# COMBINATION OF ALKALINE SOLUBILIZATION WITH MICROWAVE DIGESTION AS A SLUDGE DISINTEGRATION METHOD: EFFECT ON GAS PRODUCTION AND QUANTITY AND DEWATERABILITY OF ANAEROBICALLY DIGESTED SLUDGE

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# ABSTRACT

## COMBINATION OF ALKALINE SOLUBILIZATION WITH MICROWAVE DIGESTION AS A SLUDGE DISINTEGRATION METHOD: EFFECT ON GAS PRODUCTION AND QUANTITY AND DEWATERABILITY OF ANAEROBICALLY DIGESTED SLUDGE

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The significant increase in the sewage sludge production in treatment plants makes anaerobic digestion more important as a stabilization process. However hydrolysis is the rate-limiting step of anaerobic digestion because of the semi-rigid structure of the microbial cells. Pretreatment of waste activated sludge (WAS) leads to disruption of cell walls and release of extracellular and intracellular materials. Therefore biodegradability of sludge will be improved in terms of more biogas production and sludge minimization. Among the pretreatment methods, alkaline, thermal and thermochemical pretreatments are effectual ones. Considering the effect of thermal pretreatment, microwave technology in which the sample reaches to elevated temperatures very rapidly is a very new pretreatment method. However no previous research has been conducted to test the effectiveness of microwave (MW) irradiation combined with alkaline pretreatment. Since both of these techniques seem to be highly effective, their combination can act synergistically and even more efficient method can be obtained. Therefore the main objective of this study was to investigate the effect of combination of a chemical method (alkaline pretreatment) and a physical method (microwave irradiation) in improving anaerobic digestion of WAS.

In the first part of the study, alkaline and MW pretreatment methods were examined separately, then their combinations were investigated for the first time in the literature in terms of COD solubilization, turbidity and CST. Highest SCOD was achieved with the combined method of MW+pH-12. In the second part, based on the results obtained in the first part, alkaline pretreatments of pH-10 and pH-12; MW pretreatment alone and combined pretreatments of MW+pH-10 and MW+pH-12 pretreated WAS samples were anaerobically digested in small scale batch anaerobic reactors. In correlation with the highest protein and carbohydrate releases with MW+pH-12, highest total gas and methane productions were achieved with MW+pH-12 pretreatment reactor with 16.3% and 18.9% improvements over control reactor, respectively. Finally the performance of MW+pH-12 pretreatment was examined with 2L anaerobic semi-continuous reactors. 43.5% and 53.2% improvements were obtained in daily total gas and methane productions. TS, VS and TCOD reductions were improved by 24.9%, 35.4% and 30.3%, respectively. Pretreated digested sludge had 22% improved dewaterability than non-pretreated digested sludge. Higher SCOD and $NH_3$-N concentrations were measured in the effluent of pretreated digested sludge; however, $PO_4$-P concentration did not vary so much. Heavy metal concentrations of all digested sludges met Soil Pollution Control Regulation Standards. Finally a simple cost calculation was done for a MW+pH-12 pretreatment of WAS for a fictitious WWTP. Results showed that, WWTP can move into profit in 5.5 years.

**Key words:** Alkaline pretreatment, biogas, dewaterability, microwave pretreatment, sludge minimization

# ÖZ

## ALKALİ SOLUBİLİZASYONU VE MİKRODALGA ÇÜRÜTME TEKNOLOJİLERİNİN BİRLEŞİK BİR ÖN ARITIM METODU OLARAK KULLANILMASI: YÖNTEMİN ANAEROBİK ÇÜRÜTÜCÜDE GAZ ÜRETİMİNE VE ÇAMURUN MİKTARI İLE SUSUZLAŞTIRILMASINA OLAN ETKİSİ

