TOC and color removals were 29% and 91%, respectively at pH 7. Percent AOX removal (62.4%) at pH 7 was also higher than those obtained at pH 3 and 11. These observations indicated that COD removal could be simply achieved via both reaction pathways of ozone whereas the reaction pH had to be at least 7 to enhance decomposition by ozone for high TOC, color and AOX removals. For this reason, further ozonation experiments were carried out at pH 7. In another ozonation study, optimum pH value was also found to be 7 for the treatment of pharmaceutical wastewater (Balcıoglu & Otker, 2003).

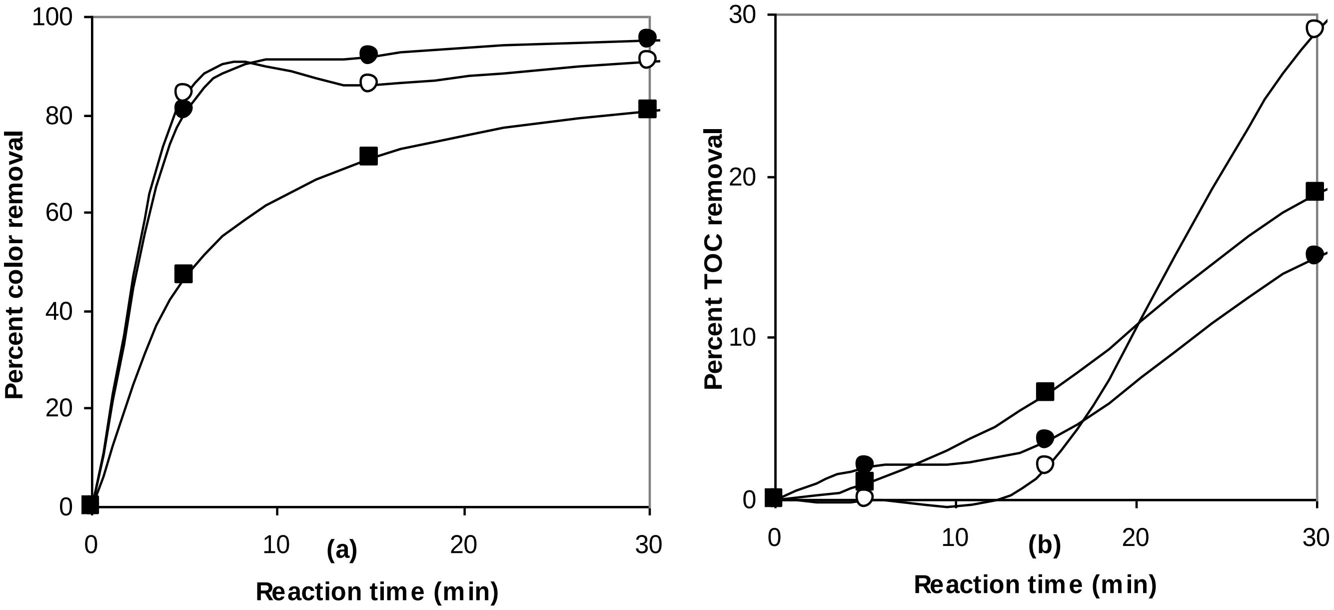

Figure 5.34 Variations of (a) percent color and (b) percent TOC removals with time at different initial pH levels in ozone treatment. pH: (●) 3, (○) 7 and (■) 11 (Ozone 4.7 g/h, reaction time 30 min).

5.3.2.5.2 Effects of Ozone Feeding Rate. Ozone concentration and therefore ozone feeding rate to the reactor is an important variable affecting the rate and the extent of oxidation. Ozone was fed to the reactor with a rate of 4.7-11.9 g/h while the pH of the wastewater was kept at pH 7 for a reaction period of 30 minutes.

Figure 5.35 depicts variations of percent color and TOC removals by ozonation at three different ozone feeding rates.

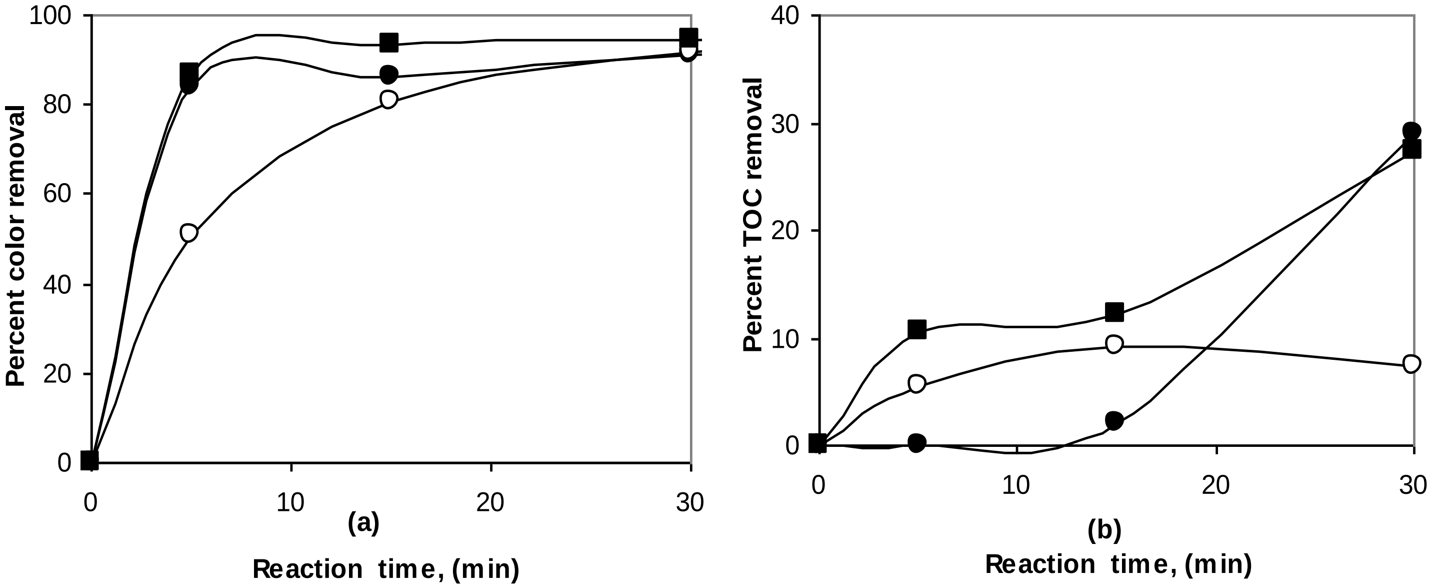

Figure 5.35 Variations of (a) percent color and (b) percent TOC removals with time for different ozone feeding rates. Ozone (g/h): (●) 4.7, (○) 5.1 and (■) 11.9 (pH 7, reaction time 30 min).

Percent color and TOC removals were not significantly affected by the increases in ozone feeding rate. Percent color removals were nearly 93% at the end of 30 minutes of reaction time independent from the ozone dose. The highest TOC removal of 29% was obtained with the lowest ozone feeding rate of 4.7 g/h which was slightly higher than that obtained with the highest ozone feeding rate of 11.9 g/h. However, final percent AOX removal increased from 62.4% to 80.2% when ozonation rate was increased from 4.7 to 11.9 g/h. Therefore, the lowest ozonation rate (4.7 g/h) was found to be satisfactory for color and TOC removals, although AOX removals required much higher rates of ozonation. In another experimental study for the treatment of pulp mill effluent, 12% TOC removal was obtained by ozonation (Freire *et al.*, 2000). Zhou and Smith showed that the ozonation of biologically pretreated pulp mill effluents resulted in up to 80% reduction in colour and 60% reduction in adsorbable organic halogens (AOX) (Zhou & Smith, 1997b). In addition, color, COD and AOX removals of 95%, 50% and 67% were reported for the treatment of pulp mill effluent by Mobius & Cordes-Talle, (1996). Percent AOX removal was reported to be 80% by Hostachy *et al.*, (1997) using ozone treatment.

As compared with the photo-Fenton treatment, which yielded 82.5% color removal, ozonation has improved the color removal to 91% while the TOC removal decreased from 82.8% to 29% by ozonation. Therefore, ozone treatment was found to be relatively inefficient for the removal of total organic carbon (TOC) or mineralization as compared to the photo-Fenton treatment.

5.3.2.6 Peroxone Treatment (O_3/H_2O_2)

Combination of ozone with hydrogen peroxide is considered to be a promising alternative for refractory organics removal from wastewater (Masten & Davis, 1994). In order to improve the percent color and TOC removals, ozone was supplied to the pulp mill effluent in the presence of H_2O_2 up to 100 mM concentration.

5.3.2.6.1 Effects of Initial pH. Peroxone treatment of the pulp mill effluent was realized at three different pH levels of 3, 7 and 11 with an ozone feeding rate of 4.7 g/h.

Figure 5.36 depicts variations of percent color and TOC removals with time by the peroxone treatment at three different pH levels. Color removals at the end of 30 minutes varied between 73.4 and 95% depending on the pH. Percent TOC removals increased from 14% to 14.3% and further to 16% when pH was increased from 3 to 7 and further to 11. The ozone decomposition rate increased with increasing pH, sincee

H_2O_2 was dissociated to HO_2^- ions. For this reason, pH 11 was considered to be the most suitable pH for the peroxone treatment.

