DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

APPLICATION OF AEROBIC SLUDGE STABILIZATION SUPPORTED WITH DIFFERENT PRETREATMENT TECHNIQUES

by
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İZMİR

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We have read the thesis entitled **"APPLICATION OF AEROBIC SLUDGE STABILIZATION SUPPORTED WITH DIFFERENT PRETREATMENT TECHNIQUES"** completed by **UTKU ALBAYRAK** under supervision of **PROF. DR. AYŞE FİLİBELİ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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APPLICATION OF AEROBIC SLUDGE STABILIZATION SUPPORTED WITH DIFFERENT PRETREATMENT TECHNIQUES

ABSTRACT

In this lab-scale study, alkali and microwave pretreatment methods were used as pretreatment techniques to modify sludge stabilization. The study consists of three main parts. In the first optimization part, optimum operational conditions of microwave pretreatment alone and combined alkaline and microwave pretreatment applications were determined to obtain the most effective sludge stabilization. Central composite design (CCD) was used as a statistical method and disintegration degree (DD) was used as a criteria of solubilization.

In the second part of the study, effect of previously determined optimum pretreatment method on performance of organic matter degradation and dewaterability characteristics of mesophilic aerobic digestion as a stabilization process was investigated by operating a lab-scale semi – batch aerobic digester during 30 d. Results were compared with the results of a parallel unpretreated sludge fed aerobic digester. Inoculum sludge which was provided from aerobic digester of municipal wastewater treatment plant (WWTP) in Manisa, and feed sludge which was provided from return line of secondary sedimentation of domestic WWTP in Izmir were mixed to prepare content of aerobic digester.

In the third part of the study, thermophilic aerobic digestion was operated for 30 d, and the effect of thermophilic temperature range on performance of organic matter degradation were evaluated. Analysis were carried out periodically and feeding were carried out daily. Organic matter degradation efficiency of reactors were evaluated according to vector attraction requirements of US Environmental Protection Agency (EPA). As different from other parameters, oxygen uptake rate (OUR) and observed yields (Yobs.) were carried out to demonstrate the accuracy of findings of this study.

Keywords: Microwave pretreatment, alkali pretreatment, central composite design, aerobic digestion, aerobic stabilization, partial nitrification, free ammonia inhibition.

FARKLI ÖN ARITMA TEKNİKLERİYLE DESTEKLENMİŞ ÇAMURUN AEROBİK STABİLİZASYON UYGULAMASI

ÖZ

Bu laboratuar ölçekli çalışmada çamurun stabilizasyonunu iyileştirmek için, ön arıtma teknikleri olarak alkali ön arıtım ve mikrodalga parçalama yöntemleri kullanılmıştır. Çalışma 3 ana bölümden oluşmaktadır. Birinci optimizasyon bölümünde, yalnızca mikrodalga ön arıtmanın çamura uygulanması halinde ve alkali ön arıtma ile mikrodalga ön arıtmanın çamura birlikte uygulanması halinde, en yüksek stabilizasyon veriminin elde edilmesini sağlayacak en uygun ön arıtma koşulları belirlenmiştir. Bunun için merkezi kompozit dizayn (CCD) istatistiksel metodundan yararlanılmış ve çözünebilirlik kriteri olarak dezentegrasyon derecesi (DD) kullanılmıştır.

Çalışmanın ikinci bölümünde, ilk bölümde seçilen en uygun ön arıtma şeklinin, bir aerobik stabilizasyon metodu olan aerobik çürütmenin mezofilik sıcaklık aralığındaki organik madde indirgeme performansı ve çamurun su verme özellikleri üzerindeki etkisi, laboratuar ölçekli yarı – kesikli bir aerobik çürütücünün 30 gün boyunca işletilmesi ile incelenmiştir. Ön arıtma yapılmadan beslenen ve paralel çalıştırılan aerobik çürütücünün sonuçları ile de kıyaslama yapılmıştır. Aerobik çürütücüler hazırlanırken Manisa'daki bir kentsel atıksu arıtma tesisinin aerobik çürütücüsünden alınan aşı çamuru ile İzmir'deki bir evsel atıksu arıtma tesisinin son çökeltim havuzunun geri devir hattından alınan besleme çamurunun karışımı kullanılmıştır.

Çalışmanın üçüncü bölümünde de ikinci bölümde gerçekleştirilen 30 günlük aerobik çürütücü işletmesi termofilik sıcaklık aralığında gerçekleştirilerek sıcaklığın organik madde indirgeme verimi üzerindeki etkisi ortaya konmuştur. Beslemeler günlük olarak ve analizler belirli periyodlarla gerçekleştirilmiştir. İşletme süresi boyunca reaktörlerin organik madde giderme veriminin, Amerikan Çevre Koruma Ajansının (EPA) vektör çekimi gereksinimlerini karşılayacak düzeyde olup olmadığı incelenmiştir. Diğer parametrelerin yanısıra bulguların doğruluğunu desteklemek amacıyla oksijen tüketim hızı (OUR) ve gözlenen verim (Yobs.) analizleri yapılmıştır.

Anahtar Kelimeler: Mikrodalga ön arıtma, alkali ön arıtma, merkezi kompozit tasarım, aerobik çürütme, aerobik stabilizasyon, kısmi nitrifikasyon, serbest amonyak inhibisyonu.

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CHAPTER ONE
INTRODUCTION

In recent years, discussions of people authorities and broadcast about value and importance of clean water have reached to a significant level, as a consequence of damaged natural resources, climate change, increasing demand of world population. Therefore, wastewater which is produced by everyday human activities, and by a variety of industrial, agricultural and municipal usage (Lue - Hing et al., 1998) has became an indirect potential source for clean water via treatment. Biological treatment which based on exploiting microorganisms to degrade organic matter in wastewater by providing appropriate conditions, is an old and effective method.

The activated sludge process is the most known and commonly used biological treatment process in the world (Yasui et al., 1996; Ahn et al., 2002). Combination of microorganism population and inert solid particles (where population settle on and carry out degradation) called biomass. Biomass is the main component of sewage sludge. Most of pollution load that exist in water, are absorbed by biomass. As degradation proceeds, a small part of biomass is left from system in effluent water and has to be brought back via return stream from secondary sedimentation tank. Excess part of this return sludge is called waste activated sludge (WAS) and it is a by-product of activated sludge process. Raw WAS is a brown or dark brown biologically active liquid which has 0.8 % – 1.2 % total solids (TS) content and 59 % - 88 % of TS content is volatile solids (VS) content (US EPA, 1979).

The two major sludge stream produced by domestic and municipal wastewater treatment plants are primary sludge (PS) which is drawn from the bottom of primary sedimentation tank, and WAS. The combination of PS and WAS is called mixed sludge. Typical values of sludge production rates for a plant are between 0.2 and 0.3 kg sludge produced per m^3 treated wastewater (Turovskiy & Mathai, 2006).

Production of sewage sludge in large volumes by wastewater treatment plants (WWTPs), is a comprehensive environmental issue to manage due to disposal challenges and potential adverse effects on public health, and it is required treatment inevitably. Hence, sludge treatment and disposal are essential factors for design, operation and cost of a plant to consider (Erden et al., 2010). Cost of sludge treatment is approximately 25 % – 65 % of total plant operation cost (Liu, 2003).

The major objective of this study is to enhance and simplify stabilization of waste activated sludge by using different pretreatment techniques prior to aerobic digestion as a stabilization method. Other objectives can be summarized as follows:

- To investigate the effect of microwave digestion as a pretreatment technique on sludge disintegration.
- To investigate the effect of combined alkaline pretreatment and following microwave digestion on sludge disintegration.
- To determine optimum pretreatment conditions by conducting an optimization study.
- To evaluate the assistance, simplicity and accuracy of Central Composite Design as a statistical method in optimization study.
- To investigate the effects of temperature and solids retention times on biological degradation during aerobic digestion process.
- To demonstrate the success of combined alkaline pretreatment and microwave digestion as a pretreatment technique on sludge stabilization.
- To give ideas for future projects about sludge stabilization and sludge management.

CHAPTER TWO
LITERATURE REVIEW

2.1 Sludge Stabilization

Stabilization is an essential method for treatment and disposal of sewage sludge (Hartman et al., 1979), and it is defined as controlled decomposition of easily biodegradable organic matter, resulting in a decrease in offensive odor and a significant reduction of volatile solids and pathogen content (Arnaiz et al., 2006; Borowski & Szopa, 2007). According to Spinosa & Vesilind (2001), stabilized sludge should not pose a health risk and should not have bad odor. Also, unstabilized sludge have a potential of putrefaction (Tchobanoglous et al., 2003).

In addition to the health risk, bad odor and putrefaction, stabilization is used for volume reduction, methane production and improvement dewaterability (Tchobanoglous et al., 2003), but this does not include all stabilization methods.

Commonly used principal stabilization methods are as follows (Turovskiy & Mathai, 2006) :

- Conventional Aerobic Digestion
- Autothermal Thermophilic Digestion
- Anaerobic Digestion
- Alkaline Stabilization
- Composting
- Thermal Drying

2.1.1 Aerobic Digestion as a Stabilization Method

Aerobic digestion is one of the commonly used stabilization methods in WWTPs. It has been widely used in small-scale treatment plants due to smaller tank volumes.

But in recent years aerobic digestion has been employed in larger treatment plants which has capacities up to 2 m^3/s (WEF, 1998).

Conventional aerobic digesters which have longer sludge retention times (from 15 to 60 days) requires large tank volumes (Li et al., 2008). But capital costs are low due to simple construction of usual tank geometry. Oxygen or air is difficult to provide effectively to each dead zone of these large tank volumes, hence oxygen transfer needs high energy consumption during digestion. Unlike anaerobic digestion, there is no recovery of energy in the form of biogas (Bernard & Gray, 1999). In this case, aerobic digestion is not totally feasible to operate and serve for large quantities of sewage sludge. Moreover, the ease of operation, process stability and volatile solids reduction slightly less than that obtained in anaerobic digestion are major features of aerobic digestion (Tchobanoglous et al., 2003). In anaerobic digestion, ongoing process considerably sensitive to content of feed, inhibitors and surrounding environmental conditions. Therefore, there are more parameters have to be checked to maintain process stability such as pH, temperature, alkalinity, total volatile fatty acids (TVFA) concentration, alkalinity / TVFA ratio, sulfate concentration.

EPA regulations part 503 contains conventional aerobic digestion (which is operated at 15 ºC and 20 ºC) in processes significantly reduce pathogens (PSRP) and thermophilic aerobic digestion in processes further reduce pathogens (PFRP) as stabilization processes. According to part 503, sewage sludge which stabilized by application of thermophilic aerobic digestion might define as class A and sewage sludge which stabilized by application of conventional aerobic digestion might define as class B respect to pathogens in case of requirements are met. It is stated in alternative 2 and 3 under class A biosolids, and alternative 5 and 6 under class B biosolids in pathogen reduction subpart apparently (US EPA, 1979).

The achievement of aerobic digestion is determined by measuring principally volatile solids reduction (38 % or more) and specific oxygen uptake rate (1.5 mg O_2 g TS^{-1} h^{-1} or less) parameters as criteria for vector attraction requirements. Densities of fecal coliform (less than 1000 MPN g TS $^{-1}$) and *Salmonella sp.* (less than 3 MPN 4 g TS $^{-1}$) are main parameters to use for the classification of biosolids and to indicate achievement of aerobic digestion process in pathogen reduction (US EPA, 1979).

2.1.2 Mechanisms of Aerobic Digestion

Aerobic digestion is the oxidative microbial stabilization of sludge (Mcfarland, 2000). When the soluble substrate is completely depleted by the biomass, microorganisms begin to consume their own protoplasm for cell maintenance. Energy obtaining from cell material in this manner known as endogenous respiration which is the major reaction in aerobic digestion The cell tissue is oxidized aerobically to carbon dioxide, water, and ammonia. (Tchobanoglous et al., 2003). Destruction of proteins to aminoacids results ammonium nitrogen (NH_4^+ - N) release. As digestion proceeds, nitrification occurs due to presence of ammonium ion ($NH_4^+{}_{(aq)}$).

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad (2.1)$$

The irreversible reaction represented in equation 2.1 directly depends on pH of aqueous solution (Tchobanoglous et al., 2003). It means both NH_4^+ ion and its conjugate base NH_3 are present in the digester in practice, and as pH increases the reaction shifts to right. Thus, a part of nitrogen is stripped from digester as in the form of free ammonia gas, and remaining ammonium is either converted to nitrate (NO_3^-) or accumulate in digester.

Biochemical reactions occurring during aerobic digestion can be represented with following equations:

$$C_5H_7O_2N + 5O_2 \rightarrow 4CO_2 + H_2O + NH_4HCO_3 \qquad (2.2)$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad (2.3)$$

$$C_5H_7O_2N + 4\ NO_3^- + H_2O \rightarrow 10\ CO_2 + 7H_2O + N_2 \qquad (2.4)$$

Equation 2.2 represents reaction of the destruction of biomass which produces ammonium ion and 1 mol of alkalinity. Equation 2.3 and 2.4 represents nitrification and denitrification respectively. As it shown in Eqn 2.3, 2 moles of H^+ ion are produced on the contrary Eqn 2.2. Hence, pH of system starts to decrease slightly due to 2 moles of alkalinity are destroyed during nitrification. This pH drop continues until buffering capacity of sludge (total alkalinity) is completely utilized, and finally inhibits nitrification. Therefore, one of the essential operational boundaries is level of pH 5.5. Below this level, system is in risk of acid inhibition and requires alkalinity loading. The other essential boundary is level of 1 mg/L dissolved oxygen (DO) concentration. Below this level nitrification does not occur. These boundaries have great importance during operation to keep process work stable.

In practice, partial nitrification which is presented in Eqn 2.5 occurs in system. In partial nitrification, a portion of nitrogen is left from the system in the forms of $NH_{3(g)}$ and $N_{2(g)}$, and nitrification continues with presence of both NO_3^- and NH_4^+ ions.

$$2C_5H_7O_2N + 12O_2 \rightarrow 10CO_2 + 5H_2O + NH_4^+ + NO_3^- \qquad (2.5)$$

2.1.3 Aerobic Digester Design Considerations

Living microorganisms, bad odor, putrefaction and health risks are results of presence of biodegradable substrate in raw sludge. In other words, volatile solids content of sludge is main reason of all decomposition activities. Therefore, solids retention time (SRT) and temperature which are the main design parameters are used to meet required reduction of volatile solids. The graphic of US EPA below is commonly used to select design SRT according to required VS reduction (US EPA, 1979).

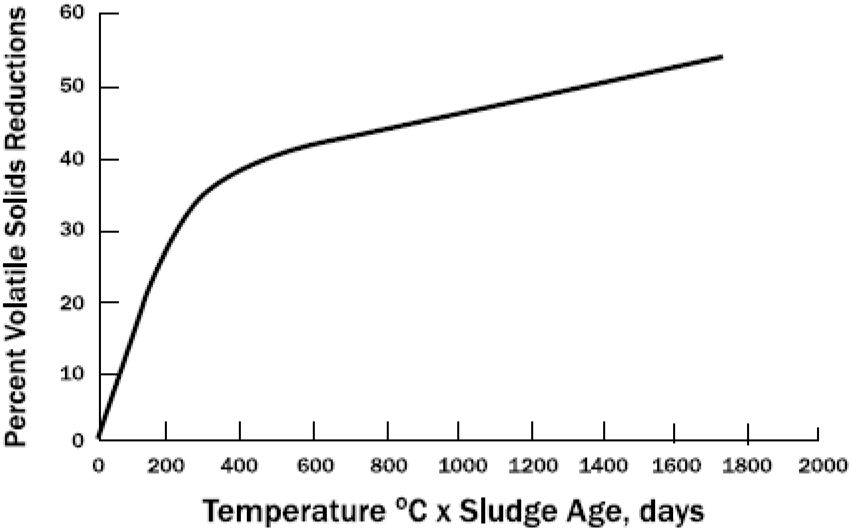


Figure 2.1 VS Reductions versus Temperature and SRT.

Volume of feed to be added daily is determined as represented in the Eqn 2.6 below.

$$V_{\text{aerobic digester}} = SRT_{\text{design}} \text{ x } V_{\text{feed sludge}} \tag{2.6}$$

The rest of design such as digester volume, feed sludge volume, air and energy requirements are calculated after determining design SRT.

2.2 Sludge Disintegration

2.2.1 Mechanisms of Disintegration and Disintegration Degree

Sludge disintegration can be defined as disruption of microbial cells in sludge as a result of external physical, chemical and biological forces (Erden & Filibeli, 2010), and it is improved via different pretreatment techniques, to accelerate the digestion processes (Erden et al., 2010). Current sludge treatment studies is composed of two major steps commonly. The first step is, changing characterization of sludge to be degraded biologically, and the second step is, reducing quantity of sludge by subsequent biological reactor (Tokumura et al., 2007).

In the first step, microbial cell walls are damaged as the result of pretreatment. After that pretreatment provide the solubilization of extracellular polymeric substances (EPS) which form bioaggregates with microbial cells such as sludge flocs (Nielsen & Jahn, 1999), and intracellular polymeric substances (IPS) into the aqueous phase (Dogan & Sanin, 2009). Released EPS and IPS are another source of nitrogen which mostly bonded in amino acids and an extra contribution to the soluble organic content of sludge to be degraded.