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Arıtma tesislerindeki önemli miktardaki çamur artışı, anaerobik çürütme proseslerinin önemini daha da arttırmaktadır. Fakat mikrobiyal hücrelerin parçalanmaya dayanıklı olan hücre duvarı yapısından dolayı, hidroliz, anaerobik çürütmenin kısıtlayıcı adımını oluşturmaktadır. Anaerobik çürütmeden önce bir ön arıtım prosesi uygulamak hücre duvarlarının parçalanmasını ve hücre dışı ve içi maddelerinin salımını sağlar. Bu sebeple, ön arıtım hem hücrelerin hidrolizini hızlandırır hem de çürütmenin ve gaz üretiminin artmasını sağlar. Ön arıtım metotları arasında, alkali, termal ve termokimyasal metotlar etkili olanlarındandır. Termal metodun etkisi göz önüne alınarak, istenilen sıcaklığa daha çabuk ulaşılmasını sağlayan mikrodalga teknolojisi de bir ön arıtım metodu olarak araştırılmaya başlanmıştır. Fakat mikrodalga ve alkali ön arıtım metotlarının birleşiminin araştırılması literatürde henüz denenmemiştir. Her iki metodunda çok etkili olduğu düşünülecek olursa, birleşik metodun sinerjistik bir sonuç vermesi beklenmektedir. Bu nedenle bu çalışmanın amacı, kimyasal bir metot olan alkali ön arıtımı ve fiziksel bir metot olan mikrodalga ışımasını birleştirip, metodun anaerobik çürütme üzerindeki etkisi araştırmaktır.

Araştırmanın ilk aşamasında, ayrı ayrı alkali ve mikrodalga ön arıtım metotları ve bunların birleşimlerinin neden olduğu KOİ salımı, bulanıklık ve çamurun susuzlaştırılabilme özellikleri literatürde ilk kez incelenmiştir. En yüksek KOİ salımı MD+pH-12 birleşik metodu ile elde edilmiştir. Çalışmanın ikinci aşamasında alkali ön arıtımlardan pH-10, pH-12; yalnız MD ön arıtımı ve birleşik metotlardan MD+pH-10 ve MD+pH-12 metotları ile ön arıtılan atık aktif çamur küçük ölçekli anaerobik kesikli reaktörlerde çürütülmüştür. En fazla protein ve karbonhidrat salımının elde edildiği MD+pH-12 ön arıtımı yine en fazla toplam gaz ve metan üretimini sağlamıştır. Artışlar kontrole oranla sırasıyla %16,3 ve %18,9'dur. Son olarak MD+pH-12 ön arıtımının performansı anaerobik yarı-sürekli reaktörler ile incelenmiştir. Günlük toplam gaz ve metan üretimleri açısından kontrole oranla %43,5 ve %53,2 artışlar gözlenmiştir. Ön arıtım uygulanmış reaktörlerde toplam katı madde, uçucu katı madde ve toplam KOİ değerlerindeki azalış sırasıyla %24,9, %35,4 ve %30,3 oranında artmıştır. Ön arıtım uygulanmış anaerobik çürütülmüş çamurun üst suyunda daha yüksek miktarlarda çözünmüş KOİ ve $NH_3$-N tespit edilmiştir. $PO_4$-P konsantrasyonu ise çok fazla değişmemiştir. Tüm anaerobik çürütmeye tabi tutulmuş olan reaktörlerdeki ağır metal konsantrasyonları Toprak Kirliliğinin Kontrolü Yönetmeliği'nce konulan limitlerin altında çıkmıştır. Son olarak atık aktif çamura MW+pH-12 ön arıtımının uygulandığı hipotetik bir tesis için maliyet hesapları yapılmıştır. Sonuçlar bu tesisin 5,5 yılda kâra geçebileceğini göstermiştir.