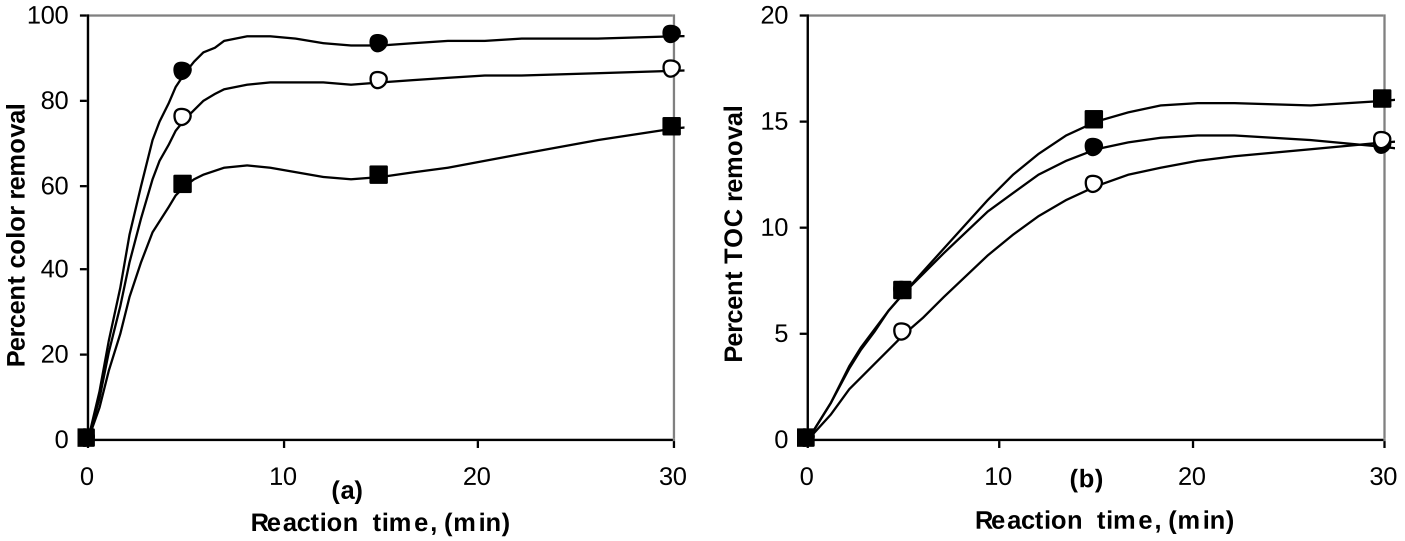

Figure 5.36 Variations of (a) percent color and (b) percent TOC removal with time at different initial pH levels in the peroxone treatment. pH: (●) 3, (○) 7 and (■) 11. (Ozone 4.7 g/h, reaction time 30 min).

In hydrogen peroxide treatment alone, percent color and TOC removals were 24% and 5%, respectively at the end of 30 minutes at pH 11 with a H_2O_2 dose of 50 mM. Color and TOC removals increased to 73.4% and 16% by the peroxone treatment at pH 11 with a H_2O_2 dose of 50 mM at the end of 30 minutes indicating the significant advantage of using ozone along with H_2O_2 in the peroxone treatment.

5.3.2.6.2 Effects of Initial H_2O_2 Concentration. Hydrogen peroxide concentrations were varied between 5 and 100 mM in the peroxone treatment of the paper mill effluent while the ozone feeding rate was 4.7 g/h at pH of 11 for a reaction period of 30 minutes. Variations of percent color and TOC removals with time are depicted in Figure 5.37 for different H_2O_2 concentrations. Percent color removal varied between 69 and 81.2% with the highest percent removal at 5 mM H_2O_2 concentration at the end of 30 minutes. Percent TOC removal showed fluctuations with time and the highest (34.7%) percent removal was obtained at 100mM H_2O_2 dose while TOC removal (30.9%) at 5 mM H_2O_2 was comparable with that. The fluctuations in TOC concentrations with peroxone treatment (Figure 5.37) was probably due to release of soluble compounds by ozone from suspended solids as stated by Fonteniera *et al.*, (2006).

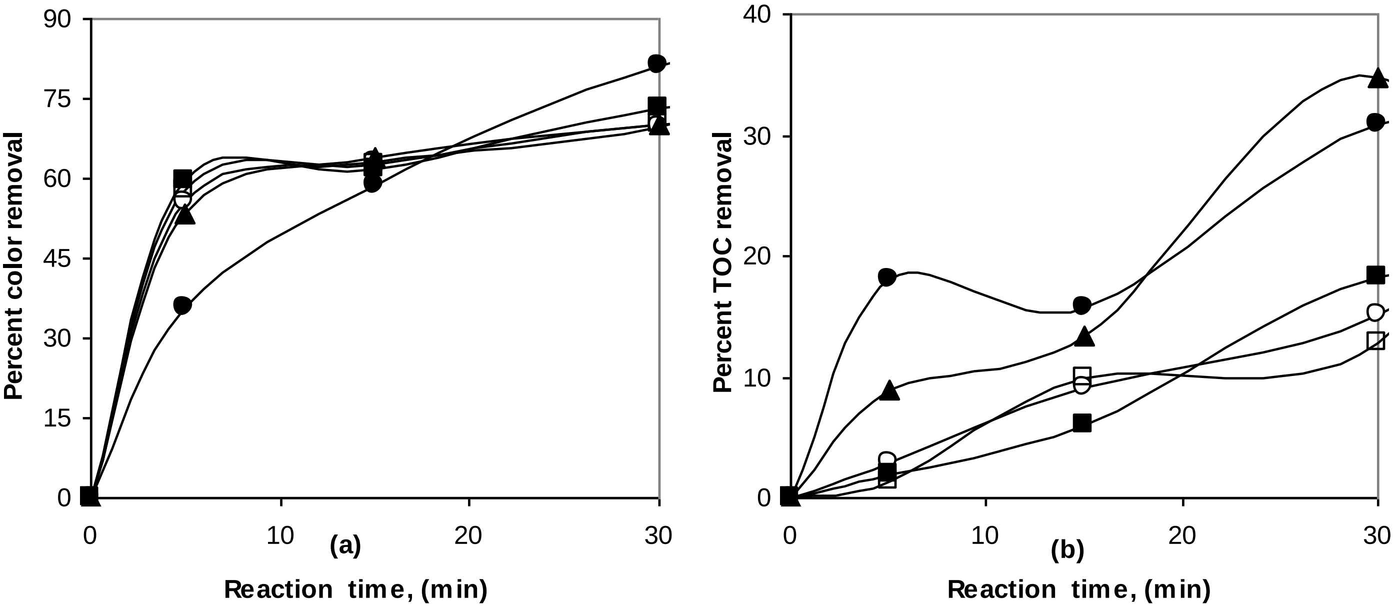

Figure 5.37 Variations of (a) percent color and (b) percent TOC removals with time at different initial H_2O_2 concentrations in the peroxone treatment. H_2O_2 (mM): (●) 5 (○) 25 (■) 50 (□) 75 and (▲) 100. (pH 11, Ozone 4.7 g/h, reaction time 30 min)

On the basis of those results the most suitable H_2O_2 dose was found to be 5 mM with an optimum peroxide/ozone ratio of 1.06 maximizing the reaction rate. Maximum percent color, TOC and AOX removals of 81.2%, 30.9% and 95% were obtained with 5 mM H_2O_2, 4.7 g/h ozone feeding rate at pH 11 at the end of 30 minutes. Murphy *et al.*, (1993) studied the removal of colour from three effluent streams from a pulp and paper mill and reported that the O_3/H_2O_2 process could achieve colour removal up to 85% from the caustic extract stream, up to 90% from the acidic stream, and up to 50% from the final effluent.

Peroxone treatment did not significantly improve percent color and TOC removals even at the highest hydrogen peroxide dose as compared to the ozone treatment. Color and TOC removals were around 81% and 19%, respectively after 30 min of ozonation at pH 11 while only 81.2% color and 30.9% TOC removals were obtained with the peroxone treatment in the presence of 5 mM H_2O_2 at pH 11. Therefore, peroxone treatment improved TOC removal slightly as compared to the ozone treatment alone.

5.3.2.7 Comparison of Advanced Oxidation Processes (AOPs) for Pulp Mill Effluent Treatment

Table 5.22 summarizes the conditions and the performances of the AOPs used for treatment of the paper mill wastewater. Hydrogen peroxide treatment alone resulted in very low TOC (5.1%), AOX (34%) and color (24%) removals at an extreme pH of 11. Fenton's reagent (H_2O_2/Fe(II)) yielded very high color (85%), TOC (88%) and AOX (89%) removals at a pH of 5 which makes this treatment more favorable among the others tested.