Recently conducted studies have reported that EPS are major organic fraction of activated sludge (Park et al., 2008). The term of EPS is used to express different classes of polysaccharides, proteins, enzymes, nucleic acids, lipids and other polymeric compounds which are produced during growth in intracellular space and are present at or outside the cell wall surface (Flemming & Wingender, 2001). Also extracellular enzymes have an important effect principally on the hydrolysis of extracellular proteins and polysaccharides (Goel R. et. al., 1998). However, EPS are key substances for microbial cells and also disintegration.

Sludge disintegration is measured commonly with two parameters in recent studies. These are COD solubilization and disintegration degree (DD). Equation 2.7, 2.8 and 2.9 below, represent COD solubilization and commonly used DD methods.

$$\text{COD solubilization (\%)} = (SCOD_a / TCOD_a) \times 100 \qquad (2.7)$$

where $SCOD_a$ is soluble COD after pretreatment (mg L^{-1}); $TCOD_a$ is total COD after pretreatment (mg L^{-1}).

$$\text{DD (\%)} = ((SCOD_a - SCOD_i) / (TCOD_i - SCOD_i)) \times 100 \qquad (2.8)$$

where $SCOD_a$ is the soluble COD after pretreatment (mg L^{-1}); $SCOD_i$ is the soluble COD before pretreatment (mg L^{-1}); $TCOD_i$ is the total COD before pretreatment (mg L^{-1}) (Muller, 1996).

$$DD\ (\%) = ((COD_f - COD_i) / (COD_{NaOH} - COD_{NaOHi})) \times (COD_{original} / COD_{homogenization}) \quad (2.9)$$

where COD_f is the final COD of supernatant after pretreatment (mg L^{-1}); COD_i is the initial COD of supernatant of raw sludge (mg L^{-1}); COD_{NaOH} is the COD of supernatant after 22 h addition of 1M NaOH (mg L^{-1}); COD_{NaOHi} is the COD of supernatant just after addition of 1M NaOH (mg L^{-1}); $COD_{original}$ is the COD of original sample right after addition of 1M NaOH (mg L^{-1}), $COD_{homogenization}$ is the COD of original sample after homogenization (mg L^{-1}) (Kunz & Wagner, 1994).

2.3 Commonly Used Pretreatment Techniques

Alkaline pretreatment, fenton oxidation, microwave digestion, ozone oxidation, thermal hydrolysis and ultrasound were introduced in this chapter as commonly used effective pretreatment techniques. Combined alkaline pretreatment and following microwave digestion is used as pretreatment technique to investigate the effect of pretreatment on COD solubilization and subsequent aerobic digestion.

2.3.1 Alkaline Pretreatment

Alkali pretreatment is a commonly used pretreatment method due to its simple operation and high efficiency (Weemaes & Verstraete, 1998). In the past, low dose alkaline pretreatment is used to assist thermal hydrolysis (Carrére et al., 2010). In recent years, use of alkaline pretreatment as a major pretreatment method raised. Many investigations which including combination of alkaline pretreatment with ultrasound and microwave digestion prior to anaerobic digester operation were conducted until present.

Addition of alkali substances to the sludge disrupt floc structure and bacteria cells such as other disintegration methods. Thus, cellular organic materials are released (Kim et. al., 2003). Moreover, chemically bonded water which can not be extracted by dewatering processes is also released due to disruption of flocs (Carrére et. al., 2010).

Commonly used alkali substances for pretreatment are solutions of NaOH, KOH, $Ca(OH)_2$ and $Mg(OH)_2$. But addition of $Ca(OH)_2$ or $Mg(OH)_2$ connects cells and EPS because of bivalent cations Ca^{2+} and Mg^{2+} (Urbain et al., 1993). Also in the presence of Ca^{2+} cations, dissolved organic polymers reflocculate (Neyens et al., 2004). Therefore addition of monovalent cations (especially NaOH is mostly used) provides more COD solubilization and dewaterability.

2.3.2 Fenton Oxidation

Fenton oxidation is one of the commonly used pretreatment methods. Actually, it can be defined as hydrogen peroxide (H_2O_2) oxidation in the presence of iron salts.

In order to make oxidation process more effective, free radicals (which are stronger than usual oxidants) are generated during process. Although hydrogen peroxide (H_2O_2) is a strong oxidant, it can be activated by transition metals, ozone and UV-light to form free radicals (Neyens & Baeyens, 2002). Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxil radicals ($OH^{\bullet}$) according to the reaction below (eqn 2.10) (Kitis et al., 1999).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \qquad (2.10)$$

This is catalysed dissociation reaction of H_2O_2 via $Fe2^{+}$ ions, and directly depends on the pH of solution. In the case of pH value is less than 2, the reaction slowed down due to formation of complex iron compounds and oxonium ion ($H_3O_2^{+}$) (Kwon et al.,1999). On the other hand, at pH values of more than 4, generation of free hydroxil radicals gets slower due to formation of ferric-hydroxo complexes (Kuo, 1992).

Intermediate free radicals cause starting of complex chain reactions in aqueous solution. These reactions can be summarized with Eqn. 2.11, 2.12, 2.13 and 2.14 (Rigg et al., 1954; Buxton & Greenstock, 1988).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (2.11)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \quad (2.12)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{-}OOH^{2+} + H^{+} \quad (2.13)$$

$$Fe\text{-}OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (2.14)$$

2.3.3 Microwave Pretreatment

Microwave technology have been widely applied in communication, navigation, food processing, minerals processing and activated carbon regeneration for the years (Jones et al., 2002). But in the last decade, number of microwave applications on the field of environmental engineering have been rised especially for sludge disintegration.

Microwave irradiation is a term that defines frequency range of 300 MHz – 300 GHz in electromagnetic spectrum (Banik S., Bandyopadhyay S., Ganguly S., 2003). According to spectrum, each radiation wavelength value has an equivalent frequency value, and industrial microwave ovens generally operate at a frequency of 2.45 GHz (Jacob et al., 1995).

Materials which show dielectric properties have ability to absorb microwave irradiation. Polar molecules such as water in sludge matrix, have dipoles which cause molecular friction inside dielectric material by rotating due to electromagnetic field (Jones et al., 2002; Wojciechowska, 2005). Kinetic energy of water dipoles leads to burst microbial cell and release organic material and bound water (Wojciechowska, 2005). Thus disintegration and dewaterability of sludge are enhanced (Saha et al., 2011). Also microwave pretreatment is very effective on inactivation of pathogens (Pino-Jelcic et al., 2006).

2.3.4 Ozone Oxidation

Ozonation process is used primarily for water supply treatment and effluent water disinfection up to now. But ozone oxidation is another oxidation process which is used for sludge disintegration recently.

Electrical current is passed through the high – purity oxygen gas flow in industrial type ozone generators. Thus oxygen molecules dissociate into atomic oxygen ($O^{\bullet}$) and ozone gas (O_3) is produced (Tchobanoglous et al., 2003).

After ozone gas produced, it dissociates into free radicals and reacts with soluble, particular, organic and mineral fractions of sludge during ozonation (Cesbron D. et. al., 2003). Free radicals have vital importance on ozonation similar to other oxidation processes. Ozonation reactions can be summarized in Equations 2.15, 2.16, 2.17 and 2.18 below (Tchobanoglous et al., 2003).

$$O_3 + H_2O \rightarrow HO_3^{\bullet} + OH^- \qquad (2.15)$$

$$HO_3^{\bullet} + OH^- \rightarrow 2HO_2^{\bullet} \qquad (2.16)$$

$$O_3 + HO2^{\bullet} \rightarrow HO^{\bullet} + 2O_2 \qquad (2.17)$$

$$HO^{\bullet} + HO2^{\bullet} \rightarrow H_2O + O_2 \qquad (2.18)$$

2.3.5 Thermal Hydrolysis

Thermal hydrolysis is another commonly used pretreatment method both in experimental studies and industrial applications. Haug et al. (1978) first used thermal hydrolysis to improve sludge dewaterability, but various studies including thermal hydrolysis have been conducted as sludge pretreatment alternatives for the last two decades.

Basically, thermal hydrolysis works with the same mechanism which other treatment methods have. At temperatures above 150 ºC, it provides release of linked water of sludge, thus, enhances dewaterability (Fisher & Swanwick, 1971). When thermal pretreatment combined with subsequent anaerobic digestion, energy requirement for pretreatment may be balanced with the energy of produced biogas (Neyens & Baeyens, 2002).

Thermal pretreatments are usually carried out in the moderate temperature range of 60 – 100 ºC, in the medium temperature range of 100 – 175 ºC and in the high temperature range of 175 – 225 ºC (Vlyssides & Karlis, 2003). Temperatures above 200 ºC can cause formation of toxic compounds such as dioxins (Stuckey & McCarty, 1984). According to studies conducted recently, optimum temperature range varies between 160 ºC and 180 ºC, and treatment time varies between 30 and 60 minutes (Dohanyos et al., 2004; Valo et al., 2004; Bougrier et al., 2006). Although optimum treatment time range is certain, studies showed that treatment times have a little effect on the success of thermal pretreatment (Neyens & Baeyens, 2003).

2.3.6 Ultrasonic Pretreatment

Ultrasonic pretreatment is known as most effective method on sludge disintegration, thereby it has been installed in many large capacity treatment plants (Zhang et al., 2007). It is used extensively as a pretreatment of anaerobic digestion in industry (Carrére et al., 2010).

The ultrasound is a kind of sound pressure with frequency greater than 20 kHz (Pilli et al., 2011). According to Carrére et al. (2010), frequency range between 20 and 40 kHz is optimum for sludge pretreatment.

Mechanism of ultrasonic pretreatment is based on two major factors: High shear forces and free radicals. Ultrasound waves push and pull solvent molecules periodically. Applied positive and negative pressures, cause rarefaction and expansion of each molecule and formation of bubbles. This is called as acoustic cavitation (Tiehm et al., 2001). When microbubbles (cavitation bubbles) grew and reached a critical size, they violently collapse due to enormous temperature and pressure inside each bubble. And this collapse causes formation of high shear tensions which disrupt cell walls. Moreover, extreme conditions provide a thermal destruction of compounds inside bubbles, and generate free hydroxil radicals (Young, 1989).

Although ultrasonic pretreatment is very effective, it is an energy-intensive process (Zhang et al., 2008). Therefore, combination with another pretreatment method may provide a synergetic effect and enhance applicability of ultrasound systems (Kim et al., 2010).

2.4 Previously Conducted Studies on Combined Alkaline and Microwave Pretreatment

Low dose alkaline pretreatment was combined with thermal hydrolysis to assist and enhance the sludge solubilization in previous studies (Carrére et al., 2010). Vlyssides & Karlis (2003) studied combined thermal hydrolysis (50 – 90 ºC) and alkaline pretreatment (pH 8 – 11) prior to anaerobic digestion to determine the effects on hydrolysis rate. They used VSS reduction (%), SCOD concentration (mg L^{-1}) and yield (L CH_4 kg VSS^{-1}) as parameters. After 10 hours hydrolysis at 90 ºC and pH 11, almost 45 % VSS reduction, more than 90 % SCOD release and 0.28 L CH_4, kg VSS^{-1} were obtained.

Li et al. (2007) studied to investigate the effects of different alkaline doses (0 – 0.5 mol L^{-1}). NaOH and $Ca(OH)_2$ were used as alkali substances. Alkali contact times 0 – 30 min., 30 min. – 6h, 6h – 24 h were tried for each NaOH dose. 60 – 70 % of total COD solubilization occurred in the first 30 min. of pretreatment. Also 0.5

mol L^{-1} NaOH dose was found the most efficient. SCOD concentration increased from 275 mg L^{-1} to more than 3000 mg L^{-1} with 0.5 mol L^{-1} dosage. pH value did not change significantly (around 12) due to additions more than 0.5 mol L^{-1} dosage.

$Ca(OH)_2$ was also tried for disintegration, but obtained results were insufficient according to NaOH disintegration. SCOD concentration increased from 275 mg L^{-1} to 821 mg L^{-1} with 0.5 mol L^{-1} dosage. The situation is a result of reflocculation of dissolved organic materials due to presence of bivalent cations (Ca^{2+}). Neyens et. al. (2003) also previously stated the important role of bivalent cations to connect EPS with cells.

Li et al. (2008) compared combined alkaline and ultrasonic pretreatment, alkaline pretreatment alone and ultrasonic pretreatment alone by using NaOH and $Ca(OH)_2$ as alkali substances. After alkaline pretreatment with $Ca(OH)_2$ (30 min, 0.04 mol L^{-1}), SCOD concentration was slightly more than untreated sludge. This situation confirmed reported results of studies which previously done (Neyens et al., 2003; Li et al., 2007). Alkaline pretreatment with NaOH (30 min, 0.04 mol L^{-1}) and ultrasonic pretreatment alone (3750 kJ kg DS^{-1}) released 3 times greater SCOD concentration than untreated sludge. On the other hand, combined ultrasonic and alkaline pretreatment with NaOH released 6 times greater and combined ultrasonic and alkaline pretreatment with $Ca(OH)_2$ released 4 times greater SCOD concentration than untreated sludge. Combined ultrasonic and alkaline pretreatment with NaOH gave best results. For better investigation of combined pretreatment, simultaneous pretreatment, alkaline (NaOH) pretreatment followed by ultrasonic and ultrasonic pretreatment followed by alkaline (NaOH) were compared by using same doses. Ultrasonic pretreatment followed by alkaline gave the most insufficient results for disintegration. This means when alkaline pretreatment was applied to a disintegrated sludge, leads to a decrease on dewaterability.

Based on these findings, combined ultrasonic (7500 kJ kg DS^{-1}) and alkaline pretreatment (30 min, 0.04 mol L^{-1}) were used and subsequent aerobic digester operated for 17 d. 50.7 % VSS reduction was obtained by Li et. al. (2008).

Kim et al. (2010) conducted a study in order to investigate the simultaneous effects of combined alkaline and the following ultrasonic pretreatment. Difference from related previous studies is experimental design used in this study. pH values in the range of 8 – 13 and ultrasound dosage in the range of 3750 – 45000 kJ kg TS^{-1} were entered as variables (inputs) and DD (%) was entered as response in software to establish a 2 factorial central composite design model. Model was established and analyzed. DD increased as pH values increased. On the other hand, DD decreased as the dose of ultrasound exceeds 20000 kJ kg TS^{-1}. Also good synergetic effect was observed when low dose ultrasound applied to alkaline pretreated sludge. Finally, sludge pretreated with low dose alkali (pH 9) and ultrasound (7500 kJ kg TS^{-1}) fed to an anaerobic sequencing batch reactor to determine the effects of combined pretreatment. Reactor was operated during 70 days. Methane production yield increased from average 81.9 (mL CH_4 g COD_{added}) to 127.3 (mL CH_4 g COD_{added}).

Microwave digestion of inoculum acclimated thickened waste activated sludge was investigated in the temperature range of 50 – 175 °C (Eskicioglu et al., 2009). Microwave digester was used instead of household microwave ovens first time. Average 1.2 – 1.4 °C min^{-1} were used to estimate duration time and digestion was ended when it reached to target temperature. SCOD TCOD^{-1} ratios increased from 9 (untreated sludge) to 24 at 120 °C, to 28 at 150 °C and to 35 at 175 °C.

Dogan & Sanin (2009) studied combined alkaline pretreatment (NaOH) and microwave irradiation prior to anaerobic digestion. pH values of 10, 11, 12, 12.5 and stable dose MW pretreatment (average 160 °C for 30 min.) were tried. First, effects of each alkaline dose and MW pretreatment alone on COD solubilization examined separately. SCOD TCOD^{-1} ratios measured as 0.005, 0.10, 0.17, 0.20, 0.29 for untreated sludge, pH 10 dose, pH 11 dose, pH 12 dose and pH 12.5 dose respectively. It was observed that CST values were increased as the pH value of dose increased.

SCOD release after MW pretreatment alone was observed that it is very close to pH 11 alkaline pretreatment. Also SCOD TCOD^{-1} ratios of combined pH 10 + MW, pH 11 + MW, pH 12 + MW and pH 12.5 + MW pretreatments measured as 0.18, 0.27, 0.34 and 0.37 respectively.

In the second part, sludge samples pretreated with NaOH (pH 10 and pH 12), MW alone and combined pretreatment (MW + pH 12) were digested in anaerobic reactor. Combined pH 12 + MW pretreatment produced the highest amount of total gas (16.3 % more than control) and methane gas (18.9 % more than control). Based on this result, pH 12 + MW pretreatment examined with semi – continuous anaerobic reactors. Reactors were operated at 15 d SRT for 92 d. Total gas production was measured 55 % more than control reactor and methane production was measured 43.5 % more than control. Moreover, TS, VS and TCOD reductions were measured as 24.9 %, 35.4 % and 30.3 % less than control reactor respectively.