**Anahtar Kelimeler:** Alkali ön arıtımı, biyogaz, çamur minimizasyonu, mikrodalga ön arıtımı, susuzlaştırılabilme

To my family,

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# ABBREVIATIONS

ATAD: Autothermal Thermophilic Digestion

ADS: Anaerobic Digested Sludge

BMP: Biochemical Methane Potential

Ca: Calcium

Cd: Cadmium

CFU: Colony Forming Unit

CH: Conventional Heating

COD: Chemical Oxygen Demand

Cr: Chromium

CST: Capillary Suction Time

Cu: Copper

DS: Dry Solids

ECP: Extracellular Polymer

F/M: Food to Microorganism Ratio

GC: Gas Chromatography

HCl: Hydrochloric Acid

Hg: Mercury

HRT: Hydraulic Residence Time

M: Molar

MBR: Membrane Bioreactor

METU: Middle East Technical University

Mg: Magnesium

min: Minute

MLSS: Mixed Liquor Suspended Solids

MLVSS: Mixed Liquor Volatile Suspended Solids

MW: Microwave
N: Normal
NaOH: Sodium Hydroxide
Ni: Nickel
nm: Nanometer
NTU: Nephelometric Turbidity Units
OLR: Organic Loading Rate
Pb: Lead
rpm: Rotations per Minute
SCOD: Soluble Chemical Oxygen Demand
sec: Seconds
SOUR: Specific Oxygen Uptake Rate
SRF: Specific Resistance to Filtration
SRT: Solids Retention Time
SS: Suspended Solids
TCOD: Total Chemical Oxygen Demand
TS: Total Solids
TWAS: Thickened Waste Activated Sludge
W: Watt
WAS: Waste Activated Sludge
WWTP: Wastewater Treatment Plant
w/v: weight/volume
VFA: Volatile Fatty Acids
VS: Volatile Solids
VSS: Volatile Suspended Solids
VOC: Volatile Organic Compound
v/v: volume/volume
Zn: Zinc

# CHAPTER 1

# INTRODUCTION

Large quantities of sludge production are the main drawback of biological wastewater treatment plants. Produced sludge contains high quantities of organics, pathogens, nutrients and lots of water which forces sludge to be further treated to enable an environmentally safe disposal. In a wastewater treatment plant, handling, treatment and disposal of sludge accounts for 50-60% of the total operating costs (Saby et al., 2002).

In order to prevent the adverse affects of sludge on environment, there exist different stabilization methods which are anaerobic digestion, aerobic digestion, autothermal thermophilic digestion (ATAD), composting and thermophilic composting (Metcalf and Eddy, 2003). Among these stabilization methods, anaerobic digestion is the most commonly used one in terms of biogas production, sludge stabilization, mass and odor reduction, and dewaterability improvement (Baier and Schmidheiny, 1997). Anaerobic digestion of sludge is achieved by following the steps of hydrolysis, acidogenesis, acetogenesis and methanogenesis. First, insoluble organics are hydrolyzed by extracellular enzymes. In the second step acid formers degrade soluble organics to produce acids. As a third step organic acids are converted into acetic acid and finally methane formers convert the organic acids into methane and carbon dioxide (Vesilind, 1979). However hydrolysis is the rate limiting step of anaerobic digestion because of the semi-rigid structure of the bacterial cells (Müller, 2001). Incomplete solubilization of insoluble organics limits the following acidogenesis and methanogenesis and therefore leads to a poor digestion. There are also other limitations of anaerobic digestion which are difficulty in degrading facultative anaerobic microorganisms, foaming and bulking, low volatile solids reduction, low quality or quantity biogas production, poor dewaterability and high amounts of sludge volume after digestion which is a really significant problem especially in populated nations (Vera et. al., 2005). In many nations the deposition of sludge in landfills has been exclusively forbidden such as in Germany and Switzerland (Strünkmann et. al., 2006). Therefore, in order to overcome the limitations of anaerobic digestion, pretreatment of sludge before anaerobic digestion has been studied so far.

Pretreatment of sludge is the application of external forces in order to destruct sludge (Müller et. al., 2004). By destroying the microbial cell walls, facultative anaerobic microorganisms and intracellular materials become soluble. Therefore, hydrolysis step of anaerobic digestion is accelerated which leads to an improved anaerobic digestion in terms of more volatile solids (VS) destruction, more biogas production and solids reduction. With a pretreatment process, filamentous and pathogenic microorganisms are also disintegrated. As a result pretreatment processes can lead to reduction in bulking and foaming problems and sludge becomes disinfected especially with the thermal pretreatment. Moreover some pretreatment methods can improve the dewaterability of sludge as well.

There are many kinds of pretreatment methods which are physical (thermal treatment, microwave, freezing and thawing), chemical (use of ozone, acids, alkali and other chemicals), mechanical (ultrasound, homogenizers, mills, and others), biological hydrolysis with or without enzyme addition and combined methods (such as thermochemical) (Müller, 2001).