Table 5.22 Comparison of paper mill effluent treatment performances of different advanced oxidation processes at the end of 30 minutes of treatment

Post-treatment method	**pH**	**H_2O_2 (mM)**	**Fe (II) (mM)**	**O_3 (g/h)**	**Color Removal (%)**	**TOC Removal (%)**	**AOX Removal (%)**
H_2O_2	11	50	–	–	24	5.1	34
H_2O_2/Fe(II)	5	50	2.5	–	84.6	88	89
UV	3	–	–	–	6.6	4.1	17
UV/H_2O_2	11	50		–	41	11.1	18.5
UV/H_2O_2/Fe(II)	5	50	2.5	–	82.5	82.8	94
UV/H_2O_2/Fe(II)*	5	50	2.5	–	82	85	93
O_3	7	–	–	4.7	91	29	62.4
O_3/H_2O_2	11	5	–	4.7	81.2	30.9	95

* Percent removals at the end of 5 min reaction time

UV treatment alone is an ineffective treatment method yielding low color, TOC and AOX removals. Performance of the UV/H_2O_2 treatment was also unsatisfactory yielding low color, TOC and AOX removals. Percent removals obtained with the photo-Fenton treatment were comparable with those obtained with the Fenton treatment. Photo-Fenton treatment yielded high TOC (85%), color (82%) and AOX (93%) removals within 5 minutes indicating the effectiveness of this treatment.

However, the contribution of UV radiation to the Fenton treatment was marginal. Ozone treatment alone was not as effective as the Fenton treatment yielding low TOC and AOX removals. Peroxone treatment improved the AOX removal, however reduced the color and TOC removals as compared to the ozone treatment alone. On the basis of the experimental results summarized in Table 5.22, either Fenton or photo-Fenton treatment can be used for effective removal of color, TOC or AOX from the paper mill wastewater. However, photo-Fenton treatment seems to be more advantageous requiring much less reaction times and therefore smaller reactor volumes as compared to the Fenton treatment.

5.3.3 Treatment of Pulp and Paper Mill Effluents II using UV/TiO_2 and UV/TiO_2/H_2O_2

5.3.3.1 Treatment by UV/TiO_2

Semiconductor materials used in environmental applications include titanium oxide (TiO_2), strontium titanium trioxide and zinc oxide (ZnO). TiO_2 is generally preferred for use in commercial AOP applications because of its high level of photoconductivity, availability, low level of toxicity, low cost and relatively high chemical stability (Konstantinou & Albanis, 2004).

The resulting hydroxyl radicals are strong oxidizing agents and can oxidize most of the organic compounds (Maurino *et al.*, 1999). Major drawback of photo-catalytic processes is the need to remove the catalyst after treatment and the limited surface area of semiconductors. In order to investigate the effects of both pH and titanium dioxide concentrations on TOC and toxicity removals, a number of experiments were carried out with UV/TiO_2 treatment.

5.3.3.1.1 Effects of Initial pH. Acidic (pH 3), neutral (pH 7) and alkaline (pH 11) pH levels were used in order to determine the most suitable pH for UV/TiO_2 treatment in terms of percent TOC and toxicity removals from the pulp mill effluent. TiO_2 concentration was constant at 1 g/L and the reaction time was 60 minutes throughout this set of experiments. Figure 5.38 shows variation of percent TOC and toxicity removals at different pH levels.

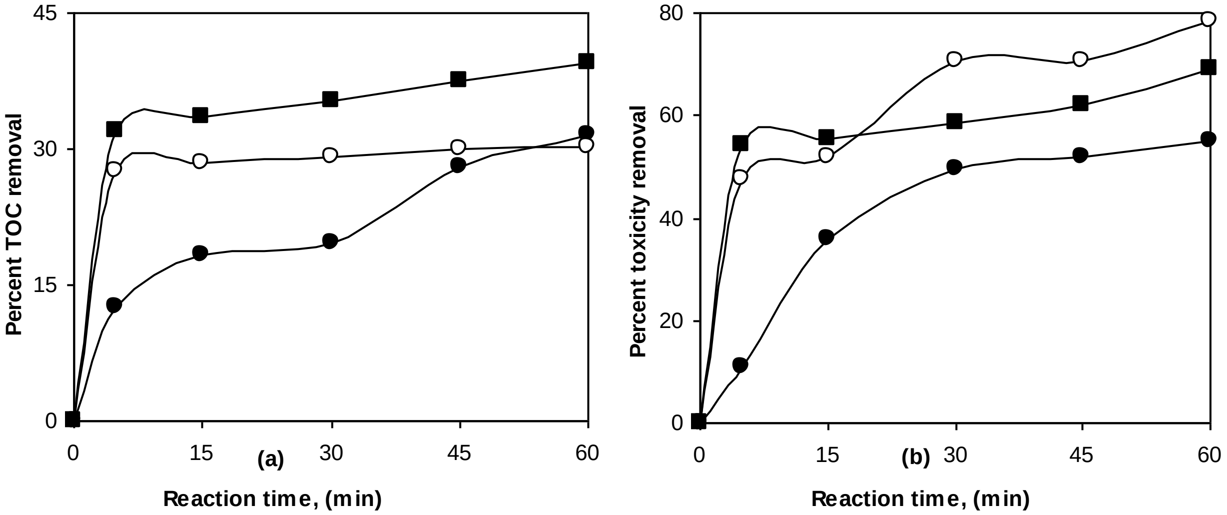

Figure 5.38 Variations of percent TOC (a) and toxicity (b) removals with the initial pH in UV/TiO_2 treatment at 1 g/L TiO_2. pH: ● 3, ○ 7, ■ 11

Maximum percent toxicity removal (78.34 %) was observed at pH 7 at the end of 60 minutes. TOC removal was 30.12% at pH 7. Decomposition of pulp mill effluent by photocatalytic treatment was represented with the first-order kinetics by other investigators (Chang *et al.*, 2004).

Table 5.23 First-order rate constants (k_1) for TOC and toxicity removals from the pulp mill effluent by UV/TiO_2 treatment at different pH values. (TiO_2 1 g/L)

UV/TiO_2 Treatment	**k_1 (min^{-1})**	
	TOC	**Toxicity**
pH 3	0.027	0.023
pH 7	0.064	0.129
pH 11	0.077	0.156

Table 5.23 summarizes the calculated first-order rate constants for removal of TOC and toxicity using UV/TiO_2 treatment for the first 5 minutes. The results clearly indicated that decreasing initial pH adversely affected the first order reaction rate constant (k_1) which decreased from 0.077 min^{-1} to 0.027 min^{-1} when the initial pH was decreased from 11 to 3 for TOC removal. High TOC removals at alkaline pH 11 can be explained by the increased amount of •OH ions on the surface of TiO_2 which combined with h_{VB+} to produce more •OH radicals (Poulios & Tsachpinis, 1999).

Percent toxicity removal at the end of 60 min was higher at pH 7 as compared to the other pH levels tested.

5.3.3.1.2 Effects of Initial TiO_2 Dose. A set of experiments with UV/TiO_2 were carried out with variable TiO_2 concentration at pH 11. Figure 5.39 depicts variation of percent TOC and toxicity removals with the TiO_2 concentration at a constant initial pH of 11 and titanium dioxide doses of between 0.25 g/L and 2 g/L at the end of 60 min reaction time. After addition of TiO_2 and turning on the UV lamp, a sharp TOC decrease was observed in five minutes. TOC removal after 5 minutes of reaction time was negligible at all TiO_2 concentrations and the effluent pH remained almost constant.