Chang et al. (2011) studied the effects of MW irradiation alone (600 W, 85 °C, 2 min. up to boiling), thermal hydrolysis alone (80 °C, 12 min.) and alkali pretreatment alone (NaOH addition up to pH 12, 30 min. contact time) on COD solubilization in the first part of study. SCOD TCOD^{-1} ratios were measured as 0.085, 0.07 and 0.18 for MW irradiation, thermal hydrolysis and alkaline pretreatment respectively.

Combined alkaline pretreatment (NaOH addition up to pH 12, 10 min. contact time) and following MW irradiation (600 W, 85 °C, 2 min. up to boiling) sequence, MW irradiation and following alkaline pretreatment (MW – alkali) sequence were also tried. SCOD TCOD^{-1} ratio of combined MW irradiation and the following alkaline pretreatment was measured as 0.46. On the other hand, SCOD TCOD^{-1} ratio of alkaline pretreatment and the following MW irradiation was measured as 0.39.

Tyagi & Lo (2012) studied MW pretreatment (900 W, 95 ºC, 2 min.) and following alkaline pretreatment (2.5 g NaOH L^{-1} sludge, addition up to pH 12, 30 min. contact time) as optimum combined pretreatment with subsequent mesophilic aerobic digestion (6 d SRT) for 20 d. 81 % TCOD reduction was obtained in pretreatment reactor and 46 % in control at the end of 20 d. Also 62 % VSS reduction was obtained in pretreatment reactor in first 5 days of digestion.

Based on the results above, in the second part of the study, combined MW irradiation and the following alkaline pretreatment with subsequent aerobic digestion operation were investigated for the first time. Aerobic digesters were batch operated at room temperature and 16 d of SRT for 30 d. 63 % VSS reduction were obtained after pretreatment (20 % more than control reactor).

CHAPTER THREE
MATERIALS & METHODS

3.1 Sludge Samples Used In This Study

The inoculum sludge was obtained from conventional aerobic digester unit of municipal WWTP of Manisa city and only used in the start-up phases of digesters. Inoculums sludge is used to form alive and stable biomass culture in digester.

The feed sludge was taken from return line of secondary sedimentation tank of Izmir Guneybati Domestic WWTP periodically. It was added and drawn to the reactors everyday during start-up and reactor operation periods. Characterization of both inoculum and feed sludges used in optimization study is given in Table 3.1. The properties of inoculum and feed sludge used in mesophilic and thermophilic aerobic reactor operation studies are, given in Table 3.2 and Table 3.3.

Table 3.1 Characterization of inoculum and feed sludge in optimization study.

Parameters	Inoculum Sludge	Feed Sludge
pH	7.47	6.58
EC, ms/cm	1.398	13.12
T, °C	15	15
TS, %	0.92	1.02
OM, %	57.15	38.62
CST, s	174.23	23.37

Table 3.2 Characterization of inoculum and feed sludge in mesophilic aerobic digestion.

Parameters	**Inoculum Sludge**	**Feed Sludge**
pH	7.61	7.47
EC, ms/cm	1.302	14.9
T, °C	15	15
TS, %	3.31	2.04
OM, %	25.44	31.8
CST, s		24.4

Table 3.3 Characterization of inoculum and feed sludge in thermophilic aerobic digestion.

Parameters	**Inoculum Sludge**	**Feed sludge**
pH	7.53	7.5
EC, ms/cm	1.501	16.8
T, °C	15	15
TS, %	3.07	1.99
OM, %	22.93	30.55
CST, s		30.3

3.2 Experimental System

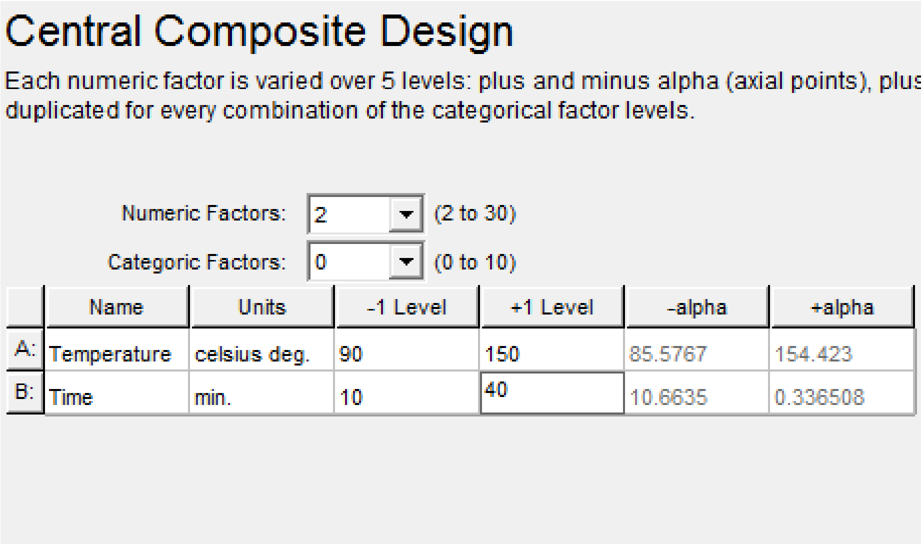
Experimental system is based on different findings of 2 parallel lab - scale digesters. One of them was fed with raw sewage sludge is control reactor, and the other one was fed with pretreated sewage sludge is pretreatment reactor. In this study, alkaline and microwave (MW) pretreatments were applied sequentially as pretreatment techniques. Observed yield coefficient (Y_{obs}, g MLVSS produced g $TCOD^{-1}$ consumed) was used as a parameter to indicate the achievement of combined pretreatments in mesophilic and thermophilic aerobic reactor operations.

This study is composed of optimization studies, mesophilic aerobic digester operation and thermophilic aerobic digester operation. Optimization part was carried out to evaluate impacts of pretreatments and determine the optimum operational conditions to be used in the study. Optimization analyses are based on chemical oxygen demand solubilization (SCOD) results of various doses of only MW and combined alkaline and microwave pretreatments (pH + MW). After SCOD results obtained, values of disintegration degree (DD) were calculated and optimum conditions for MW pretreatment and pH + MW pretreatment were selected from MW pretreatment conditions versus DD and pH + MW pretreatment conditions versus DD graphics. Thus, previously determined optimum pH + MW pretreatment condition was used in mesophilic and thermophilic aerobic reactor operations.

3.3 Optimization Studies

First step of optimization studies is optimum condition determination of MW pretreatment. Central composite designs (CCD) was used as statistical method for this purpose. Because establishment of model in CCD with 2 factors is more simple and results are as accurate as other methods in shorter experiment period.

Design Expert 7.0 software was used to conduct central composite experimental design. CCD was run to determine trial points of analysis of MW pretreatment. For design, temperature of microwave digester (X_1) is one of variables, duration of digestion (X_2) is other variable and DD (Y) is response. Range of X_1 variable entered in software is between 90 ºC and 150 ºC, and range of X_2 is between 10 min. and 40 min (Figure 3.1).



Central Composite Design

Each numeric factor is varied over 5 levels: plus and minus alpha (axial points), plus
duplicated for every combination of the categorical factor levels.

Numeric Factors: 2 (2 to 30)

Categoric Factors: 0 (0 to 10)

	Name	Units	-1 Level	+1 Level	-alpha	+alpha
A:	Temperature	celsius deg.	90	150	85.5767	154.423
B:	Time	min.	10	40	10.6635	0.336508

Figure 3.1 Ranges of factors in MW pretreatment.

Number of runs for two factorial central composite design is calculated with equation 3.1.

$$N = 2^k + 2k + c \qquad (3.1)$$

where N is the number of runs (trial points); k is the number of factors; c is the number of center points. 11 trial points were determined by software (Table 3.4).

Table 3.4 Trial points of model.

		$SCOD_a$, mg L^{-1}	**$SCOD_i$, mg L^{-1}**	**$SCOD_{NaOH}$, mg L^{-1}**	**DD_{SCOD}, %**
1	90 ºC - 10 min.	448	320	1152	15.38
2	150ºC - 10 min.	768	320	1152	53.85
3	90 ºC - 40 min.	544	320	1152	26.92
4	150 ºC - 40 min.	1120	320	1152	96.15
5	85,58 ºC - 25 min.	544	320	1152	26.92
6	154,42 ºC - 25 min.	1024	320	1152	84.62
7	120 ºC - 7,79 min.	576	320	1152	30.77
8	120 ºC - 42,21 min.	608	320	1152	34.62
9	120 ºC - 25 min.	784	320	1152	55.77
10	120 ºC - 25 min.	752	320	1152	51.92
11	120 ºC - 25 min.	768	320	1152	53.85

In this table, SCODa is the concentration of soluble COD after pretreatment (mg L^{-1}); SCODi is the concentration of soluble COD before pretreatment (mg L^{-1}); $SCOD_{NaOH}$ is the maximum COD release in the supernatant after chemical disintegration (NaOH digestion).and DD_{SCOD} is disintegration degree of SCOD (%).

After analyses completed, responses were entered and design was established. Equation and R^2 value of design represented in equation 3.2. and 3.2. are given below.

$$Y = (0.0061X_1^2) - (0.0534X_2^2) + (0.0171X_1X_2) - (1.0223X_1) + (1.2052X_2) + 38{,}7021 \quad (3.2)$$

$$R^2 = 0.9492 \text{ (model significant)} \quad (3.3)$$

Graphic of different MW conditions versus DD was drawn according to design equation. Thus optimum operational condition of MW pretreatment was determined.

After optimum operational condition of microwave pretreatment determined, optimum dose of alkaline pretreatment was determined without software. Based on the data of previous studies mentioned in literature review, 30 min. contact time and 1 N NaOH were used in the optimization part and reactor operations of this study (Li et al., 2008; Chang et al., 2011; Tyagi & Lo, 2012). Determination of optimum dose in alkali pretreatment was carried out by 1 N NaOH addition to the feed sludge to reach desired pH level. pH values of 8, 9, 10, 11, 12 and 12.5 were tried. Optimum microwave operational condition was applied after each pH value regulation and contact time. DDs were calculated according to Muller’s method for combined alkaline and microwave digestion based on SCOD concentrations. Finally pH versus DD graphic was drawn and optimum combined pretreatment was determined.

3.3.1 Statistical Methods Used In Optimization Study

Central composite designs (CCD) are one of the response surface methods (RSM). Two factorial CCDs are used to fit a second order model for a given response. CCD was selected and used as an experimental method due to its simplicity with two factors and well accuracy. Also number of replications on center points can be selected by people who will make experiment.

3.3.2 Analytical Methods Used In Optimization Study

3.3.2.1 SCOD Analysis

Liquid sample was centrifuged at 15000 rpm for 20 min and supernatant was passed through 0.45 micron pore size filter paper. After filtration, COD analysis (open reflux) was carried out according to SM 5220 B.

3.3.2.2 Chemical (NaOH) Disintegration

Chemical disintegration ($SCOD_{NaOH}$) is done for maximum COD release in the supernatant. This experiment was carried out by mixing sludge sample and 1 N NaOH in the ratio of 1:2 for 10 min. at 90 °C. After disintegration, sample was centrifuged at 15000 rpm for 20 min and SCOD concentration of supernatant was analyzed. Clifton model thermostatic bath was used to provide desired temperature in chemical disintegration experiment and mesophilic and thermophilic aerobic reactor operations.

3.3.2.3 Disintegration Degree

Disintegration degree of SCOD was calculated according to Equation 3.4.which Muller proposed.

$$DD_{SCOD}, \% = (SCOD_a - SCOD_i) / (SCOD_{NaOH} - SCOD_i) \qquad (3.4)$$

where $SCOD_a$ is the concentration of soluble COD after pretreatment (mg L^{-1}); $SCOD_i$ is the concentration of soluble COD before pretreatment (mg L^{-1}); $SCOD_{NaOH}$ is the maximum COD release in the supernatant after chemical disintegration (NaOH digestion).

3.4 Semi-Batch Aerobic Digester Operations

3.4.1 Semi-Batch Aerobic Digesters

3 L glass beakers were used as lab-scale aerobic digesters. These 2 beakers (control and pretreatment) were filled with same sludge sample and put into a thermostatic bath to obtain and keep desired temperature (mesophilic and thermophilic). Water in the thermostatic bath was fulfilled at the end of everyday because of high evaporation rate. Also top of the beakers were covered with streched film all the time (except drawing sample and adding feed) to prevent evaporation of sludge liquid. A Resun model aquarium pump which has air flowrate of 110 L/min. was connected to 2 silicone tubing which have diffuser stones at the heads. Air was provided by aquarium pump continuously, thus DO concentration in the beakers was kept 2 mg/L ±0.5.

Figure 3.2 Semi-batch aerobic digesters

Semi – batch aerobic digesters and air pump are shown in Figure 3.2 and Figure 3.3.

Figure 3.3 Air pump

First certain volume of sludge sample in the beaker was drawn to analyze, and then same volume of feed was added every operation day. This volume of feed sludge was determined according to appropriate SRTs and Eqn 2.6 mentioned in previous chapters.

3.4.2 Operational Conditions for Reactor Operations

The graphic in Figure 2.1 was considered to have an idea about probable VS reductions in mesophilic and thermophilic aerobic digestion operations according to the SRT and reactor temperature. SRT, temperature and feed sludge volume values which were used in digester operations are given in the Table 3.5 below. Where, SRT_{design} is design solid retention time (d), $T_{operation}$ is operation temperature (ºC), and V_{feed} is feed sludge volume (mL d^{-1}).

Table 3.5 Solids retention times used in reactor operations.

	SRT_{design}, d	**$T_{operation}$, °C**	**SRT x T, d x °C**	**V_{feed}, mL d^{-1}**
Mesophilic Aerobic Digestion	15	35 ± 2	525 ±30	200
Thermophilic Aerobic Digestion	6	55 ± 2	330 ±12	500

3.4.3 Start-up Phase

Both control and pretreatment reactors were fulfilled with 2 L inoculum sludge and 1 L feed sludge at the beginning. 200 mL of sludge was drawn from reactors and same volume of feed sludge added everyday for mesophilic aerobic digestion. 500 mL of sludge was drawn from reactors and same volume of feed sludge added everyday for thermophilic aerobic digestion. This feeding was continued until pH, electrical conductivity (EC), dissolved oxygen (DO), total solids (TS) and volatile solids (VS) concentrations of reactors remain stable.

3.4.4 Alkaline Pretreatment

According to predetermined optimum dose, 1 N NaOH was added to 200 mL of feed sludge in mesophilic aerobic digestion and 500 mL of feed sludge in thermophilic aerobic digestion until pH reached to 12. NaOH added sludge was stirred by Chiltern Hotplate HP31E magnetic stirrer for 30 min and prepared for subsequent microwave pretreatment.

3.4.5 Microwave Pretreatment

Berghoff Speedwave MWS 2+ model microwave digester device (2.45 GHz frequency, 1000 W max. power) which consists of 12 vessels was used in microwave pretreatment. Each vessel (DAP 60) has 60 mL capacity. Device and vessels are represented in Figure 3.4 and Figure 3.5 below.

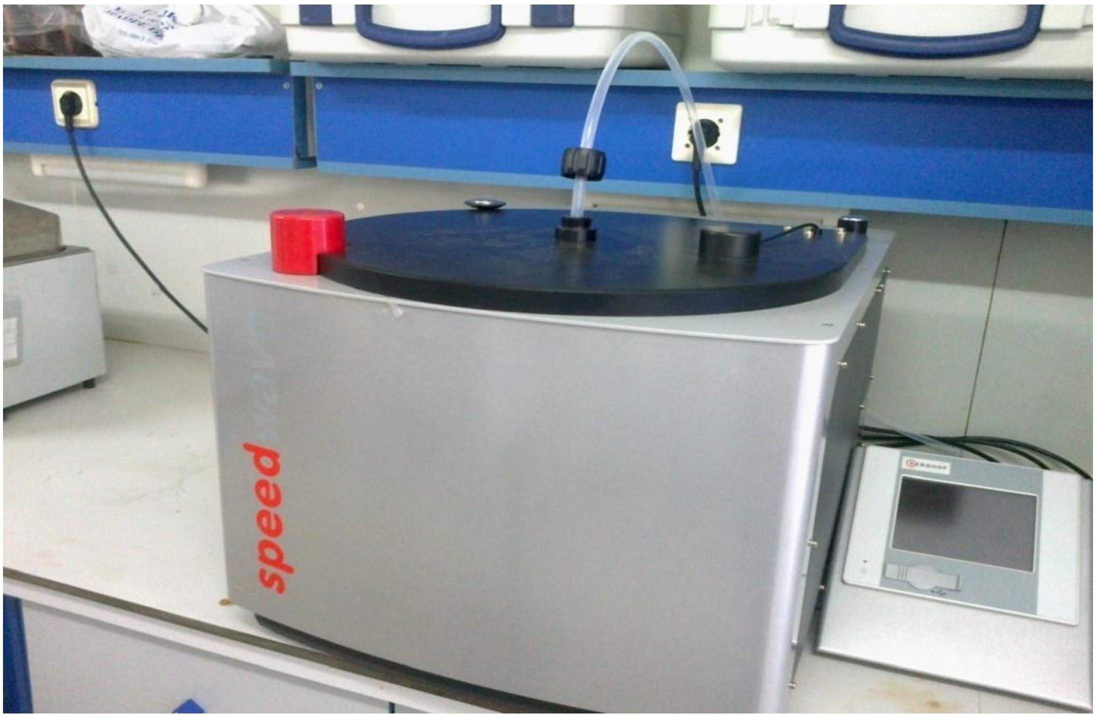


Figure 3.4 Microwave digester.