So far, there are many studies about pretreatment processes involving laboratory scale and full scale testing. For instance, the first full scale thermal hydrolysis pretreatment unit of Cambi Process was established in Hamar, Norway. Thermal hydrolysis temperature reaches up to 180°C. By applying the Cambi Process, digester volume was reduced over 50%. Solids reduction was increased by 23% and the mass reduction is increased by 50% due to better dewaterability. Total disinfection was achieved as well (Kepp et. al., 2000). There are other full scale applications of Cambi Process in Ireland, England, Denmark and Sweden (Ødegaard, 2003).

Another example for a full scale pretreatment method is MicroSludge process that was first established in Vancouver, BC, Canada. The pretreatment process depends on the combination of a chemical and a mechanical pretreatment method. Thickened waste activated sludge (WAS) is firstly alkaline pretreated and then exposed to high pressure homogenizer mechanical disintegration unit. As a result the process provides savings in the transportation and disposal costs of sludge (MicroSludge Official Website).

Considering the effect of thermal pretreatment, microwave (MW) technology in which the sample reaches elevated temperatures very rapidly is a very new method for pretreatment of WAS. Even though thermochemical pretreatment techniques for sludge minimization and biogas production have been studied widely, no previous research has been conducted to test the effectiveness of this recent MW irradiation technique combined with alkaline pretreatment. Since both of these techniques seem to be highly effective, their combination can act synergistically leading to a more efficient method. Therefore, the main objective of this study was to investigate the effect of combination of a chemical method, alkaline pretreatment and a physical method, microwave irradiation in improving anaerobic digestion of WAS.

The study consists of three parts: preliminary investigation of both techniques separately and combined, setting up anaerobic batch reactors and operation of anaerobic semi-continuous reactors. In the first part, MW application alone was applied, the effects of different alkaline doses were tested and the combinations of the two methods were studied in terms of chemical oxygen demand (COD) solubilization, turbidity and capillary suction time (CST). For selected pretreatment methods, carbohydrate and protein releases of WAS were also examined.

Based on the results obtained in the first part, anaerobic batch reactors were set up for selected pretreatment techniques. Total gas productions and methane productions were observed during anaerobic digestion. After digestion, reductions in mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) values were determined as rough indication of sludge reduction. Qualities of anaerobically digested sludges were examined in terms of turbidity, SCOD and CST as well.

Screening of the anaerobic batch reactor results indicated the most effective pretreatment technique; so finally anaerobic semi-continuous reactors were set up accordingly in the last part of the study. During 3 months of operation of the digesters, the efficiency of pretreatment method in terms of biogas production and sludge minimization were observed. The effects of pretreatment on the quality of the digested sludge were also examined. Finally a cost calculation was done for a fictitious WWTP that applies MW+pH-12 pretreatment of WAS.

# CHAPTER 2

# LITERATURE SURVEY

## 2.1 Wastewater Sludge

Wastewater treatment plants are designed in order to reduce adverse effects on environment. On the other hand wastewater treatment plants lead to large quantities of sludge production and the production rates increase with the extended demands on effluent water quality (Strünkmann et. al., 2006).

Wastewater can be treated by physical, chemical and biological methods (Metcalf and Eddy, 2003). Treatment process starts from preliminary treatment then follows primary, secondary, tertiary or advanced treatment. In primary pretreatment settleable solids are removed from wastewater, therefore wastewater becomes less offensive. The solids removed from the bottom of the primary clarifier are called as raw primary sludge which have solids concentration of 4-8%, gray-brown color, bad odor, and are mechanically dewaterable. Most commonly used secondary treatment process is the activated sludge system. In the process, microorganisms consume dissolved organic material and produce carbon dioxide, water and more microorganisms. Biomass in the aeration tank is settled in the secondary clarifier and returned to the head of the aeration system to be reused. However some portion of the settled biomass in the secondary clarifier is wasted since the required amount is exceeded in the aeration tank. Wasted biomass in the secondary clarifier is called as waste activated sludge

(WAS) or secondary sludge which is very active biologically, has a solids concentration of 0.5-1.5%, yellow-brown color, little odor and difficult dewaterability (Vesilind, 1979).

## 2.2 Sludge Stabilization

From all the aforementioned steps of wastewater treatment, sludge is produced which has high quantities of organics, pathogens, lots of water and nutrients. Therefore sludge should be further treated for an environmentally safe disposal in a way that stabilized sludge should not have an undesirable rate of degradation and adverse effects on the existing ecology (Vesilind, 1979).