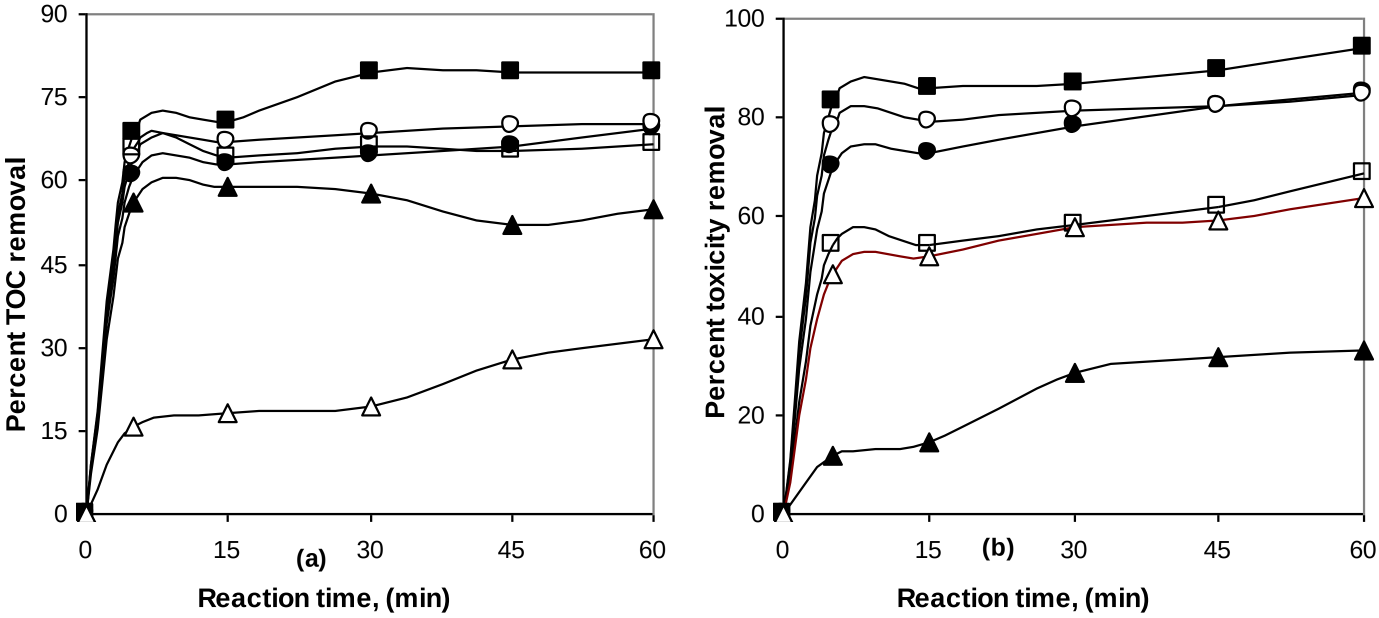

Figure 5.39 Variations of percent TOC (a) and toxicity (b) removals with initial TiO_2 concentration in UV/TiO_2 treatment at pH 11. TiO_2 (g/L): ● 0.25, ○ 0.50, ■ 0.75, □ 1, ▲ 2, Δ 0.

The reaction rate for the UV/TiO_2 treatment was reported to be fast so that the treatment can be completed within a short period of time (Lanzalunga & Bietti, 2000; Tanaka *et al.*, 2000). The reason for negligible TOC removal after the first five minutes of reaction time may be because of the fact that adsorption of the organic matter on the catalyst surface may form a layer hindering degradation by reducing the O_2 supply to the surface of TiO_2. It is well known that high TiO_2 concentrations may inhibit the photo-catalytic oxidations (Legrini *et al.*, 1993; Chen & Ray, 1998).

Percent TOC and toxicity removals sharply increased with TiO_2 concentration up to 0.75 g/L and then decreased with further increases in TiO_2. Excessive TiO_2 dosages above the optimum level cause a shadowing effect, which interferes with the transmission of UV light so that the formation of electron hole pairs cannot effectively occur resulting in low TOC and toxicity removals. Addition of TiO_2 to the UV system improved both TOC and toxicity removals considerably as compared to UV treatment alone even at low TiO_2 concentrations. When UV treatment was used alone without TiO_2, only 31.6% of TOC and 63.7% of toxicity were removed within 60 min of reaction time (Figure 5.39). The results indicated that the UV/TiO_2 treatment was quite effective with 0.75 g/L TiO_2, and at pH 11 resulting in 79.6% TOC and 94.2% toxicity removals.

Table 5.24 First-order rate constants (k_1) for TOC and toxicity removals from the pulp mill effluent by UV/TiO_2 treatment at different TiO_2 concentrations. (pH 11)

UV/TiO_2 Treatment	**k_1 (min $^{-1}$)**	
	TOC	**Toxicity**
UV only (TiO_2 = 0)	0.034	0.132
TiO_2 (0.25 g/L)	0.188	0.240
TiO_2 (0.5 g/L)	0.204	0.305
TiO_2 (0.75 g/L)	0.233	0.359
TiO_2 (1 g/L)	0.215	0.156
TiO_2 (2 g/L)	0.165	0.025

As presented in Table 3, the first-order rate constant (k_1) for TOC removal increased from 0.034 min^{-1} to 0.233 min^{-1} when TiO_2 was increased from 0 to 0.75 g/L. The first-order rate constant (k_1) for toxicity removal increased to 0.132 min^{-1} and 0.359 min^{-1} when only ultraviolet irradiation and addition of 0.75 g/L TiO_2 in UV irradiation were used, respectively. 50% TOC removal and 50% toxicity reduction were obtained using 42 mg/L TiO_2 in UV/TiO_2 process by Yeber *et al.*, (2000).

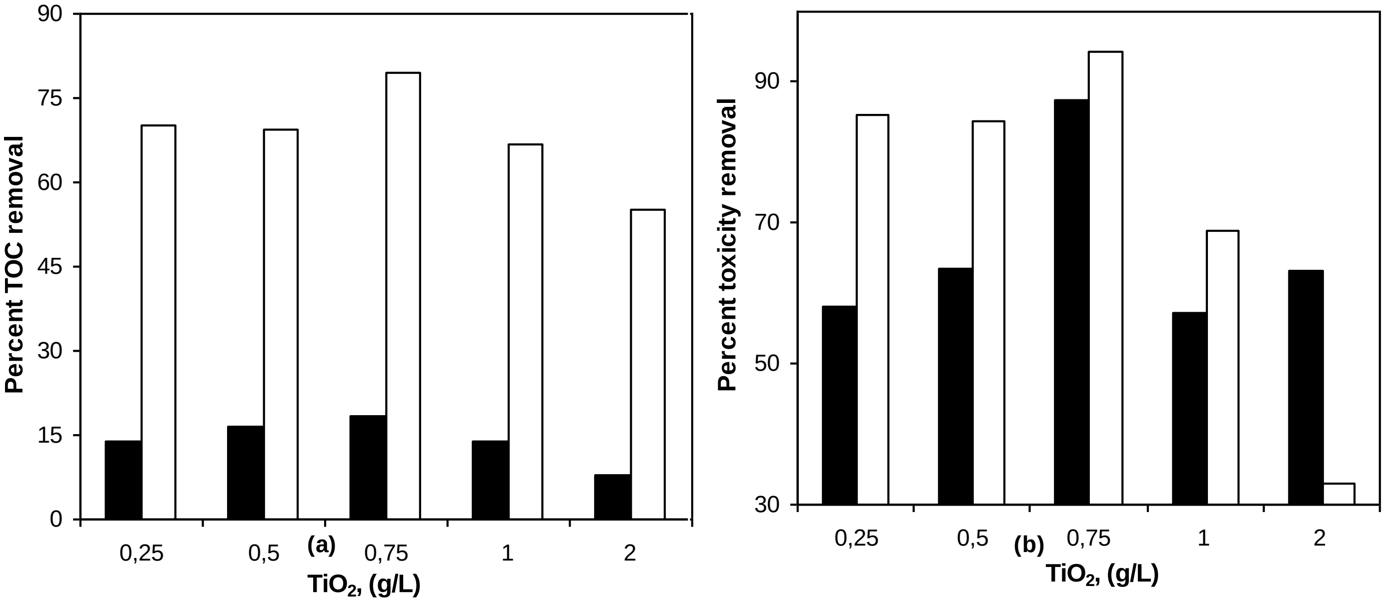

Figure 5.40 Variations of percent TOC (a) and toxicity (b) removals with TiO_2 concentrations in UV/TiO_2 treatment at pH 11: (■) in the absence of light and (□) in the presence of light.

In order to clarify the effect of photolysis on the treatment of pulp mill effluent, a number of experiments with titanium dioxide were performed in the dark. As presented in Figure.5.46, percent removals obtained with TiO_2 in the dark were lower than those of TiO_2/UV experiments because of formation of $OH^{\bullet}$ in UV/TiO_2 treatment. The results indicated that TOC removal in UV/TiO_2 treatment was not only due to adsorption of pollutants on TiO_2 surfaces, but by photo-catalytic degradation. A sharp oxidation of the organic matter (TOC removal) in UV/TiO_2 treatment during the first five minutes was by means of heterogeneous photo-catalysis and direct photolysis. This removal mechanism is mentioned by Machado *et al.*, (2000) for the treatment of the peroxy-formic acid-lignin and biphenyl-lignin compounds. Addition of irradiation (UV), also significantly enhanced the toxicity removals obtained by TiO_2 in the dark.

5.3.3.2 Treatment by UV/H_2O_2/TiO_2

Titanium dioxide (TiO_2) is known to be more effective due to the formation of electron-hole pairs under illumination with UV light. However, recombination of electrons and holes inhibit the photo-catalytic reaction process as mentioned in UV/TiO_2 treatment. Some oxidants (oxygen, hydrogen peroxide, oxyhalogens) improve the performance of UV/TiO_2 treatment by capturing the electrons ejected from TiO_2 and therefore, reducing the probability of recombination of e^- and h_{VB}^+, yielding higher number and long survival time for h_{VB}^+ (Irmak *et al.*, 2004). Recently, some investigators examined the effect of H_2O_2 on oxidation of organic pollutants, such as chlorophenols and atrazine mediated by TiO_2 (Wong & Chu, 2003). Addition of small amounts of hydrogen peroxide can significantly increase the generation rate of hydroxyl radicals, thereby enhancing the oxidation efficiencies of organic pollutants mediated by TiO_2.

In order to improve the performance of UV/TiO_2 treatment, hydrogen peroxide was added at the most suitable operating conditions determined. Experiments were carried out using hydrogen peroxide concentrations ranging between 5 and 100 mM with the presence and absence of UV light at an optimum titanium dioxide concentration of 0.75 g/L.