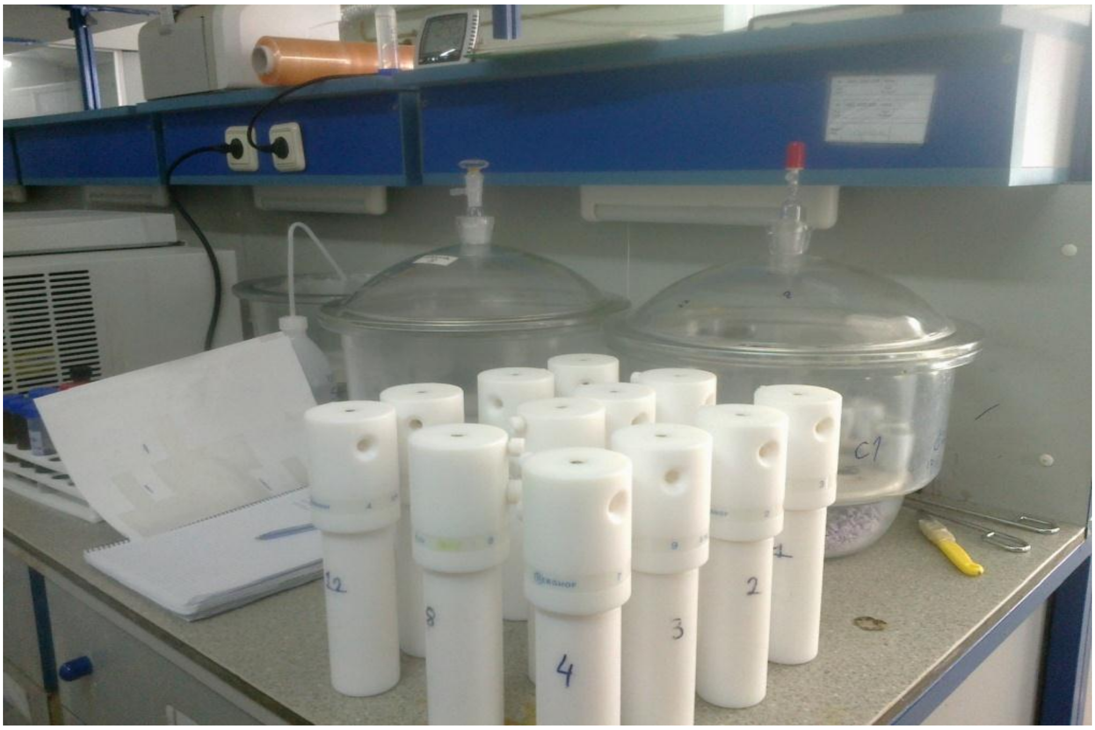


Figure 3.5 Vessels of microwave digester.

Alkali pretreated sludge was equally shared and same volumes of sludge was put into each vessel. Microwave digestion was processed according to application which represented in Table 3.6 below.

Table 3.6 Microwave application.

Temperature, °C	**Ramp, min.**	**Time, min.**	**Power, %**
50	1	1	99
100	1	1	99
150	2	35	99
50	1	1	80
50	1	1	80

The most appropriate application was written in digester’s software to provide predetermined optimum microwave pretreatment condition (150 °C, 35 min). In order to reach desired temperature rapidly and obtain the most accurate results, ramp time was kept as short as possible. Thus, period of ramp between 0 °C and 150 °C was assumed as negligible for pretreatment.

When microwave digestion finished, vessels were taken outside to warm. After pretreated feed was cooled down to room temperature, was fed to mesophilic / thermophilic pretreatment reactor. Any pH regulation was not carried out before feeding pretreatment reactor.

3.4.6 Mesophilic Aerobic Digestion Operation

Control and pretreatment reactor were reached to stable condition after start-up phase. Temperature was kept at 35 ±2 °C during operation. pH, EC, DO and T was measured with probe and recorded before drawing sludge samples from reactors every operation day. 200 mL of sludge was drawn from each reactor at the same time of the every operation day. TS, VS, MLSS, MLVSS, TCOD, CST and NH_4-N concentration of drawn sludge samples were measured periodically. OUR analysis was carried out separately on the days after these analysis were done. 200 mL of untreated feed sludge was added to control reactor and 200 mL of pretreated feed sludge was added to pretreatment reactor just after drawing samples every operation day.

3.4.7 Thermophilic Aerobic Digestion Operation

Control and pretreatment reactor were reached to stable condition after start-up phase. Temperature was kept at 55 ±2 °C during operation. pH, EC, DO and T was measured with probe and recorded before drawing sludge samples from reactors every operation day. 500 mL of sludge was drawn from each reactor at the same time of the every operation day. Total solids (TS), volatile solids (VS), mixed liquour suspended solids (MLSS), mixed liquour volatile suspended solids (MLVSS), total soluble COD (TCOD) concentrations and capillary suction time (CST) values of drawn sludge samples were measured periodically. Oxygen utilization rate (OUR) analysis was carried out separately. 500 mL of untreated feed sludge was added to control reactor and 500 mL of pretreated feed sludge was added to pretreatment reactor just after drawing samples every operation day.

3.4.8 Analytical Methods Used In Semi - Batch Aerobic Digester Operations

3.4.8.1 pH, EC, DO And T Analysis

pH, EC, DO and T measurements were carried out by WTW model 340i multi analyzer.

3.4.8.2 TS,VS, MLSS And MLVSS Measurements

TS, VS, MLSS and MLVSS measurements were carried out according to standard methods 2540 B, 2540 E, 2540 D and 2540 E respectively. Mettler Toledo AB 204-S model digital weigher, Nüve FN 055 model incubator and Nüve MF 120 model oven were also used in measurements.

3.4.8.3 TCOD Analysis

Total COD analysis was carried out according to standard methods 5220 B (open reflux method).

3.4.8.4 OUR Analysis

Oxygen uptake rate analysis was carried out according to standard methods 2710 B. WTW model 340i multi analyzer and Chiltern Hotplate HP31E magnetic stirrer were also used in analysis.

3.4.8.5 CST Measurements

Capillary suction time measurement was carried out according to standard methods 2710 G. Triton Type 304 M model capillary suction timer device which represented in Figure 3.6. below was also used in measurements.

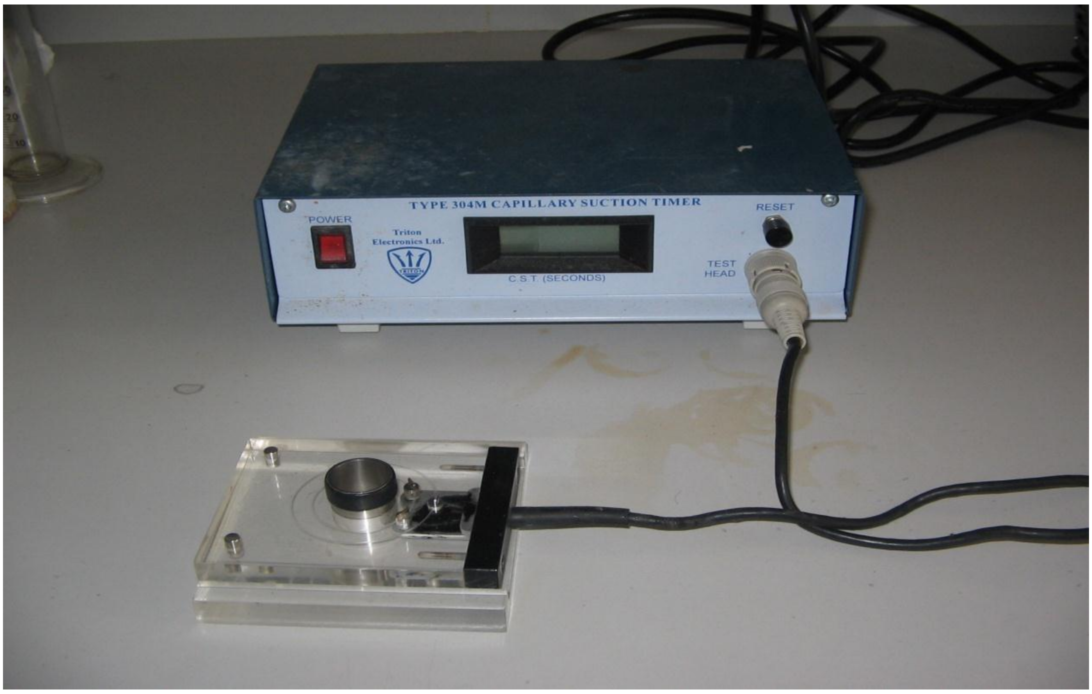


Figure 3.6 Capillary Suction Timer.

3.4.8.6 NH_4 - N Measurement

NH_4-N measurements were carried out by using Merck Ammonium Cell Test 114559.

3.4.8.7 Y_{obs} Determinations

Y_{obs} values were calculated by dividing MLVSS concentrations to TCOD concentrations during reactor operations.

CHAPTER FOUR

RESULTS & DISCUSSIONS

4.1 Results of Optimization Study

4.1.1 Optimum Condition Determination of Microwave Pretreatment Alone

Variation of disintegration degree of microwave pretreatment with microwave duration time is illustrated in Figure 4.1. Curves of different temperatures are in sequence vertically. After each curve reached its peak, DDs tend to decrease due to mineralisation phenomenon for higher doses per g TS (Bougrier et al., 2006). At 150 ºC temperature and 35 min. duration time, DD reached the highest level (89.54 %) for microwave pretreatment alone. This point was assumed as optimum condition of microwave pretreatment and used to determine the optimum condition of combined alkaline and microwave pretreatment in the next optimization step.

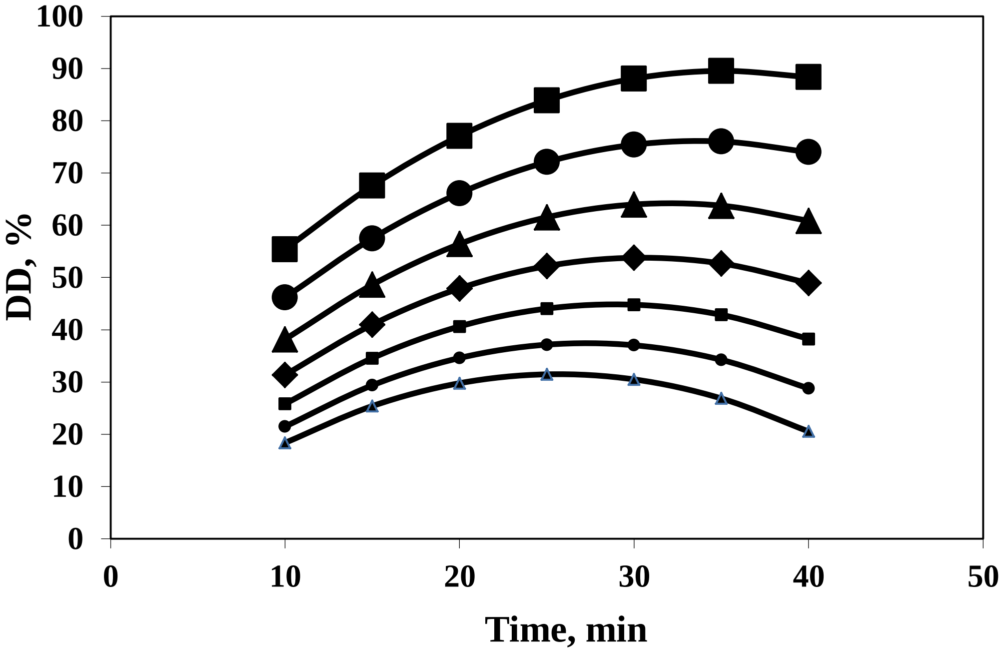


Figure 4.1 Variation of disintegration degrees (DD) with different duration times. Microwave set temperatures : (■) 150 °C, (●) 140 °C, (▲) 130 °C, (♦) 120 °C, (▪) 110 °C, (•) 100 °C, (▲) 90 °C.

In previously conducted studies including microwave digestion, SCOD/TCOD ratio was commonly used for COD solubilization instead of DD as a parameter. For comparison, SCOD/TCOD ratio increased from 0.06 (raw sludge) to 0.22 at this optimum point (150 ºC, 35 min.). Dogan & Sanin (2009) observed SCOD/TCOD ratio increase from 0.005 (raw sludge) to 0.18 at average 160 ºC temperature and 600 W power input for 30 min. total duration time. Chang et al. (2011) observed SCOD/TCOD ratio increase from 0.0033 (raw sludge) to 0.085 and sludge reached 85 ºC temperature at the end of 2 min. reaction time (600 W power input). Tyagi & Lo (2012) obtained SCOD/TCOD ratio increment from 0.006 (raw sludge) to 0.159 and sludge reached to 95 ºC at the end of 2 min. reaction time (900 W power input). But our results are slightly better than results of Eskicioglu et al. (2006) where SCOD/TCOD ratio increased from 0.06 (raw sludge) to 0.15 at 96 ºC.

4.1.2 Optimum Condition Determination of Combined Pretreatment

Variation of disintegration degree of combined pretreatment (alkali + MW) with alkali dose is shown in Figure 4.2.

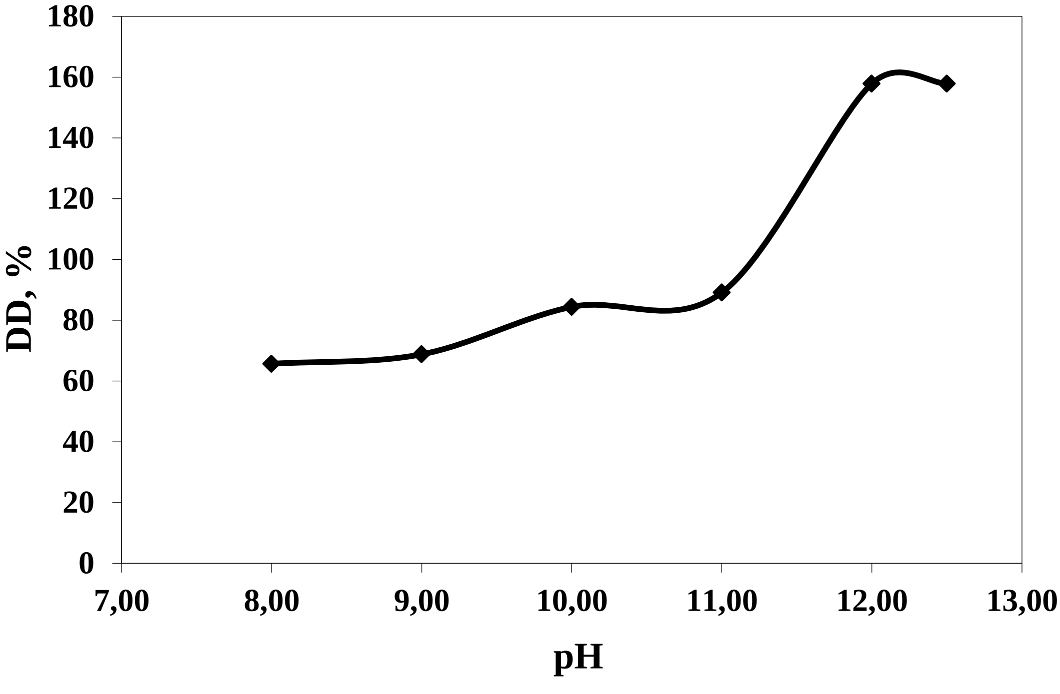


Figure 4.2 Variation of disintegration degrees (DD) with pH.

Considerable changes on DD were not observed from pH 8 to pH 12. At pH 12 and pH 12.5, DD rapidly increased and reached the same highest level (157.81 %). But alkaline solution consumption to reach pH 12.5 level is much higher than the consumption to reach pH 12 level. Therefore, alkaline dosage to pH 12 is more feasible.

Kim et al. (2010) employed a central composite design by using software and used DDs as response to determine the individual effects of pretreatments. They reported DD value as 21.4 % at pH 12 alkaline dose, and also they estimated DD value of Dogan & Sanin (2009) as 19.5 % at pH 12 alkaline dose by using same model. Based on these results, a considerable synergetic effect is present in our DD value (157.81 %) of combined alkaline (pH 12) and MW pretreatment. Dosages at this point were used in reactor operations as optimum combined pretreatment dosage. Dogan & Sanin (2009) also obtained the highest total gas and methane productions by applying combined MW (160 °C, 16 min.) and subsequent alkaline (pH 12) pretreatment prior to anaerobic digestion (SRT 15 d).