Sludge stabilization method are alkaline stabilization, anaerobic digestion, aerobic digestion, autothermal thermophilic digestion (ATAD), composting and thermophilic composting (Metcalf and Eddy, 2003). Among these stabilization methods, the most commonly used one is the anaerobic digestion of sludge.

### 2.2.1 Anaerobic Digestion

Anaerobic digestion by fermentation occurs in a heated reactor with the absence of molecular oxygen that results in methane and carbon dioxide production (Metcalf and Eddy, 2003). Anaerobic digestion has four steps which are hydrolysis, acidogenesis, acetogenesis and methanogenesis (Figure 2.1) (Gray, 2005).

The first step is the solubilization (hydrolysis) step in which insoluble organics are degraded by extracellular enzymes and turned into soluble phase. Hydrolysis is the rate limiting step of overall anaerobic digestion because of the semi-rigid structure of the bacterial cells (Müller, 2001). In the second step, acid formers degrade soluble organics and they mainly form propionic and acetic acid and also alcohols, hydrogen and carbon dioxide. Third step is the acetogenesis in which acetogenic bacteria convert organic acids and alcohols into acetic acid. Finally methane formers convert the organic acids into methane and carbon dioxide where about 70% of methane is produced from acetic acid (Gray, 2005).

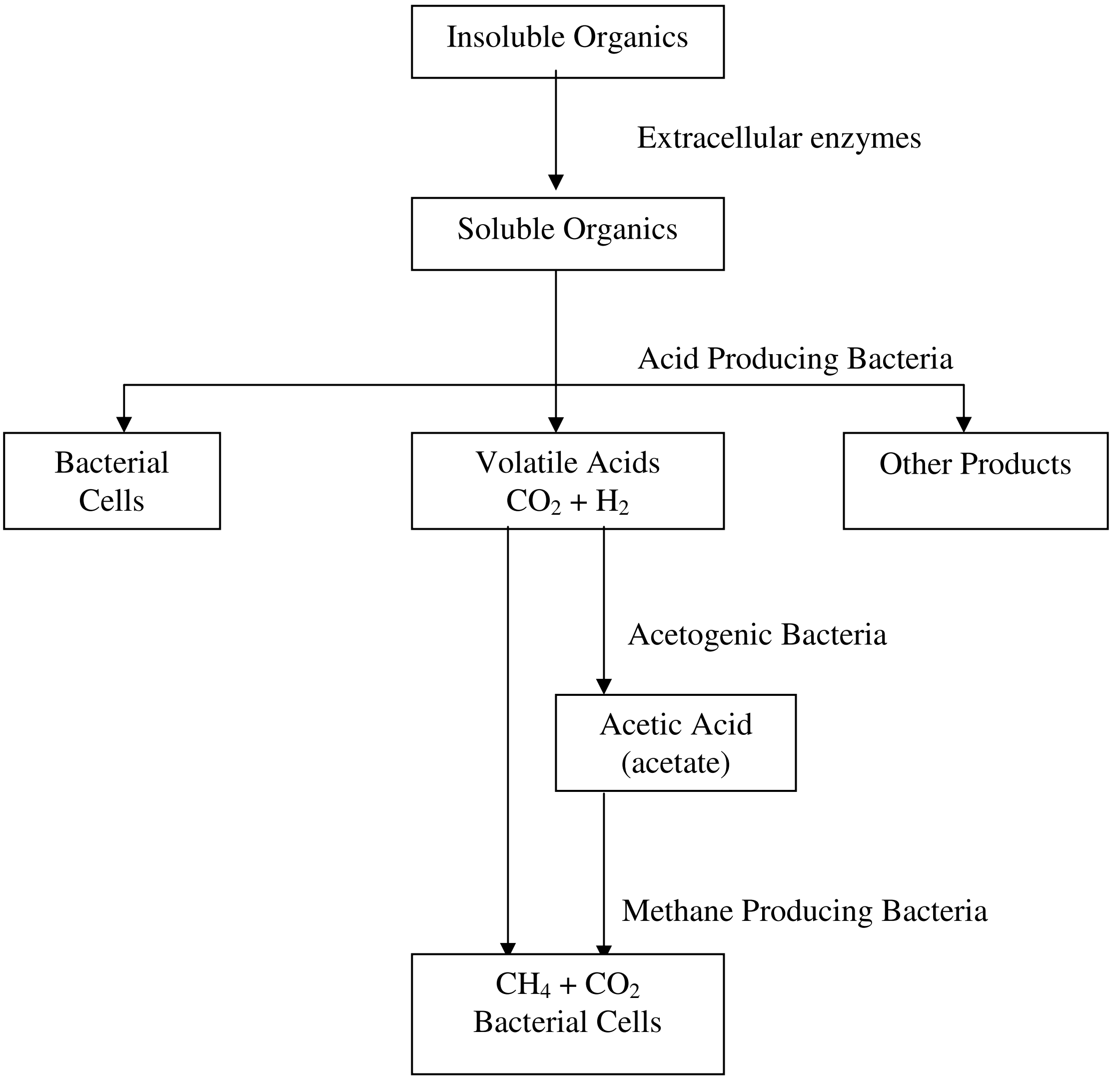

Figure 2. 1 Anaerobic digestion steps (Vesilind, 1979; Gray, 2005)

Methane formers are very sensitive to the environmental conditions. Presence of heavy metals or other toxicants negatively impact the methanogenic environment and the optimum pH range is 6.4-7.5 for anaerobic digestion (Vesilind, 1979).