5.3.3.2.1 Effects of Initial pH. Figure 5.41 depicts variation of percent toxicity and TOC removals with the initial pH at a constant hydrogen peroxide concentration of 50 mM and TiO_2 concentration of 0.75 g/L at the end of 60 min reaction time. Percent toxicity removals were low under acidic and alkaline conditions yielding a maximum toxicity removal of 47% at pH 7. However, percent TOC removals were not affected from pH changes yielding 84.5 to 84.8% TOC removals at all pH levels tested.

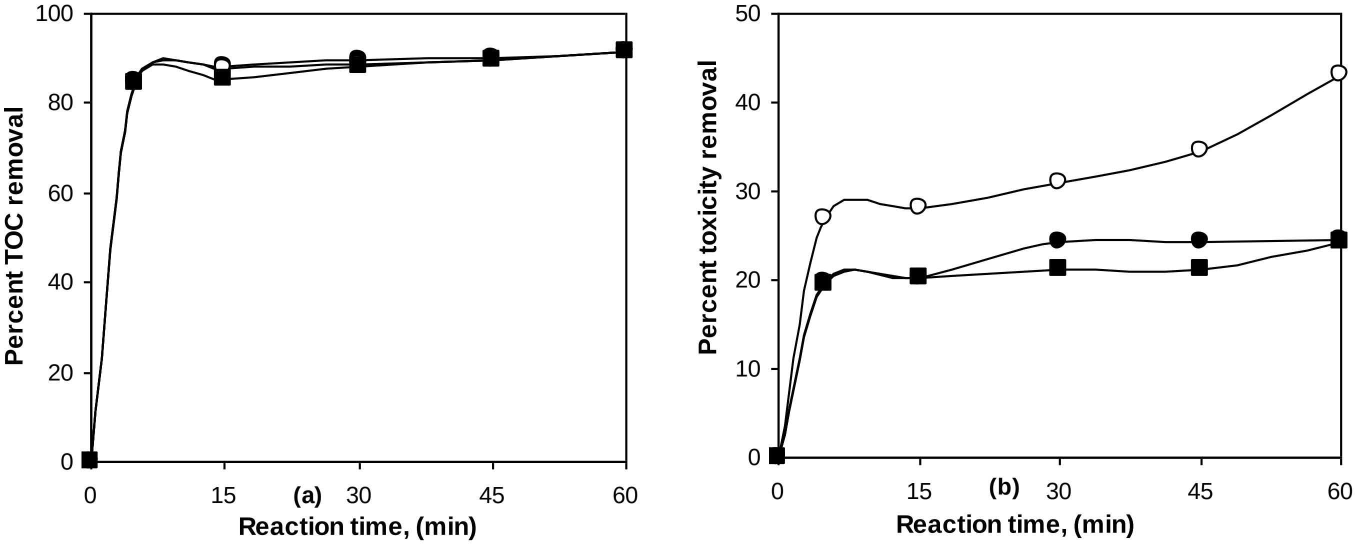

Figure 5.41 Variations of percent TOC (a) and toxicity (b) removals with the initial pH in UV/H_2O_2/TiO_2 treatment at a 0.75 g/L TiO_2 and 50 mM H_2O_2. pH: ● 3, ○ 7, ■ 11.

The first-order rate constants for TOC and toxicity removals were 0.377 and 0.063 min^{-1}, respectively at pH 7 (Table 4). Since the maximum toxicity removal was obtained at pH 7 and TOC removals were nearly same at all pH value, further experiments with UV/H_2O_2/TiO_2 were carried out at this pH. In another study, pH 7 was also found to be the optimum for the treatment of pesticides containing wastewater by UV/H_2O_2/TiO_2 (Doong & Chang, 1997).

Table 5.25 First-order rate constants (k_1) for TOC and toxicity removals from the pulp mill effluent by UV/H_2O_2/TiO_2 treatment at different pHs . (TiO_2 0.75 g/L, H_2O_2 50 mM)

UV/H_2O_2/TiO_2 Treatment	**k_1 (min^{-1})**	
	TOC	**Toxicity**
pH 3	0.374	0.044
pH 7	0.378	0.063
pH 11	0.373	0.043

5.3.3.2.2 Effects of Initial H_2O_2 Dose. A set of experiments were carried out with variable H_2O_2 concentrations between 5 and 100 mM at a pH of 7, constant titanium dioxide concentration of 0.75 g/L in the presence and absence of UV light.

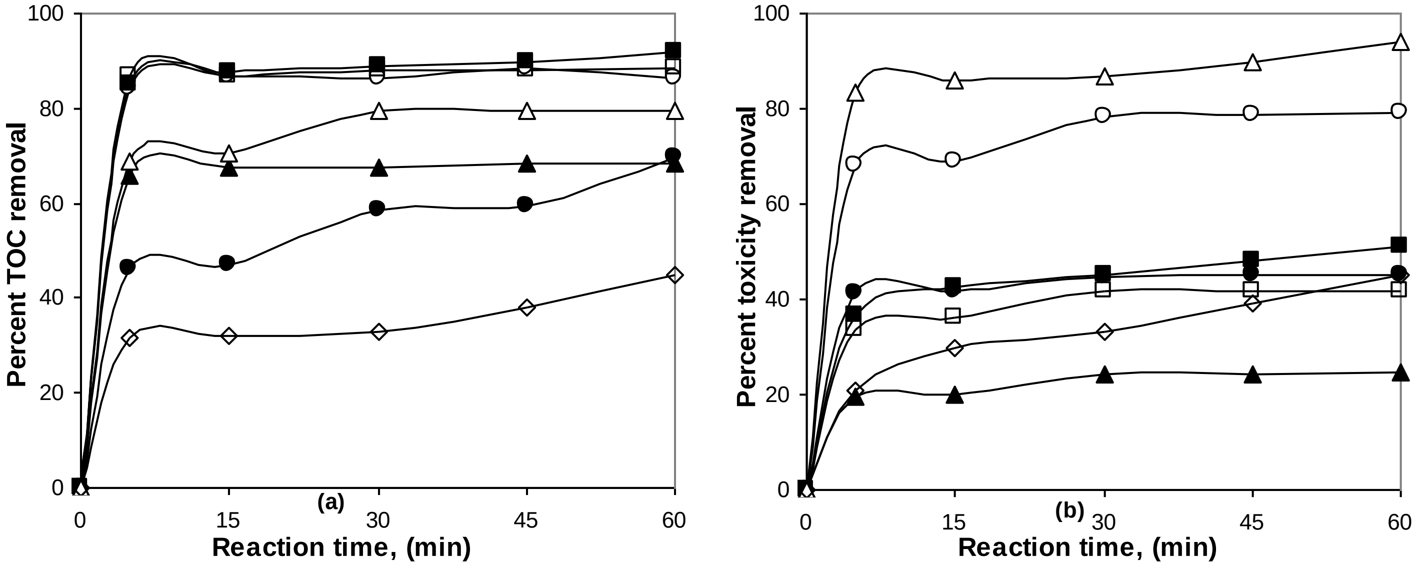

Figure 5.42 Variations of percent TOC (a) and toxicity (b) removals with initial H_2O_2 concentration in $UV/H_2O_2/TiO_2$ treatment at 0.75g/L TiO_2 and pH 7. H_2O_2 (mM): ● 5, ○ 25, ■ 50, □ 75, ▲ 100, Δ 0, ◊ TiO_2 0, H_2O_2 25 mM.

Figure 5.42 depicts variation of percent toxicity and TOC removals with the H_2O_2 concentration at constant initial pH of 7 in the presence of UV light. Addition of H_2O_2 to the UV/TiO_2 system improved TOC removals considerably as compared to UV/TiO_2 treatment alone even at low H_2O_2 concentrations. Percent TOC removals increased with H_2O_2 concentration up to 75 mM and then decreased with further increases in H_2O_2.

As presented in Table 5.26, the first-order rate constant (k_1) for TOC removal decreased from 0.406 min^{-1} to 0.215 min^{-1} when the concentration of H_2O_2 was increased from 75 mM to 100 mM. At high H_2O_2 concentrations, photo-catalytic oxidation was inhibited by the reactions of excess H_2O_2 with •OH radicals and h_{VB}^+ (Tanaka *et al.,* 2000; Konstantinou & Albanis, 2004). Reactions are presented in Eqn 3.13, Eqn 3.14 and Eqn 3.15.

However, addition of H_2O_2 to UV/TiO_2 system did not enhance toxicity removal. Toxicity removal of 94.2% obtained by UV/TiO_2 treatment decreased to nearly 50% with the addition of H_2O_2 to UV/TiO_2 treatment. Moreover, the first order rate constant (k_1) for toxicity removal decreased from 0.359 min^{-1} to 0.044 min^{-1} with the addition of 100 mM H_2O_2 to UV/TiO_2 treatment (Table 5.26). After these evaluations, the most suitable hydrogen peroxide concentration was selected as 25 mM by means of maximum first order reaction constants (0.368 min^{-1} for TOC and 0.227 min^{-1} for toxicity).