4.2 Results of Mesophilic Aerobic Digestion Operation

4.2.1 pH, EC, DO and T

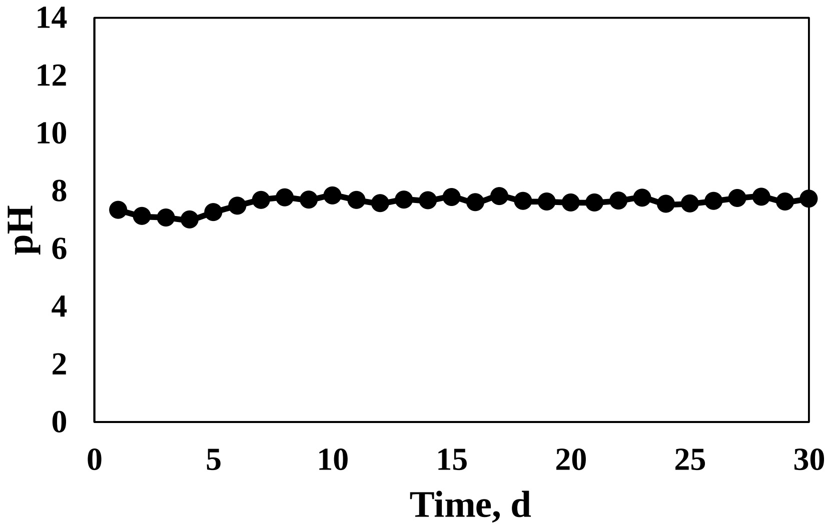


Figure 4.3 Variation of pH with time in control reactor.

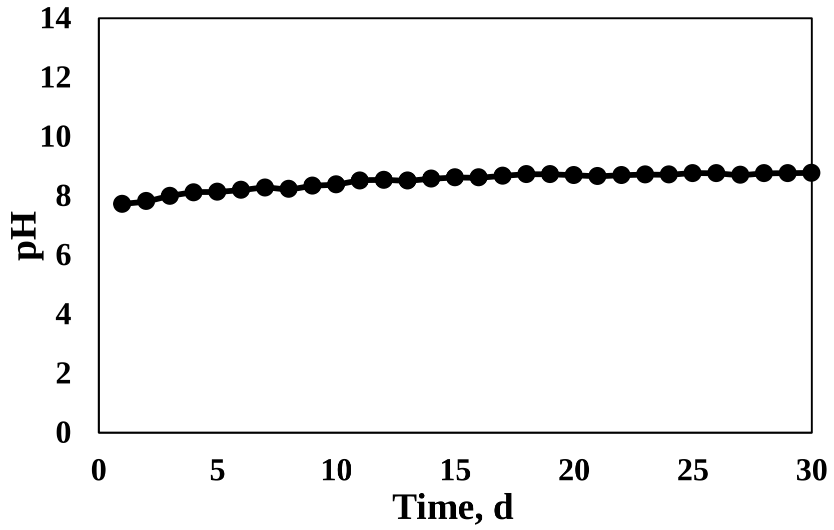


Figure 4.4 Variation of pH with time in pretreatment reactor.

Variation of pH values with time both in control and pretreatment reactors were shown in figure 4.3 and 4.4 respectively. pH values did not change significantly and stayed around 7.7 in control, but slightly increased in pretreatment and reached to 8.78 due to NaOH content of daily feed.

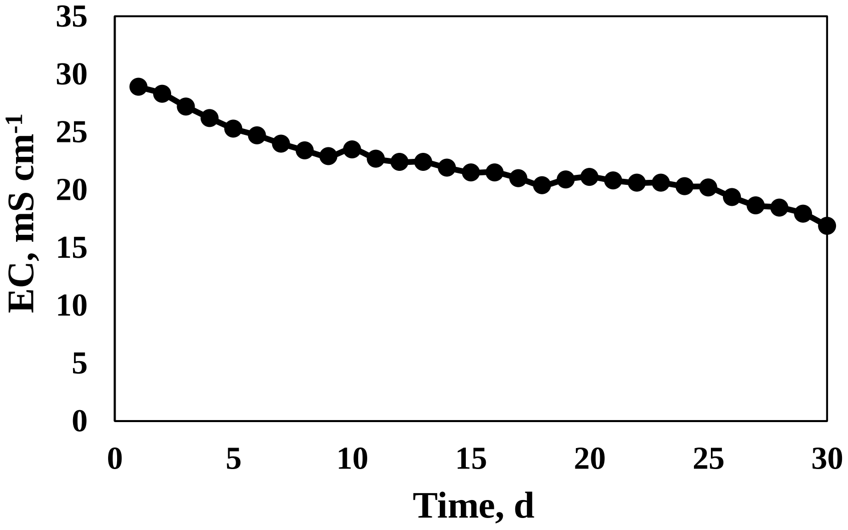


Figure 4.5 Variation of EC with time in control reactor.

EC is an indicator of total salinity in reactors. Normally, high evaporation rate in reactors leads to increase on EC. But EC reached a high level (more than concentration of feed) in reactors due to period without feeding before start-up. In this period, reactors were only aerated by air pump. After steady state, lower salinity of feed sludge started to dilute total salinity of reactor content. Variation of EC (electrical conductivity) with time both in control and pretreatment reactors were shown in figure 4.5 and 4.6 respectively.

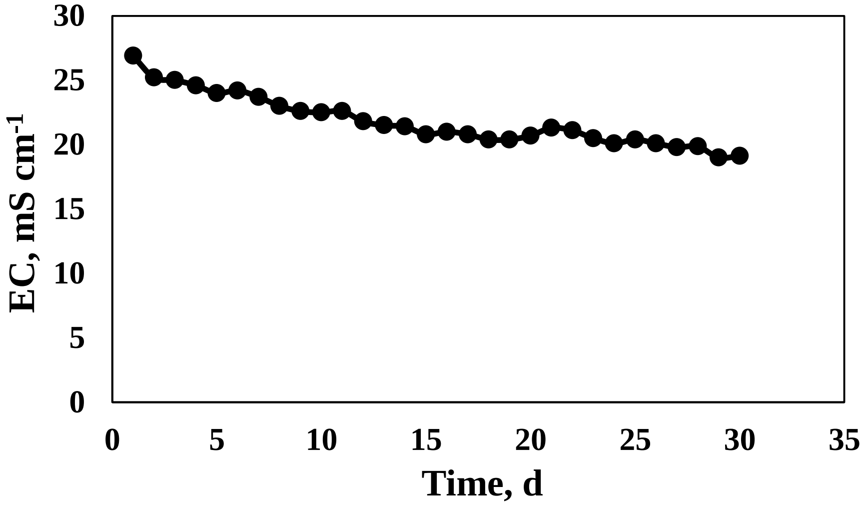


Figure 4.6 Variation of EC with time in pretreatment reactor.

DO concentration was kept at 2 mg/L (±0.5) and temperature was kept at 35 °C (± 2) in the beakers during operation.

4.2.2 TS & VS Reductions

Variation of TS reduction of reactor contents with time shown in figure 4.7. TS reduction is around 25 % in control and 38 % in pretreatment.

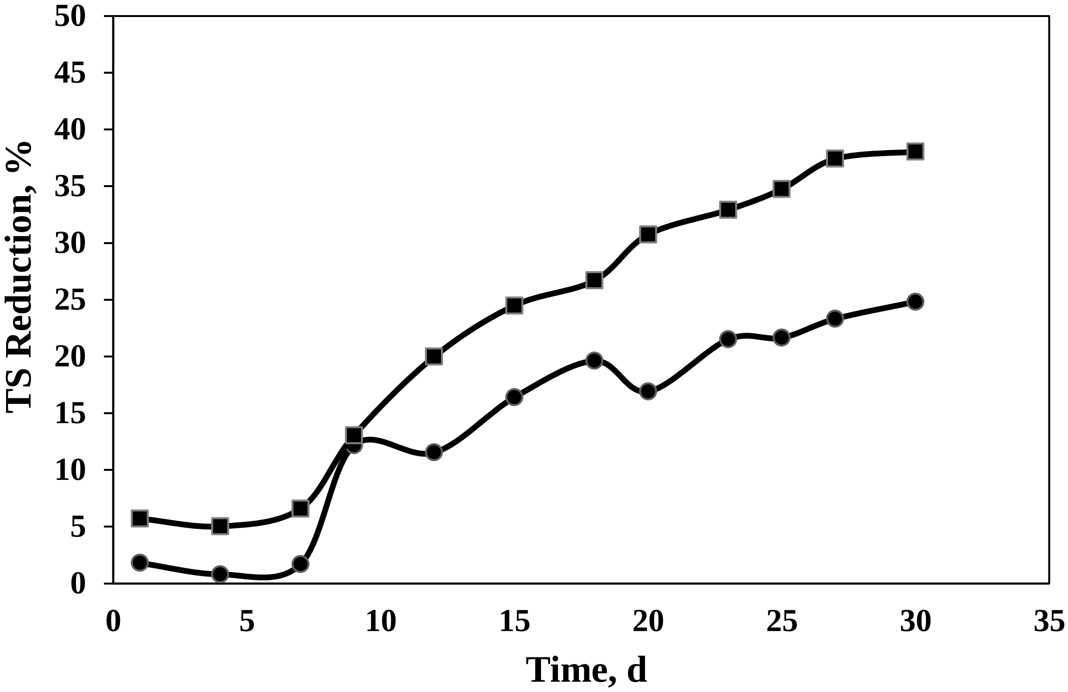


Figure 4.7 Variation of TS reduction with time. (●) Control reactor, (■) Pretreatment reactor.

Variation of VS reduction of reactor contents with time shown in figure 4.8.

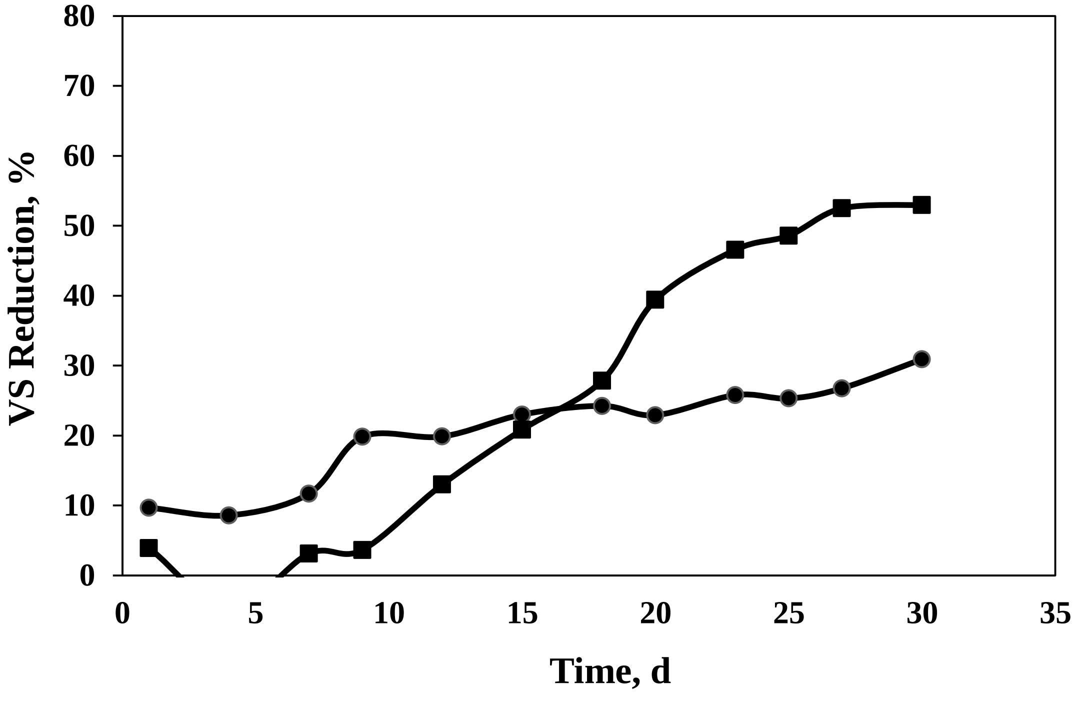


Figure 4.8 Variation of VS reduction with time. (●) Control reactor, (■) Pretreatment reactor.

VS reduction is around 31 % in control and 53 % in pretreatment. There is a considerable difference between VS degradation of control and pretreatment reactors. This result meets requirement for vector attraction (more than 38 %) in US EPA part 503. Dogan & Sanin (2009) also reported 58.5 % VS reduction in pretreatment reactor at the end of mesophilic anaerobic digestion (MW + pH 12, HRT 92 d) with combined MW and alkali pretreatment.

4.2.3 MLSS & MLVSS Reductions

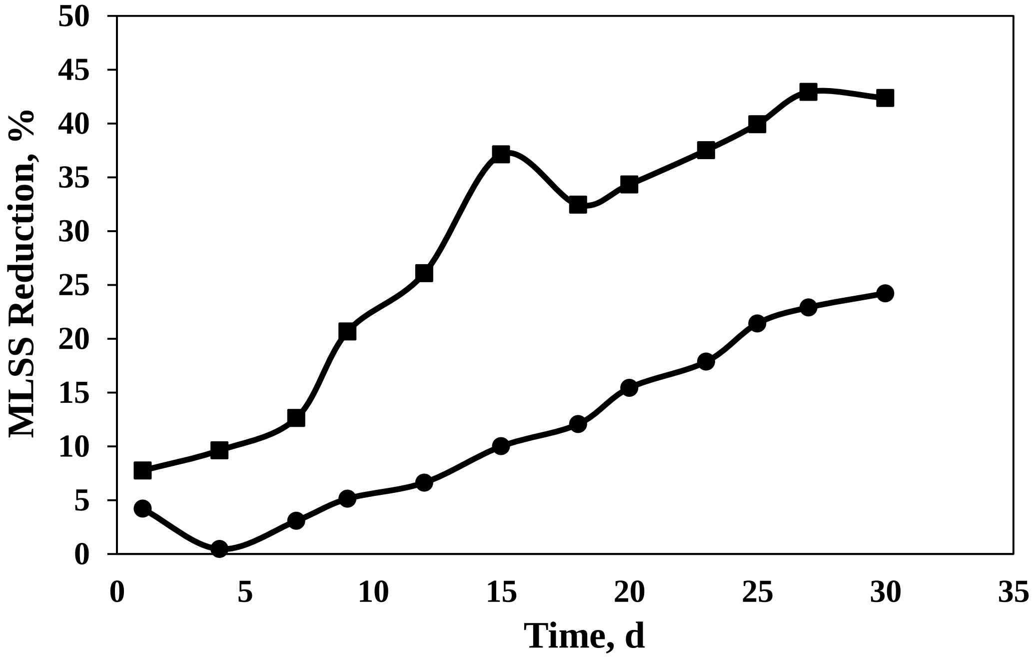


Figure 4.9 Variation of MLSS reduction with time. (●) Control reactor, (■) Pretreatment reactor.

Variation of MLSS concentrations of reactor contents with time is shown in figure 4.9. MLSS reductions were found around 24 % in control and 42 % in pretreatment. Decreasing MLSS concentrations are related with decreasing TS concentrations considerably.

Variation of MLVSS concentrations of reactor contents with time is shown in Figure 4.10. MLVSS reductions found around 13 % in control reactor and around 44

% in pretreatment. MLVSS reduction slightly increased in control but increased steadily in pretreatment. These results are indicators of endogenous respiration. Aerobic bacterias which are carrying out degradation in both reactors, are in endogenous respiration phase. Normally, an instant increase on MLVSS concentrations are expected at the beginning period of conventional aerobic digestion due to readily degradation of soluble organic matter. But instant increase was not exactly observed in this study.

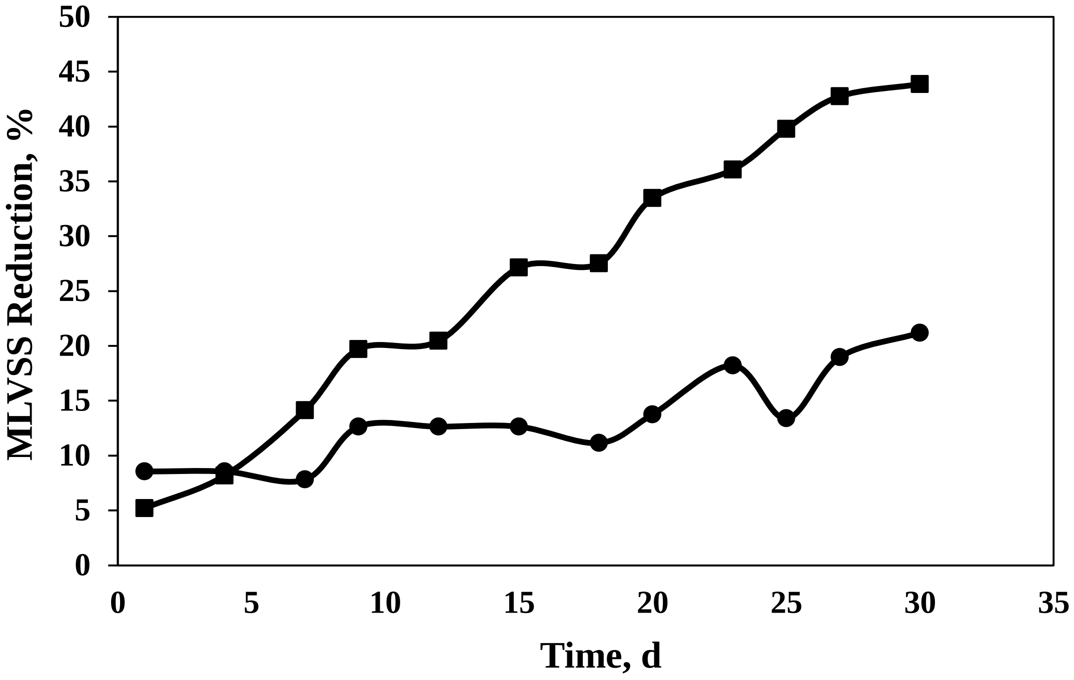


Figure 4.10 Variation of MLVSS reduction with time. (●) Control reactor, (■) Pretreatment reactor.