Anaerobic digestion can be operated in mesophilic (30-38°C) or in thermophilic (50-57°C) conditions. Higher temperature operation leads to faster reactions and more biogas productions (Metcalf and Eddy, 2003). Effect of temperature on biogas production is given in Figure 2.2. Although thermophilic anaerobic digestion leads to more biogas production, due to high energy demands, mesophilic anaerobic digestion is most commonly applied.

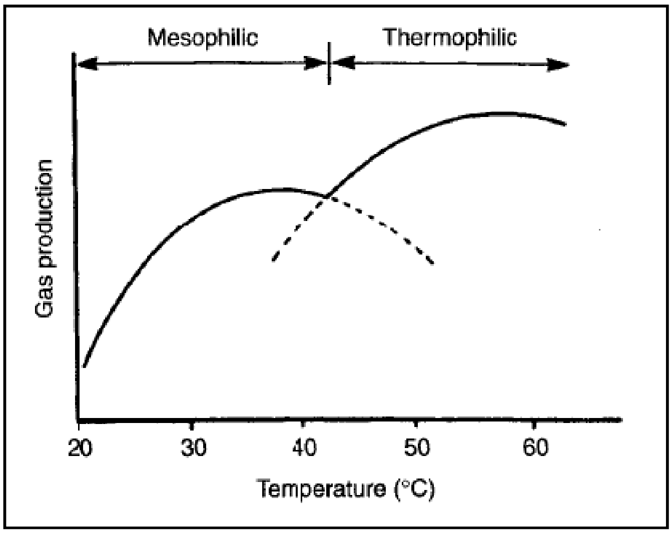

Figure 2. 2 Effect of temperature on biogas production (Gray, 2005)

High rate anaerobic digesters typically achieve 30-35% VS reduction for secondary sludge where VS reductions can reach up to 55-60% for primary sludge.

Produced gas in anaerobic digestion is called as biogas which consists of trace amounts of water vapor, hydrogen, nitrogen, hydrogen sulphide, unsaturated hydrocarbons and other gases. Major components of biogas are methane and carbon dioxide with typically 65-70% and 30-35% by volumes, respectively (Gray, 2005). Methane therefore energy production is the major advantage of anaerobic digestion processes.

Besides energy production, anaerobic digestion process control odor, reduce the net mass of sludge and improve sludge handleability (Baier and Schmidheiny, 1997). The fact that less amounts of sludge is produced with anaerobic digestion is a significant advantage over aerobic digestion (Metcalf and Eddy, 2003). On the other hand anaerobic digestion has some limitations.

The rate limiting step of hydrolysis is the most important limitation of anaerobic digestion. In WAS most of the organics are located in the microbial cell and stable semi-rigid structure of the cell walls protects the cell from lysis. Therefore there occurs a high resistance to biodegradation and this leads to long hydraulic retention time for the biological stabilization in digesters (Müller, 2001). Thus anaerobic digestion is a slow process because of the rate-limiting step of hydrolysis.