Table 5.26 First-order rate constants (k_1) for TOC and toxicity removals from the pulp mill effluent by UV/H_2O_2/TiO_2 treatment at different H_2O_2 concentrations (pH 7, TiO_2 0.75 g/L)

UV/H_2O_2/TiO_2 Treatment	**k_1 (min^{-1})**	
	TOC	**Toxicity**
UV only	0.034	0.132
UV/H_2O_2 (25 mM)	0.076	0.047
UV/TiO_2 (0.75 g/L)	0.233	0.359
UV/H_2O_2/TiO_2 (5 mM)	0.124	0.106
UV/H_2O_2/TiO_2 (25 mM)	0.368	0.227
UV/H_2O_2/TiO_2 (50 mM)	0.378	0.091
UV/H_2O_2/TiO_2 (75 mM)	0.406	0.082
UV/H_2O_2/TiO_2 (100 mM)	0.215	0.044

In order to clarify the effect of photolysis on the treatment of pulp mill effluent, a number of experiments with TiO_2 and H_2O_2 were performed in the dark. As presented in

Figure 5.43, when the pulp mill effluent was treated with the TiO_2 and H_2O_2 in the dark for 60 min, only 67.8% TOC and 79.9% toxicity were removed without irradiation. The results indicated that TOC removal (84.1%) in UV//H_2O_2/TiO_2 treatment was not only due to adsorption on TiO_2 surfaces, but by the photo-catalytic degradation. Addition of irradiation (UV) did not enhance toxicity removals (79.1%) obtained from TiO_2 experiments in the dark too (79.9%). This result showed that toxicity of intermediate products resulted in UV/TiO_2/H_2O_2 treatment is higher than ones in TiO_2/H_2O_2 treatment.

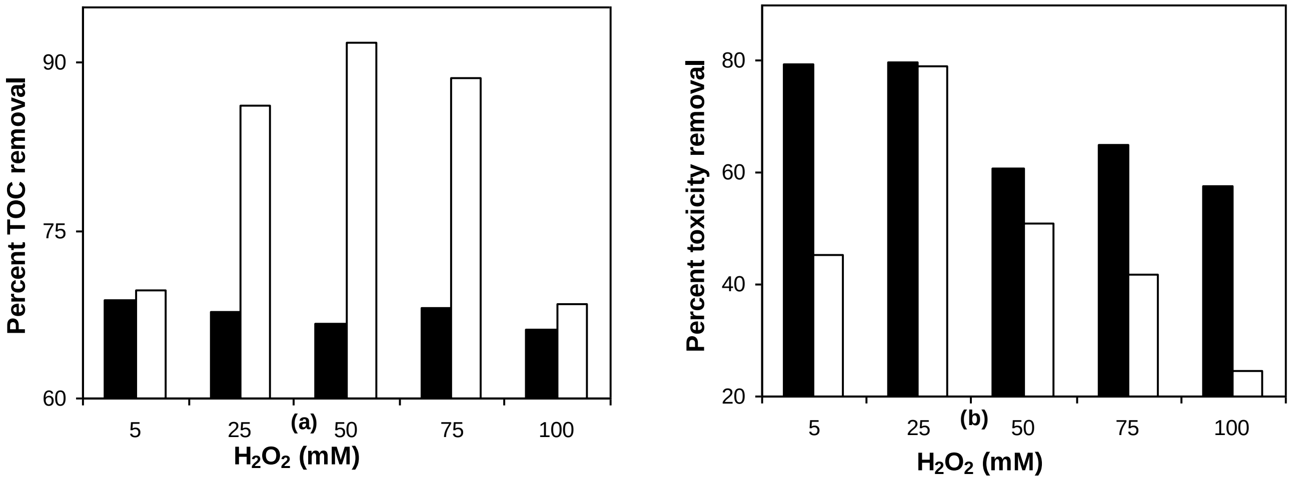

Figure 5.43 Variations of percent TOC (a) and toxicity, (b) removals with H_2O_2 concentrations in UV/H_2O_2/TiO_2 treatment at a 0.75g/L TiO_2 and pH 7. (■) in the absence of light and (□) in the presence of light.

In order to further clarify the role of TiO_2 in advanced oxidation of the pulp mill effluent, experiment with 25 mM H_2O_2 at pH 7 were also performed only with UV/H_2O_2 treatment without TiO_2. Percent toxicity and TOC removals were 44% and 45%, respectively for the UV/H_2O_2 treatment (Figure 5.42). Addition of TiO_2 to the UV/H_2O_2 system improved both toxicity and TOC removals considerably as compared to UV/H_2O_2 treatment. Moreover, the first order rate constant (k_1) for toxicity removal increased from 0.047 min^{-1} to 0.227 min^{-1} with the addition of 25 mM TiO_2 to UV/H_2O_2 treatment (Table 5.26). As a result, 84.1% TOC and 79.1% toxicity removals were obtained with UV/TiO_2/H_2O_2 treatment when 25 mM H_2O_2, 0.75 g/L TiO_2 was used at pH 7 at the end of 60 minutes reaction time.

5.3.3.3 Comparisons of Advanced Oxidation Processes (AOPs)

TOC and toxicity removals from a pulp mill effluent were investigated by using different advanced oxidation methods (AOPs). Effects of pH and concentrations of the reagents were investigated for each treatment method tested and the most suitable pH and oxidant concentrations were determined. Peak performances of each treatment method were compared for TOC and toxicity removals. Either TiO_2-assisted photo-catalysis (UV/TiO_2) or UV/H_2O_2/TiO_2 treatment can be used to obtain high percent TOC removals. However, TiO_2-assisted photo-catalysis treatment seems to be more advantageous yielding higher toxicity removal as compared with UV/H_2O_2/TiO_2. Treatment by TiO_2-assisted photo-catalysis yielded high toxicity (94%) and TOC (79.6%) removals at a pH of 11 with 0.75 g/L TiO_2 after 60 minutes of treatment.

CHAPTER SIX
CONCLUSIONS

6.1 Conclusions

Pesticide (simazine or diuron) degradation, mineralization and dehalogenation by advanced oxidation processes (Fenton, photo-Fenton and peroxone oxidation) were investigated over a large range of reactant concentrations. Box-Behnken statistical experiment design and the response surface methodology (RSM) were used for this purpose. Pesticide, peroxide, ferrous ion doses and the initial pH were considered as independent variables while percent pesticide and TOC removals were the objective functions. Experimental data was used to determine the coefficients of the response functions. Predictions obtained from the response functions were in good agreement with the experimental results indicating the reliability of the method used.

In advanced oxidation methods used for removal of diuron, high diuron removals indicated effective breakdown of diuron. However, low mineralization and TOC removals indicated formation of intermediary products (such as 3,4-dichloroaniline (DCA)) and incomplete mineralization. In photo-Fenton treatment, the highest pesticide removal (100%) and mineralization (85%) were obtained with a H_2O_2/Fe(II)/diuron ratio of 267/37/25 (mg/L). Under the same reaction conditions, 100% pesticide and 26.7% TOC (mineralization) were obtained by using the Fenton treatment in the absence of UV light. Peroxone treatment (ozone/H_2O_2) did not improve mineralization of diuron as compared to photo-Fenton treatment. Apparently, photo-Fenton treatment was the most effective method yielding the highest degree of diuron removal and mineralization.

In advanced oxidation of simazine, high simazine removals indicated effective breakdown of simazine. However, low TOC removals (low mineralization) indicated incomplete simazine degradation and formation of intermediary products (such as; 2-chloro-4,6-diamino-s-triazine (diamino chlorotriazine)) at high simazine concentrations. As compared to experimental studies with the Fenton and photo-

Fenton treatment, peroxone treatment yielded higher percent mineralization with almost no differences in simazine removals. Peroxone treatment at a pesticide dose of 3 mg/L, peroxide dose of 50 mg/L and pH of 7.0 yielded 100% simazine removal and 69% mineralization. Apparently, application of ozone into hydrogen peroxide oxidant improved degree of mineralization of simazine.

The optimum H_2O_2/pH/Simazine ratio resulting in the maximum pesticide (100%) and TOC removal (53.3%) was found to be 50/3/5 (mg/L) in peroxone oxidation, while the highest pesticide removal (100%) and mineralization (85%) were obtained with a H_2O_2/Fe(II)/diuron ratio of 267/37/25 (mg/L) in photo-Fenton oxidation. At high pesticide doses, mineralization was incomplete yielding formation of intermediate compounds.

The initial rate of simazine and diuron degradation was found to be first-order with respect to the initial pesticide concentration for Fenton and photo-Fenton processes. Simazine and diuron concentrations obtained from advanced oxidation processes were suitable for the EU pesticide standards (0.1 mg/L for any particular pesticide in drinking water).

In advanced oxidation of paper mill wastewater (PMW-I), either Fenton or photo-Fenton treatment can be used for effective removal of color, TOC or AOX. Ozone and peroxone treatment were not as effective as the Fenton’s reagent treatment yielding low TOC removals. Fenton (H_2O_2/Fe(II)) and photo-Fenton treatment produced very high color (85%), TOC (88-82%) and AOX (89-93%) removals at pH= 5. High removal efficiencies were obtained within 5 minutes indicating the effectiveness of photo-Fenton treatment as compared to the others. Therefore, photo-Fenton treatment seems to be more advantageous requiring much less reaction time and therefore smaller reactor volumes as compared to the Fenton treatment.