Dogan & Sanin (2009) obtained 48.3 % MLVSS reduction in pretreatment reactor at the end of mesophilic anaerobic digestion (MW + pH 12, HRT 49 d) and 42 % MLVSS reduction in control reactor after digestion.

4.2.4 Oxygen Uptake Rates (OUR)

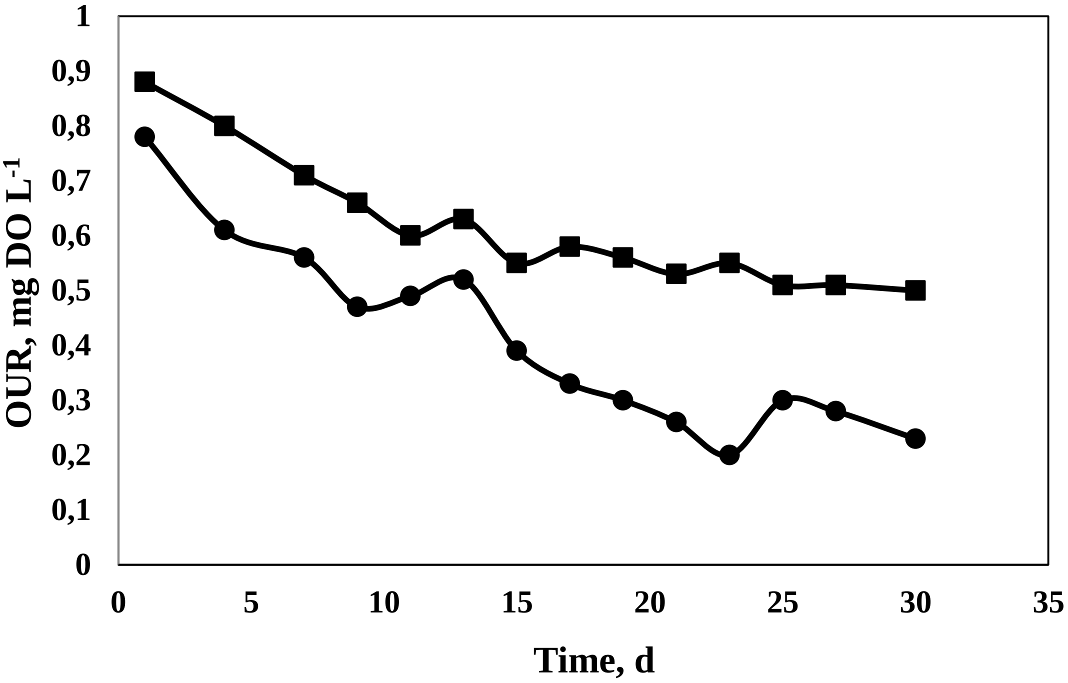


Figure 4.11 Variation of OUR values with time. (●) Control reactor, (■) Pretreatment reactor.

Oxygen uptake rates of both control and pretreatment reactors decreased during 30 d digestion due to endogenous respiration. OUR values of pretreatment reactor were higher than control during digestion and a considerable difference observed between final OUR values. Variation of OUR values with time is shown in Figure 4.11.

4.2.5 TCOD Reductions

Variation of TCOD reductions with time is shown in Figure 4.12. TCOD reductions observed around 22 % in control reactor and around 48 % in pretreatment reactor. Tyagi & Lo (2012) reported 81.1 % TCOD reduction after mesophilic aerobic digestion (MW + pH 12, HRT 20 d).

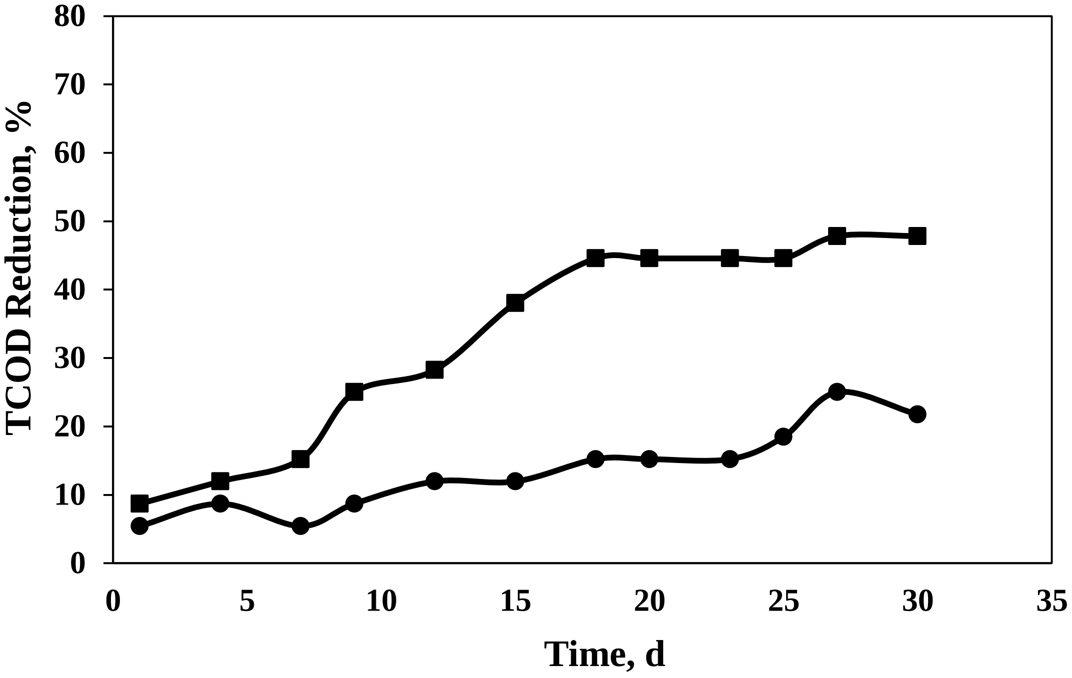


Figure 4.12 Variation of TCOD reductions with time. (●) Control reactor, (■) Pretreatment reactor.

4.2.6 Observed Yields (Y_{obs})

Parameter of Y_{obs} is an indicator of biological activity in digesters but it is mostly calculated to determine the achievement of conventional activated sludge systems. Therefore, there is a lack of literature about Y_{obs} values of digestion processes.

Variation of Y_{obs} values with time is shown in figure 4.13. Y_{obs} values of pretreatment were higher than values of control during 30 d aerobic digestion. Average Y_{obs} values of control and pretreatment were calculated as 0.19 g MLVSS g TCOD^{-1} and 0.32 g MLVSS g TCOD^{-1} respectively. These results are in agreement with OUR values of digesters and indicate endogenous respiration.

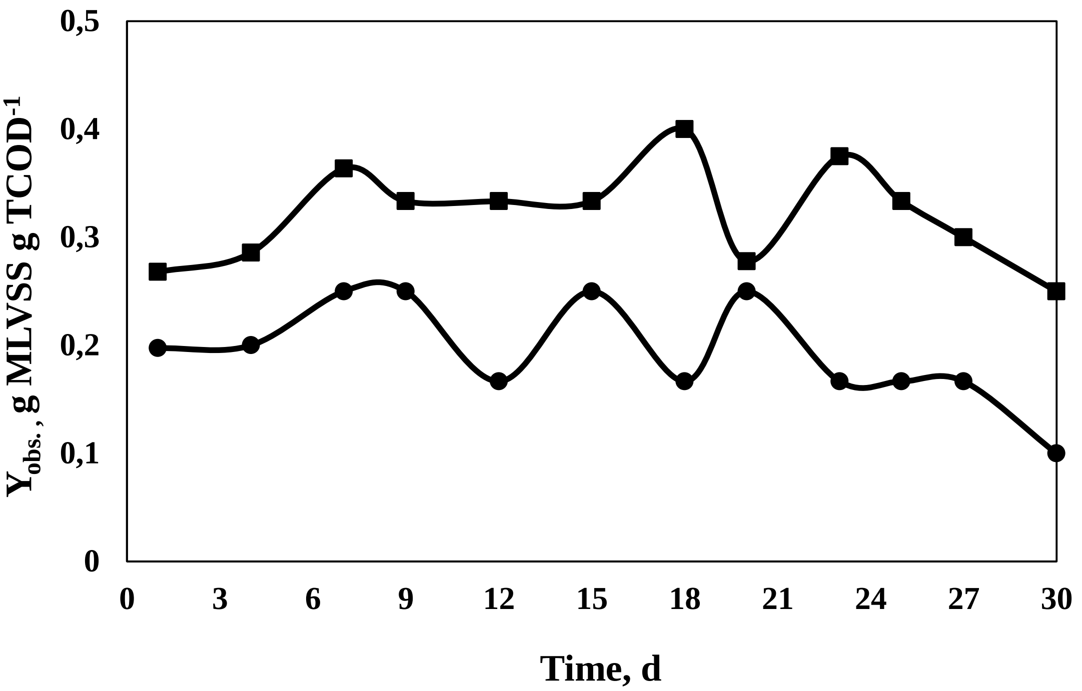


Figure 4.13 Variation of observed yield (Y_{obs}) values with time. (●) Control reactor, (■) Pretreatment reactor.

4.2.7 CST

Parameter of capillary suction time (CST) is an indicator of dewaterability of waste activated sludge. Both of reactors contains sludge that have good filterability. CST values of both control and pretreatment are very close during digestion.

In most of the studies containing microwave irradiation in combined pretreatments, microwave pretreatment was carried out prior to alkaline pretreatment. Subsequent alkaline pretreatment leads to reflocculation, thus improves sludge settleability and causes a decrease in dewaterability. But combined alkaline pretreatment with subsequent energy-intensive pretreatments (microwave irradiation, ultrasonic disintegration etc.) causes very low CST values. The main reason of this, breaking flocs which are reflocculated in previous step by high energy (low wavelength) microwave irradiation. Also reflocculation in only alkaline pretreated sludge is weaker than previously microwave pretreated sludge due to absence of EPS material.

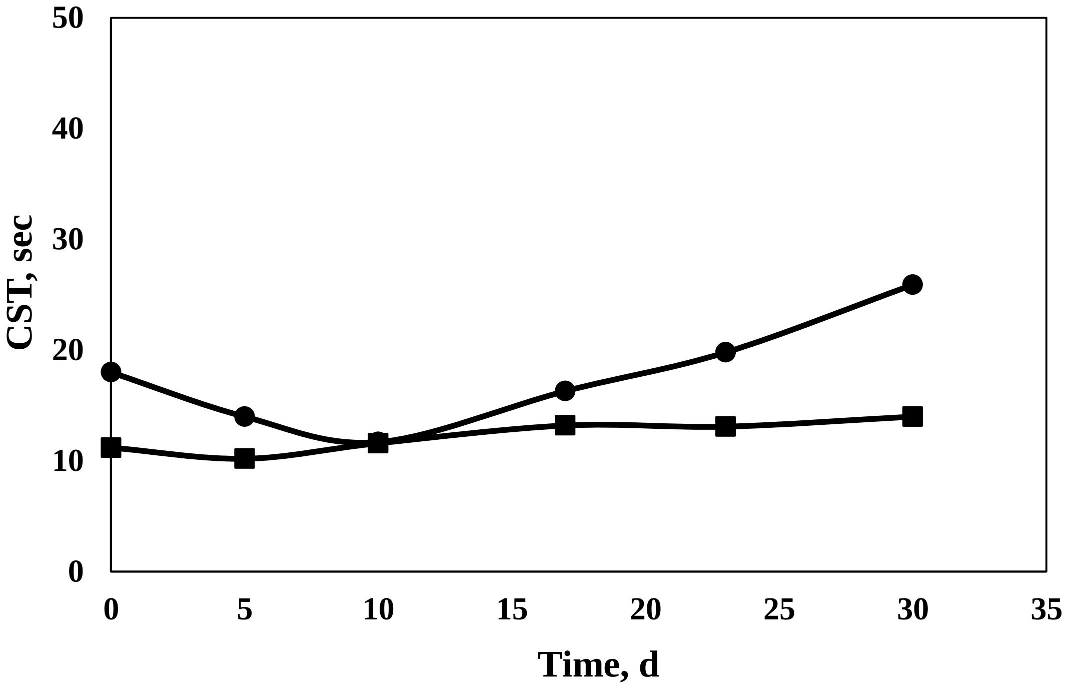


Figure 4.14 Variation of CST values with time. (●) Control reactor, (■) Pretreatment reactor.

According to US EPA Design Manual (1987), WAS which has 10 seconds or less CST value is enough to dewater by filter press. CST values of pretreatment reactor are very close to this value. Variation of CST values with time is shown in Figure 4.14.

4.2.8 NH_4-N

NH_4-N concentrations of pretreatment increased during digestion and reached to max. level of 110 mg L^{-1}. An expected considerable difference is shown between final concentrations. This is a result of released EPS and IPS into aqueous phase. Both EPS and IPS have high nitrogen content. After 20 days of digestion, NH_4-N concentrations in pretreatment reactor did not change considerably. This may be a result of nitrification. Variation of NH_4-N values with time is shown in Figure 4.15.

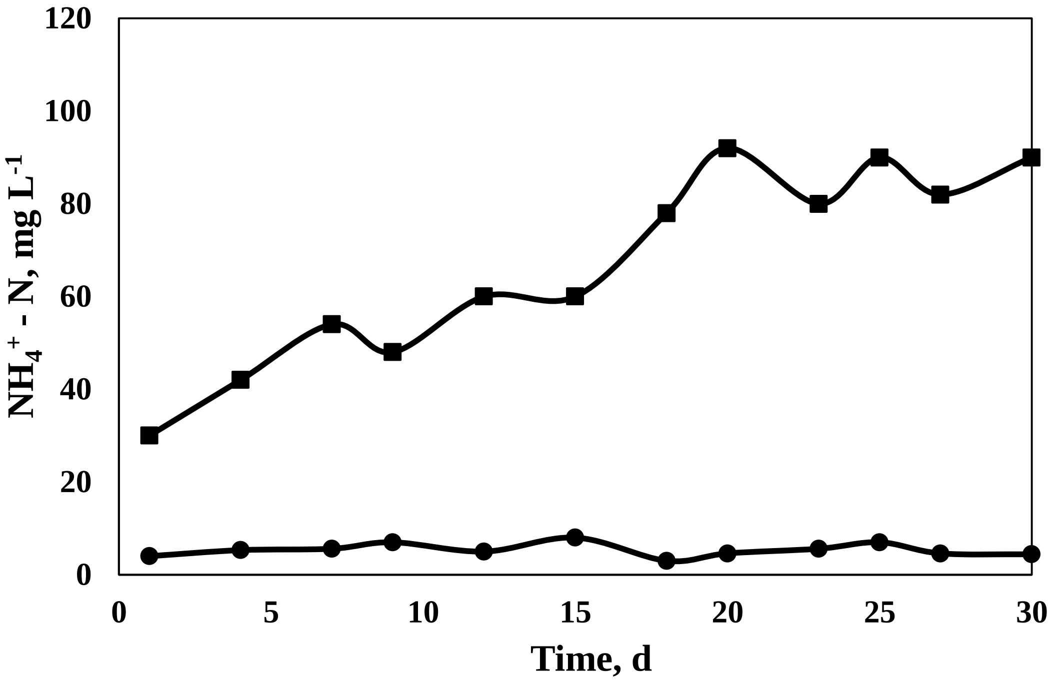


Figure 4.15 Variation of NH_4-N concentrations with time. (●) Control reactor, (■) Pretreatment reactor.

4.3. Results of Thermophilic Aerobic Digestion Operation

4.3.1 pH, EC, DO and T

Variation of pH values with time both in control and pretreatment reactors were shown in Figure 4.16 and 4.17 respectively. pH values did not change significantly in control reactor as it happened in mesophilic operation, but increased more in pretreatment reactor and reached max. level of 9.2. This is a result of bigger feed volume (more NaOH addition) in thermophilic operation.