When performances of the AOPs were compared for treatment of another paper mill wastewater (PMW-II), it can be said that, either TiO_2-assisted photo-catalysis (UV/TiO_2) or UV/H_2O_2/TiO_2 treatment should be used to obtain high percent TOC removals. However, TiO_2-assisted photo-catalysis treatment seems to be more advantageous yielding higher toxicity removal as compared to UV/H_2O_2/TiO_2

treatment. TiO_2-assisted photo-catalysis yielded high toxicity (94%) and TOC (79.6%) removals within 60 minutes pH=11 with 0.75 g/L TiO_2.

It was proven that, pesticide containing water and pulp mill wastewater can be treated and mineralized effectively by advanced oxidation processes. These compounds may be easily removed in short reaction times by using combination of different advanced oxidation processes such as photo-Fenton/ozone process. Integration of advanced oxidation processes as a pre-treatment or post-treatment step into industrial treatment plants is recommended for removal of recalcitrant compounds and for improvement of treatment efficiencies.

6.2 Recommendations for Future Research

Performances of different advanced oxidation process were compared in this study in terms of the oxidant and catalyst requirements and removal efficiencies using pesticide containing water. The optimum conditions determined in this study can be used for treatment of real groundwater, surface water or wastewater containing pesticides.

Different statical experimental design methods may be used to determine the effects of large number of varaiables on treatment performances and to determine the optimum reaction conditions.

Incorporation of advanced oxidation processes as a pre-treatment or post-treatment step into industrial treatment plants may result in improvements in overall treatment efficiency. Pilot plant studies should be carried out for this purpose.

Mineralization of pesticides may be improved and degradation of some toxic organic compounds can be accomplished by increasing the power output of UV reactor to 1000-1500 W.

Oxidation and degradation products of pesticides should be determined and toxicity of these intermediates should be assesed using other toxicologic and analytical methods.

Addition of TiO_2, ozone or other catalysts (eg, ZnO) to the advanced oxidation processes used and utilization of different reactor configurations may positively affect the treatment efficiency of toxic industrial wastewaters.

Ozone/UV and ultrasonic treatments may be used together in advanced oxidation treatment to improve TOC, toxicity and pesticide removals from toxic industrial wastewaters.

More detailed studies should be carried out on the kinetics of the AOP methods should be developed to improve mineralization of toxic compounds.

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APPENDICES
RAW EXPERIMENTAL DATA

A.1 Anova Tests for the Response Functions for Different AOPs

A.1.1 Anova Tests for Diuron Removal using Fenton Treatment

Table A. 1 ANOVA test for the response function Y_1 (% pesticide removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	12634.55	9	1403.84	102.66	<0.0001
X_1(Pest.)	472.01	1	472.01	34.52	0.002
X_2 (H_2O_2)	2299.1	1	2299.1	168.12	<0.0001
X_3 (Fe^{2+})	3845.21	1	3845.21	281.18	<0.0001
X_1X_2	1773.25	1	1773.25	129.67	<0.0001
X_1X_3	9.09	1	9.09	0.66	0.4520
X_2X_3	906.61	1	906.61	66.3	0.0005
X_1^2	31.19	1	31.19	2.28	0.1914
X_2^2	532.25	1	532.25	38.92	0.0015
X_3^2	2844.08	1	2844.08	207.97	<0.0001
Total error	68.38	3	22.79		
Total (corr)	12702.93	14			

Table A. 2 ANOVA test for the response function Y_2 (% TOC removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	2399.22	9	266.58	186.43	<0.0001
X_1(Pest.)	1516.63	1	1516.63	1060.63	<0.0001
X_2 (H_2O_2)	104.26	1	104.26	72.91	0.0004
X_3 (Fe^{2+})	131.30	1	131.30	91.82	0.0002
X_1X_2	38.19	1	38.19	26.71	0.0036
X_1X_3	10.79	1	10.79	7.55	0.0404
X_2X_3	506.70	1	506.70	354.35	< 0.0001
X_1^2	1.16	1	1.16	0.81	0.4085
X_2^2	77.66	1	77.66	54.31	0.0007
X_3^2	7.20	1	7.20	5.03	0.0749
Total error	7.15	5	1.43		
Total (corr)	2406.37	14			

A.1.2 Anova Tests for Diuron Removal using Photo-Fenton Treatment

Table A. 3 ANOVA test for response function Y_1 (% pesticide removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	7326.93	9	814.10	142.06	<0.0001
X_1(Pest.)	27.42	1	27.42	4.78	0.084
X_2 (H_2O_2)	3056.45	1	3056.45	533.35	<0.0001
X_3 (Fe^{2+})	954.85	1	945.85	166.62	<0.0001
X_1X_2	787.64	1	787.64	137.44	<0.0001
X_1X_3	814.53	1	814.53	142.13	<0.0001
X_2X_3	138.53	1	138.53	24.17	0.0044
X_1^2	524.01	1	514.01	89.69	0.0002
X_2^2	878.37	1	878.37	153.27	<0.0001
X_3^2	379.74	1	379.74	66.26	0.0005
Residual	28.65	3	5.73		
Lack of Fit	28.04		9.35	30.26	0.0322
Pure Error	0.62		0.31		
Total (corr)	7355.58	14			

Table A. 4 ANOVA test for the response function Y_2 (% TOC removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	7656.35	9	850.71	105.02	<0.0001
X_1(Pest.)	3858.37	1	3858.37	476.30	<0.0001
X_2 (H_2O_2)	1180.01	1	1180.01	145.67	<0.0001
X_3 (Fe^{2+})	38.5	1	38.5	4.75	0.0811
X_1X_2	621.26	1	621.26	76.69	0.0003
X_1X_3	856.73	1	856.73	105.76	0.0001
X_2X_3	74.74	1	74.74	9.23	0.0288
X_1^2	17.	1	17.	2.12	0.2049
X_2^2	8975	1	8975	110.79	0.0001
X_3^2	184.73	1	184.73	22.8	0.0050
Total error	40.50	5	8.1		
Lack of Fit	39.97	3	13.32	49.67	0.0198
Pure Error	0.54	2	0.27		
Total (corr)	7696.86	14			

A.1.3 Anova Tests for Diuron Removal using Peroxone Treatment

Table A. 5 ANOVA test for the response function Y_1 (% pesticide removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	365.96	9	40.66	37.19	0.0005
X_1(Pest.)	0.58	1	0.58	0.53	0.4998
X_2 (H_2O_2)	17.26	1	17.26	15.78	0.0106
X_3 (pH)	22.44	1	22.44	20.53	0.0062
X_1X_2	13.69	1	13.69	12.52	0.0166
X_1X_3	178.89	1	178.89	163.61	< 0.0001
X_2X_3	0.33	1	0.33	0.3	0.6060
X_1^2	73.53	1	73.53	67.25	0.0004
X_2^2	6.36	1	6.36	5.82	0.0607
X_3^2	54.73	1	54.73	50.06	0.0009
Residual	5.47	5	1.09		
Lack of Fit	5.47	3	1.82		
Pure Error	0.00	2	0.000		
Total (corr)	371.43	14			

Table A. 6 ANOVA test for the response function Y_2 (% TOC removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	6429.00	9	714.33	108.51	< 0.0001
X_1(Pest.)	1118.17	1	1118.17	169.85	< 0.0001
X_2 (H_2O_2)	1348.88	1	1348.88	204.9	< 0.0001
X_3 (pH)	2682.05	1	2682.05	407.41	< 0.0001
X_1X_2	56.1	1	56.1	8.52	0.0330
X_1X_3	64	1	64	9.72	0.0263
X_2X_3	528.54	1	528.54	80.29	0.0003
X_1^2	283.18	1	283.18	43.02	0.0012
X_2^2	369.05	1	369.05	56.06	0.0007
X_3^2	5.84	1	5.84	0.89	0.3896
Residual	32.92	5	6.58		
Lack of Fit	32.92	3	10.97		
Pure Error	0.000	2	0.000		
Total (corr)	6461.92	14			

A.1.4 Anova Tests for Simazine Removal using Fenton Treatment

Table A. 7 ANOVA test for the response function Y_1 (% pesticide removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	26761.07	9	2973.45	2789.45	< 0.0001
X_1(Pest.)	1.13	1	1.13	1.06	0.3514
X_2 (H_2O_2)	1.31	1	1.31	1.23	0.3177
X_3 (Fe^{2+})	18443.52	1	18443.52	17302.21	< 0.0001
X_1X_2	0.32	1	0.32	0.30	0.6077
X_1X_3	0.53	1	0.53	0.49	0.5139
X_2X_3	0.20	1	0.20	0.19	0.6844
X_1^2	0.041	1	0.041	0.038	0.8522
X_2^2	2.48	1	2.48	2.33	0.1877
X_3^2	8237.93	1	8237.93	7728.15	< 0.0001
Residual	5.33	5	1.07		
Lack of Fit	4.86	3	1.62	6.94	0.1286
Pure Error	0.47	2	0.23		
Total (corr)	26766.40	14			