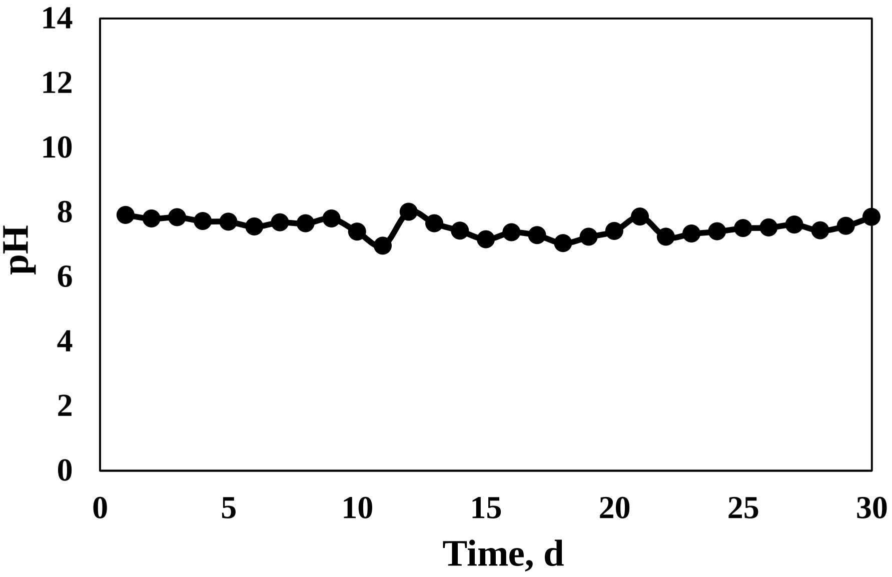


Figure 4.16 Variation of pH with time in control reactor.

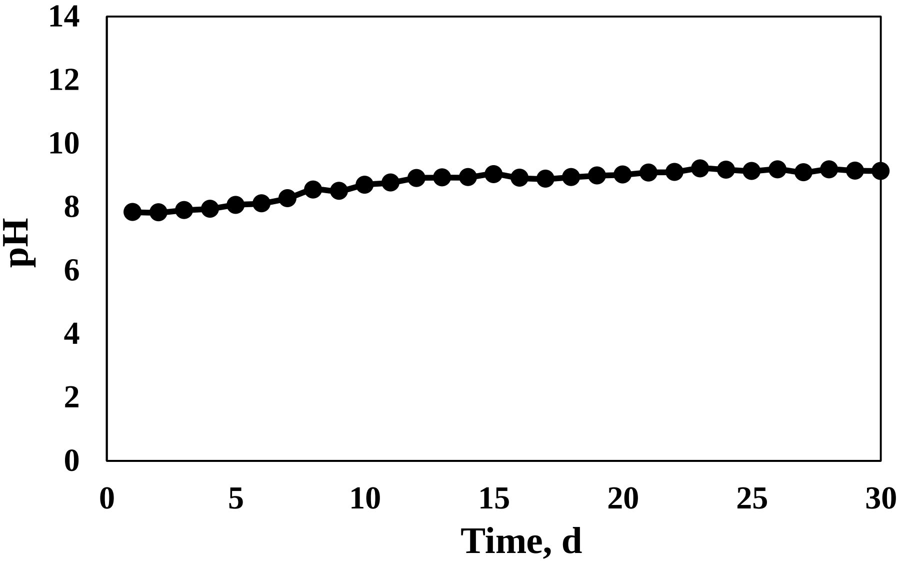


Figure 4.17 Variation of pH with time in pretreatment reactor.

Variation of EC values with time both in control and pretreatment reactors were shown in Figure 4.18 and 4.19 respectively. EC values decreased in both control and pretreatment during digestion due to dilution of total salinities.

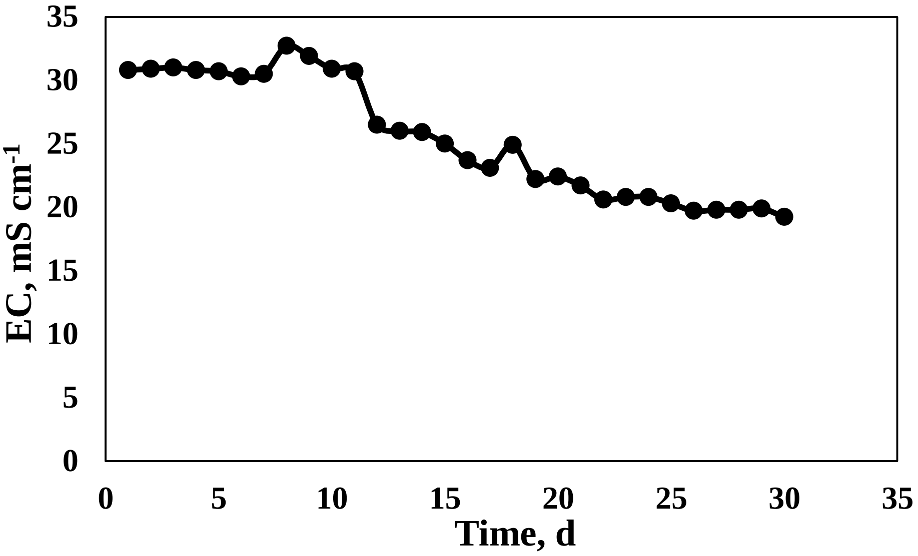


Figure 4.18 Variation of EC with time in control reactor.

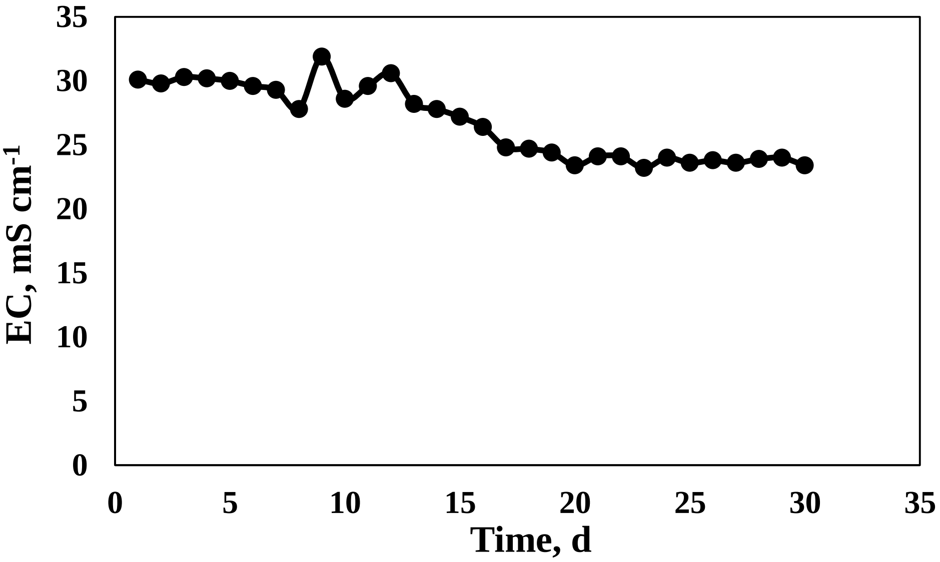


Figure 4.19 Variation of EC with time in pretreatment reactor.

DO concentration was kept at 2 mg/L (±0.5) and temperature was kept at 55 °C (± 2) in the beakers during operation.

4.3.2 TS & VS Reductions

Variation of TS reduction of reactor contents with time shown in Figure 4.20. TS reduction is around 22 % in control and 36 % in pretreatment. These results are slightly worse than mesophilic operation. This may be a result of less TS concentration of reactor content in thermophilic operation.

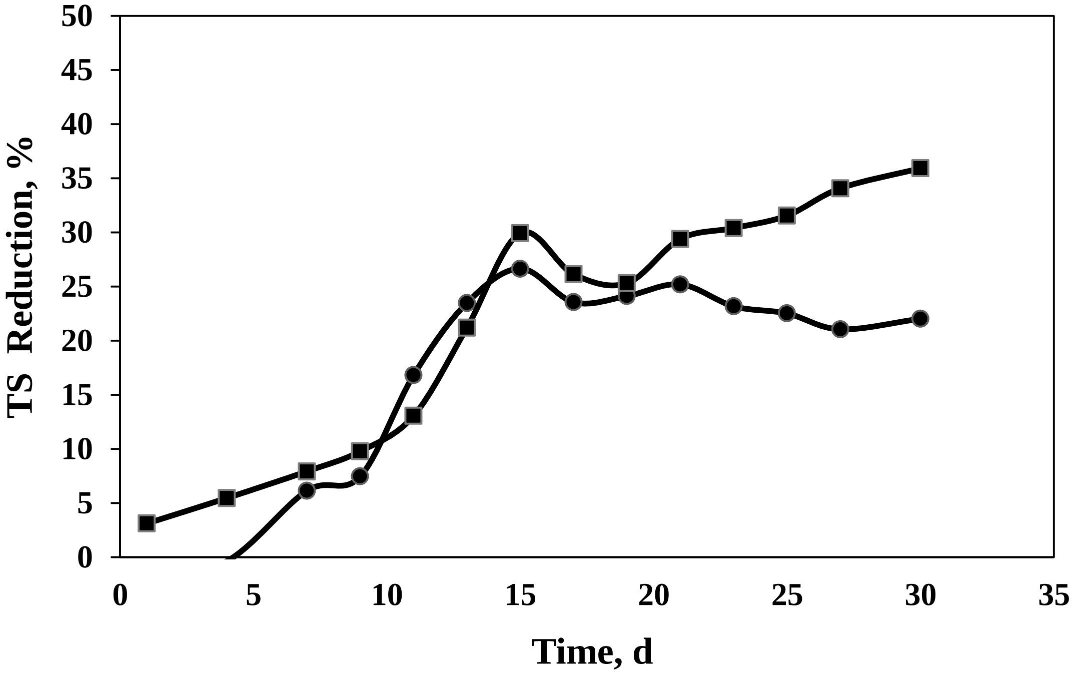


Figure 4.20 Variation of TS reduction with time. (●) Control reactor, (■) Pretreatment reactor.

VS reduction is around 39 % in control reactor and 65 % in pretreatment. A considerable difference was observed between reductions during thermophilic operation. This indicates that higher temperature of environment improved biological activity of aerobic bacterias for degradation of organic matter. Also long operation period (30 d) of thermophilic operation according to SRT led better degradation for easily degradable compounds. In other words, carbon-based substrate was depleted rapidly after feeded. On the contrary to this, nitrogen-based substrate accumulated as ammonia nitrogen (NH_3-N) in reactor during operation. This situation also led to a decrease on MLVSS concentrations considerably.

Final VS reductions in pretreatment reactor are well above the level of vector attraction requirements of EPA (38 %). Variation of VS reduction of reactor contents with time shown in figure 4.21.

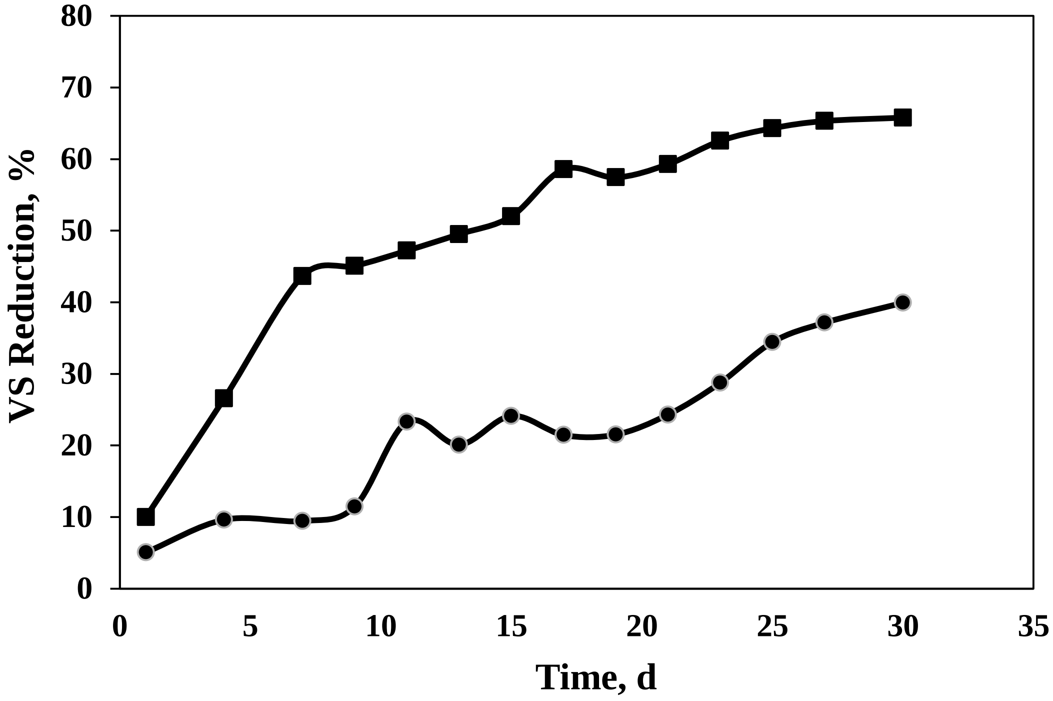


Figure 4.21 Variation of TS reduction with time. (●) Control reactor, (■) Pretreatment reactor.

4.3.3 MLSS & MLVSS Reductions

Variation of MLSS concentrations of reactor contents with time is shown in figure 4.22. Final MLSS reductions are around 23 % in control and 43 % in pretreatment. Decreasing MLSS concentrations are related with decreasing TS concentrations considerably.

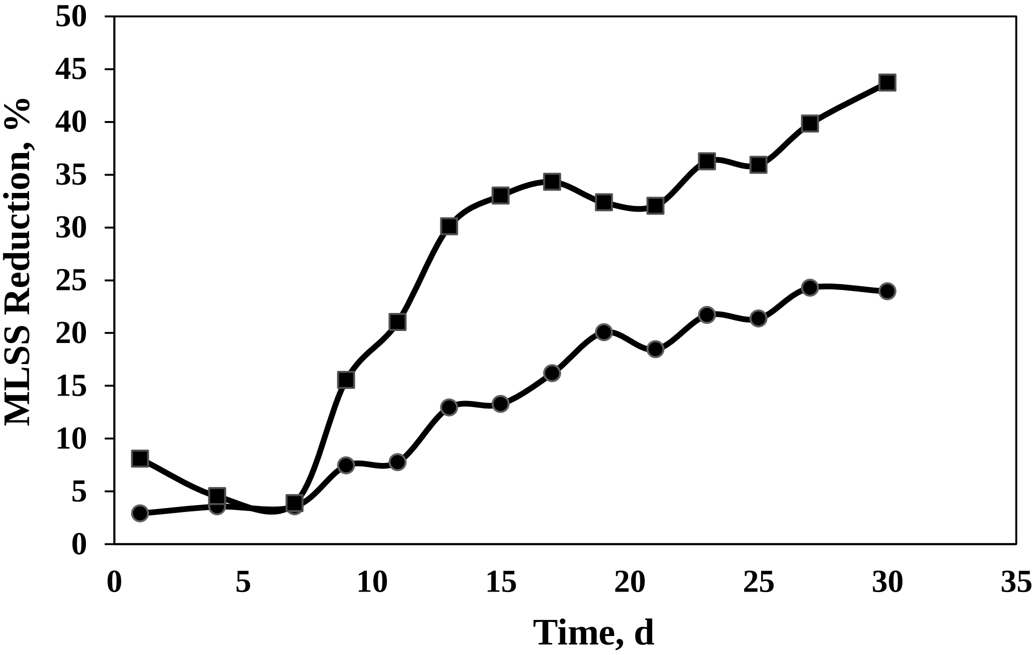


Figure 4.22 Variation of MLSS reduction with time. (●) Control reactor, (■) Pretreatment reactor.

Variation of MLVSS reductions of reactor contents with time is shown in Figure 4.23.

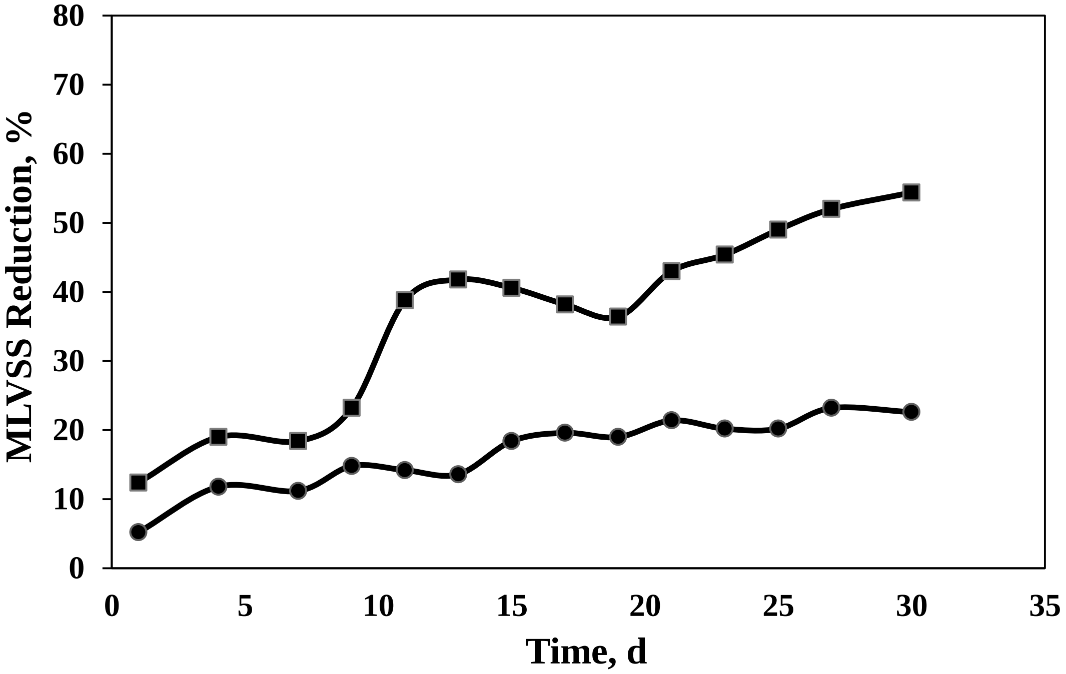


Figure 4.23 Variation of MLVSS reduction with time. (●) Control reactor, (■) Pretreatment reactor.

Final MLVSS reductions are around 21 % in control and 53 % in pretreatment reactor. MLVSS concentrations instantly increased in both control and pretreatment in first 10 days of operation as expected. After 15 th day of digestion, MLVSS reductions remained stable in control, but increased in pretreatment continuously. Free ammonia inhibition may be also a factor for this reduction.

4.3.4 Oxygen Uptake Rates (OUR)

Oxygen uptake rates of both control and pretreatment reactors decreased during 30 d digestion due to endogenous respiration and probable free ammonia inhibition. Average value of OUR of pretreatment less than average in mesophilic operation but final concentrations are close to mesophilic operation. This result is an indicator of probable inhibition in pretreatment reactor in thermophilic operation. On the other hand, average OUR value of control is equal to average in mesophilic operation. Variation of OUR of reactor contents with time is shown in Figure 4.24.

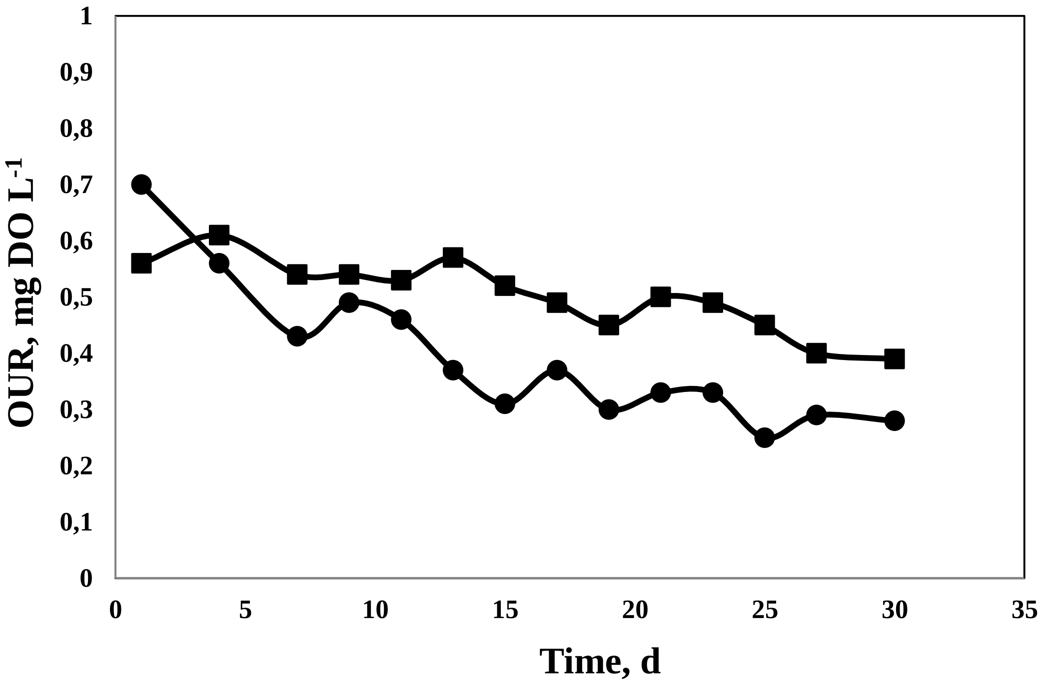


Figure 4.24 Variation of OUR values with time. (●) Control reactor, (■) Pretreatment reactor.

4.3.5 TCOD Reductions

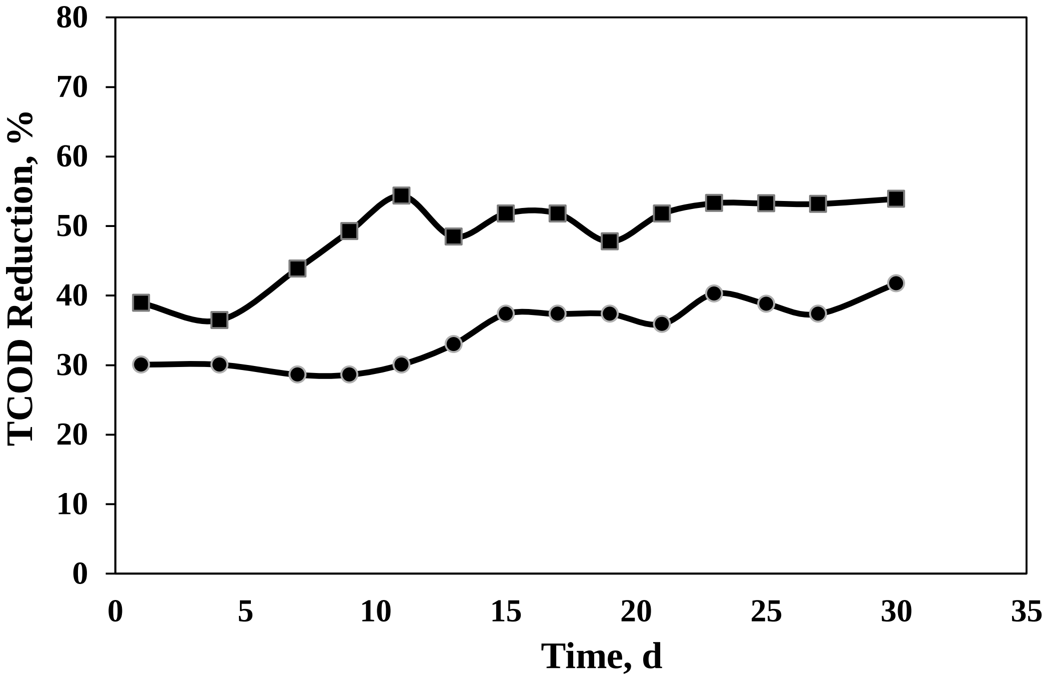


Figure 4.25 Variation of TCOD reductions with time. (●) Control reactor, (■) Pretreatment reactor.

TCOD reductions observed around 41 % in control reactor and around 53 % in pretreatment reactor. Higher temperature of environment improved degradation of TCOD in control reactor. TCOD reductions slighltly increased during digestion. But pretreatment reactor did not achieve a sufficient reduction according to mesophilic operation. Final reduction value of pretreatment are close to final reduction value in mesophilic operation (48 %). Tyagi & Lo (2012) obtained 64 % TCOD reduction in first 4 days of mesophilic aerobic digestion. Variation of TCOD reductions with time is shown in Figure 4.25.

4.3.6 Observed Yields (Y_{obs})

Average Y_{obs} values of control and pretreatment during thermophilic operation were calculated as 0.21 g MLVSS g $TCOD^{-1}$ and 0.26 g MLVSS g $TCOD^{-1}$

respectively. Average value of control is slightly higher than average of mesophilic operation due to temperature difference and related biological activity improvement. But average value of pretreatment is lower than average of mesophilic operation. This result confirmed presence of insufficient biological activity in pretreatment reactor in thermophilic operation and is in agreement with findings of other parameters. Variation of Y_{obs} values with time is shown in Figure 4.26.

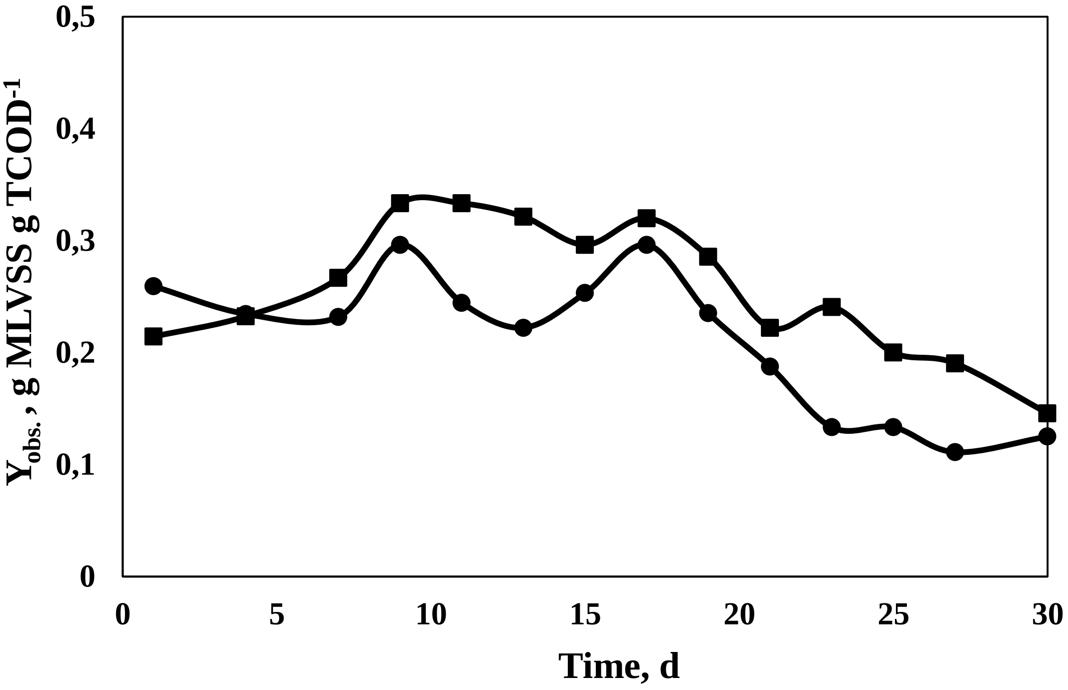


Figure 4.26 Variation of observed yield (Y_{obs}) values with time. (●) Control reactor, (■) Pretreatment reactor.

Results of all parameters which were conducted during reactor operations have been briefly shown in Table 4.1 below.

Table 4.1 Results of reactor operations

	Mesophilic Operation		**Thermophilic Operation**	
	Control	**Pretreatment**	**Control**	**Pretreatment**
pH final	7.7	8.78	7.8	9.2
EC final, mS/cm	16.89	18.26	19.23	24.9
TS reduced, %	25	38	22	36
VS reduced, %	31	53	39	65
MLSS reduced, %	24	42	23	43
MLVSS reduced, %	13	44	21	53
OUR average, mg DO L^{-1}	0.4	0.63	0.41	0.51
TCOD reduced, %	22	48	41	53
$Y_{obs.}$ average, g MLVSS g TCOD $^{-1}$	0.19	0.32	0.21	0.26
CST final, s	14.4	10.7	-	-
NH_4-N final, mg L^{-1}	4.4	98	-	-

CHAPTER FIVE
CONCLUSIONS & RECOMMENDATIONS

Conventional aerobic digestion was used as a stabilization technique in this lab-scale study. Alkaline pretreatment and energy intensive process microwave digestion were also used as pretreatment techniques to improve stabilization of WAS. Aerobically digested sludge was used as inoculum and WAS from return line of secondary sedimentation tank of domestic WWTP was used as feed sludge.

Changing composition of feed sludge which was supplied from domestic WWTP periodically, was substantially affected composition of reactor content and biological activity. High EC values of feed sludges which were used both in mesophilic (14.9 mS cm^{-1}) and thermophilic operation (16.8 mS cm^{-1}) may be inhibited biological activity in reactors. VS and TCOD reduction performance of control reactors is the main indicator for this situation.

Feeding with low TS concentration (around 1%) return sludge in intermediate sections of operations is another important issue which disturbs the influent–effluent balance of substrate and active biomass in reactors. In other words, MLSS and MLVSS concentration tends to decrease as an indirect result of decreasing TS concentration and fluctuations on MLVSS concentrations substantially affect degradation performance. Therefore, composition of feed sludge which provided from WWTP must not change considerably.

As a new finding of this study, determining appropriate SRT_{design} according to operation period is one of the important design considerations for semi-batch aerobic digestion operations. Because low SRTs according to operation period (high number of loops, $T_{operation\ period}$ / T_{SRT}) causes easily depletion of carbon-based substrate but accumulation of nitrogen-based substrate. It may be better to dispose all digester and refill at the end of a certain number of loop to avoid inhibition. Because, although sufficient NH_4-N concentration was present and conditions were suitable to start partial nitrification in digester, daily addition of soluble carbon-based substrate (refreshment) prevented to occur this in thermophilic operation. Also volume of feed according to volume of digester (V_{feed} $V_{digester}^{-1}$) increases as SRT_{design} decreases. This causes inhibition to reach intolerable levels. Maximum NH_4-N concentration was found 110 mg L^{-1} in mesophilic operation and accumulation was estimated to be more than 110 mg L^{-1} in thermophilic operation.

Final pH values at the end of operations reached 8.8 and 9.2 in pretreatment reactors of mesophilic and thermophilic operation respectively. NH_4-N is present as ammonia (NH_3) at high pH values. Increasing NH_3 concentrations may be led to free ammonia inhibition, especially in pretreatment reactor of thermophilic operation. On the other hand, an effect of nitrite inhibition may be occured due to insufficient nitrification in digester. Average $Y_{obs.}$ values of pretreatment reactors of both operations demonstrated that inhibition effect. Average Y_{obs} of pretreatment reactor in mesophilic operation was found 0.32 g MLVSS g $TCOD^{-1}$ but it was found 0.26 g MLVSS g $TCOD^{-1}$ in thermophilic operation. Also insufficient VS reduction (65 %), TCOD reduction (53 %) and excess MLVSS reduction (42 %) in pretreatment reactor of thermophilic operation are other indicators of this inhibition. On the contrary to this, effect of inhibition on degradation kinetics of mesophilic digestion operation could not be determined clearly. Despite of this, mesophilic aerobic digestion process was found more effective than thermophilic aerobic digestion due to observed advantages. These advantages are better stability of reactors, lower evaporation rate and less inhibition effect.

CST of pretreatment reactor content in mesophilic operation were found slightly lower than CST of control reactor content due to disruption of reflocculated sludge particles by subsequent microwave irradiation. Also very low CST values of both reactor contents are suitable to transfer sludge to dewatering process directly. Published studies about combined alkaline and microwave digestion prior to digestion processes until present, applied alkaline pretreatment as subsequent pretreatment. But this finding is one of the different results about filterability characteristics of sludge. Another difference of this study is pH neutralization of pretreated feed which was not carried out. Unneutralized feed raised the pH value of pretreatment reactor contents. Based on these differences of experimental study, most of the published studies in the literature that include alkaline pretreatment and microwave irradiation as pretreatment techniques are not totally appropriate to compare and give an idea about our findings. A detailed study which indicates synergetic effect of pretreatments better, with more related parameters such as SCOD and VSS should be investigated during operations. To determine the effect of potential inhibition and degradation performance clearly, respirometric devices should be used for more accurate OUR analysis and additional indicator parameters which are not present in this study should be analyzed.

A new lab-scale aerobic digestion operation with combined alkaline and microwave pretreatments should be investigated by using unneutralized pretreated feed sludge. It is recommended to operate in mesophilic temperature range to reduce effect of inhibition. Particle size distribution and specific resistance to filtration (SRF) analysis also should be analyzed with CST to demonstrate the findings of this study.

For a more comprehensive study, pathogen reduction requirements and classifications of US EPA should also be considered with vector attraction requirements. Also an effective cost analysis should be done to determine applicability of this effective aerobic stabilization method in municipal and industrial field of work.

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APPENDICES

Abbreviations

CCD	Central composite design
CST	Capillary suction time, s
DD	Disintegration degree, %
DO	Dissolved oxygen, mg O_2 L^{-1}
EC	Electrical conductivity, mS cm^{-1}
EPA	United States Environmental Protection Agency
EPS	Extracellular polymeric substances
HRT	Hydraulic residence time, d
IPS	Intracellular polymeric substances
MLSS	Mixed liquor suspended solids, mg L^{-1}
MLVSS	Mixed liquor volatile suspended solids, mg L^{-1}
MPN	Most probable number
MW	Microwave pretreatment
NH_4-N	Ammonium nitrogen, mg L^{-1}
O_3	Ozone gas
PFRP	Processes further reduce pathogens
PS	Primary sludge
PSRP	Processes significantly reduce pathogens

RSM	Response surface methodology
SCOD	Soluble chemical oxygen demand, mg L^{-1}
SRF	Specific resistance to filtration, s
SRT	Solids retention time, d
SRT_{design}	Design solids retention time, d
T	Temperature, °C
$T_{operation}$	Operation temperature, °C
TCOD	Total chemical oxygen demand, mg L^{-1}
TS	Total solids concentration, %
V_{feed}	Volume of feed sludge, mL d^{-1}
$V_{digester}$	Volume of digester, mL
VS	Volatile solids concentration, %
WAS	Waste activated sludge
WEF	Water Environment Federation
$Y_{obs.}$	Observed yields, g MLVSS g $TCOD^{-1}$