Table A. 8 ANOVA test for the response function Y_2 (% TOC removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	1403.55	9	155.95	357.07	< 0.0001
X_1(Pest.)	26.03	1	26.03	59.60	0.0006
X_2 (H_2O_2)	2.34	1	2.34	5.37	0.0684
X_3 (Fe^{2+})	12.45	1	12.45	28.51	0.0031
X_1X_2	0.28	1	0.28	0.63	0.4630
X_1X_3	18.58	1	18.58	42.53	0.0013
X_2X_3	6.05	1	6.05	13.86	0.0137
X_1^2	192.63	1	192.63	441.05	< 0.0001
X_2^2	447.41	1	447.41	1024.42	< 0.0001
X_3^2	872.87	1	872.87	1998.57	< 0.0001
Total error	2.18	5	0.44		
Lack of Fit	2.13	3	0.71	26.06	0.0372

A.1.5 Anova Tests for Simazine Removal using Photo-Fenton Treatment

Table A. 9 ANOVA test for the response function Y_1 (% pesticide removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	212.29	9	23.59	63.60	0.0001
X_1(Pest.)	31.52	1	31.52	84.99	0.0003
X_2 (H_2O_2)	42.55	1	42.55	114.73	0.0001
X_3 (Fe)	85.22	1	85.22	229.78	< 0.0001
X_1X_2	18.02	1	18.02	48.59	0.0009
X_1X_3	12.29	1	12.29	33.13	0.0022
X_2X_3	16.16	1	16.16	43.57	0.0012
X_1^2	2.14	1	2.14	5.76	0.0616
X_2^2	0.17	1	0.17	0.45	0.5338
X_3^2	3.78	1	3.78	10.19	0.0242
Residual	1.85	5	0.37		
Lack of Fit	1.19	3	0.40	1.19	0.4874

Table A. 10 ANOVA test for the response function Y_2 (% TOC removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	5988.36	9	665.37	89.08	< 0.0001
X_1(Pest.)	3288.20	1	3288.20	440.22	< 0.0001
X_2 (H_2O_2)	93.23	1	93.23	12.48	0.0167
X_3 (Fe)	12.40	1	12.40	1.66	0.2540
X_1X_2	349.88	1	349.88	46.84	0.0010
X_1X_3	548.03	1	548.03	73.37	0.0004
X_2X_3	45.02	1	45.02	6.03	0.0576
X_1^2	492.46	1	492.46	65.93	0.0005
X_2^2	1031.75	1	1031.75	138.13	< 0.0001
X_3^2	12.42	1	12.42	1.66	0.2537
Residual	37.35	5	7.47		
Lack of Fit	37.35	3	12.45		

A.1.6 Anova Tests for Simazine Removal using Peroxone Treatment

Table A. 11 ANOVA test for the response function Y_1 (% pesticide removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	232.57	9	25.84	55.95	0.0002
X_1(Pest.)	10.17	1	10.17	22.02	0.0054
X_2 (H_2O_2)	15.82	1	15.82	34.25	0.0021
X_3 (Fe)	43.57	1	43.57	94.34	0.0002
X_1X_2	4.31	1	4.31	9.32	0.0283
X_1X_3	1.78	1	1.78	3.86	0.1067
X_2X_3	57.76	1	57.76	125.06	< 0.0001
X_1^2	34.86	1	34.86	75.47	0.0003
X_2^2	14.26	1	14.26	30.87	0.0026
X_3^2	63.13	1	63.13	136.70	< 0.0001
Residual	2.31	5	0.46		
Lack of Fit	2.31	3	0.77		

Table A. 12 ANOVA test for the response function Y_2 (% TOC removal)

Source	**Sum of squares**	**Df**	**Mean Square**	**F ratio**	**P value**
Model	4119.00	9	457.67	175.80	< 0.0001
X_1(Pest.)	1431.13	1	1431.13	549.73	< 0.0001
X_2 (H_2O_2)	396.63	1	396.63	152.36	< 0.0001
X_3 (Fe)	5.30	1	5.30	2.03	0.2131
X_1X_2	26.57	1	26.57	10.21	0.0241
X_1X_3	774.79	1	774.79	297.62	< 0.0001
X_2X_3	329.42	1	329.42	126.54	< 0.0001
X_1^2	528.60	1	528.60	203.05	< 0.0001
X_2^2	625.20	1	625.20	240.16	< 0.0001
X_3^2	156.60	1	156.60	60.15	0.0006
Residual	13.02	5	2.60		
Lack of Fit	13.02	3	4.34		

A.1.7 Raw Data for Kinetic Studies on Pesticide Degradation

Table A. 13 Raw data for diuron degradation using Fenton treatment at different experimental conditions

Time (min)	**Run no**												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
0	1.0	25.0	1.0	25.0	1.0	25.0	1.0	25.0	13.0	13.0	13.0	13.0	13.0
2.5	0.743	13.35	0.351	4.782	0.651	19.6	0.3	9.6	10.66	11.15	7.37	1.275	3.42
5	0.646	13.258	0.3	0.414	0.694	18	0.29	8.8	10.76	11.5	7.756	0.741	3.23
10	0.31	13.19	0.3	0.377	0.685	16	0.292	8.5	10.73	11.45	7.78	0.463	2.9
15	0.306	13.07	0.3	0.216	0.684	14.8	0.29	8.3	10.82	11.2	8.38	0.552	2.82
30	0.294	12.69	0.0	0.198	0.622	14.8	0.293	8.3	11.05	11.03	8.54	0.642	2.39
45	0.29	12.61	0.0	0.216	0.669	14.8	0.29	9.8	10.8	11.3	8.55	0.56	2.28
60	0.286	12.61	0.0	0.0	0.66	14.8	0.3	15	11.39	11	8.59	0.539	1.35

Table A. 14 Raw data for diuron degradation using photo-Fenton treatment at different experimental conditions

Time (min)	**Run no**												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
0	1.0	25	1	25	1	25	1	25	13	13	13	13	13
2.5	0.55	16	0.309	0.533	0.408	20.38	0.3	1.05	9.99	7.42	6.6	0.4	0.32
5	0.611	15.6	0.304	0.533	0.29	17.8	0.298	0.302	9.91	4.89	5.96	0.38	0.3
10	0.465	15	0.285	0.54	0.28	15.6	0.298	0.292	9.2	1.19	5.5	0.35	0.29
15	0.411	14.24	0.285	0.505	0.262	12.457	0.316	0.291	8.624	1.46	4.12	0.328	0.33
30	0.491	13.25	0.314	0.347	0.258	5.4	0.298	0.298	7.194	0.354	4.29	0.328	0.337
45	0.495	12.29	0.282	0.318	0.26	2	0.293	0.291	5.76	0.3	4.12	0.32	0.335
60	0.641	11.44	0.28	0.303	0.263	0.76	0.291	0.294	4.763	0.286	3.48	0.32	0.333

Table A. 15 Raw data for simazine degradation using Fenton treatment at different experimental conditions

Time (min)	**Run no**												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
0	5.0000	5.0100	0.5300	0.5000	5.0000	5.0000	0.4900	0.5000	2.7500	2.7500	2.7500	2.7500	2.7500
3	0.0120	0.4420	0.0427	0.0000	0.0000	1.4000	0.0000	0.0627	0.0000	0.9560	0.0680	1.8000	0.1280
6	0.0098	0.4340	0.0000	0.0000	0.0000	0.4800	0.0000	0.0266	0.0000	0.2560	0.0259	0.9700	0.0970
9	0.0057	0.5690	0.0000	0.0000	0.0320	0.1850	0.0000	0.0000	0.0000	0.0849	0.0179	0.5840	0.0074
12	0.0000	0.4460	0.0000	0.0000	0.0123	0.0700	0.0000	0.0488	0.0000	0.0397	0.0000	0.3220	0.0448
15	0.0000	0.4410	0.0000	0.0000	0.0000	0.0330	0.0000	0.0000	0.0000	0.0309	0.0000	0.2170	0.0000

Table A. 16 Raw data for simazine degradation using photo-Fenton treatment at different experimental conditions

Time (min)	**Run no**												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
0	5.0000	5.0100	0.5300	0.5000	5.0000	5.0000	0.4900	0.5000	2.7500	2.7500	2.7500	2.7500	2.7500
3	0.5830	0.0627	0.0153	0.0000	0.0000	4.7550	0.0000	0.9520	0.0000	2.7600	0.0000	2.8100	0.1360
6	0.1910	0.0057	0.0209	0.0000	0.0760	4.8200	0.0000	0.9060	0.0000	2.7890	0.0000	2.7950	0.0270
9	0.1560	0.0030	0.0078	0.0000	0.0000	4.7700	0.0000	1.0200	0.0000	2.7990	0.0000	2.8000	0.0000
12	0.1460	0.0034	0.0148	0.0000	0.0000	4.7900	0.0000	0.9450	0.0000	2.7770	0.0000	2.7970	0.0000
15	0.1430	0.0025	0.0000	0.0000	0.0000	4.7800	0.0000	0.9280	0.0000	2.7890	0.0000	2.8100	0.0000