Another limitation of anaerobic digestion is that facultative anaerobic microorganisms are not affected in anaerobic digestion and some portions of the organics are not biodegradable which again lead to a poor anaerobic digestion (Müller et. al., 1998).

Foaming and bulking are other problems that arise in anaerobic digesters. Some certain filamentous microorganisms lead to foaming and bulking which cause operational problems in anaerobic digesters. Effective volume of the digesters is reduced and digestion periods are shortened (Barjenbruch and Kopplow, 2003).

Anaerobic digestion is sensitive to shock loads and toxic materials (Lin et. al., 1997). Methane formers can be easily affected by the unfavorable conditions which lead to a poor digestion.

Low quality or quantity biogas production and poor dewatering characteristics of anaerobically digested sludge are other problems that can arise in anaerobic digestion (Vera et al., 2005).

Although anaerobic digestion is an effective method among all the stabilization techniques there are still high amounts of sludge volume after anaerobic digestion that should be disposed of. This is a really big problem especially in populated nations. Sludge disposal costs are important part of a total operation cost of a treatment plant. Moreover in many countries sludge disposal into landfill is completely forbidden such as in Germany and in Switzerland (Strünkmann et. al., 2006).

Therefore in order to overcome the limitations of anaerobic digestion, and improve the efficiency of anaerobic stabilization, pretreatment of sludge before anaerobic digestion has been developed so far.

## 2.3 Pretreatment of Sludge before Anaerobic Digestion

Pretreatment of sludge is the application of external forces in order to destruct sludge (Müller et. al., 2004). In other words pretreatment processes lead to release of extracellular and intracellular materials into aqueous phase. Therefore breaking the cells and solubilizing the extracellular and intracellular materials improve the rate limiting step of hydrolysis in anaerobic digestion.

In a WWTP, pretreatment should be applied on WAS because excess sludge contains many microorganisms which are difficult to degrade. However the primary sludge contains substances that can be hydrolyzed more easily (Lehne et al. 2001). Eskicioglu et. al. (2008) applied microwave pretreatment to primary, secondary and mixed sludges and the highest biodegradability efficiency was achieved with the pretreated WAS.

Apart from sending pretreated WAS to anaerobic digestion, it can be returned to the aeration tank in order to achieve enhanced degradation as well. High dissolved organic carbon involving sludge can also be added to the denitrification tank for nitrogen removal (Müller, 2001).

Advantages of applying a pretreatment process before anaerobic digestion are as follows:

**Effect on Stabilization:** Since the intracellular organics are solubilized, improved and accelerated degradation of organics is achieved in anaerobic digestion (Müller, 2004). With disintegration facultative microorganisms are disrupted too and they become degradable which leads to a higher degree of degradation (Müler et. al., 1998).

After pretreatment of WAS, when primary and WAS are mixed in anaerobic digestion, VS conversion can increase from about 45% to 60% or more (Panter, 2002).

**Effect on Biogas Production:** Pretreatment processes lead to higher degrees of organics utilization and therefore more biogas production in anaerobic digestion is expected.

**Effect on Sludge Disposal:** Since organic content degradation of sludge is improved, the amount of sludge that should be disposed of is reduced. The degree of improvement depends on the anaerobic digestion conditions such as sludge age, facultative anaerobic organisms percentage, etc (Müller, 2001).

**Effect on Bulking and Foaming:** Bulking and foaming can be reduced by applying a pretreatment process. During pretreatment voluminous flocs are also disintegrated and therefore smaller size flocs become able to compact and settle better (Müller, 2001).

**Effect on Dewatering:** Extracellular polymers (ECP) which surrounds the cell represents approximately 80% of the mass of activated sludge. ECP is composed of proteins, polysaccharides, lipids and DNA either because of cellular production extracellularly or because of the cell lysis of microorganisms. ECP also involves organic materials that come from wastewater itself. ECP plays an important role in dewaterability of sludge. It was found that the increased amounts of ECP surrounding the cell deteriorate the dewaterability of sludge because of its highly hydrated nature (Neyens and Baeyens, 2003).

Sludge dewaterability can be improved by reducing the bound water captured by the cells by applying a pretreatment process. From the pretreatment methods, thermal pretreatment is a well-known conditioning method. On the other hand not all pretreatment processes can improve the dewaterability (Panter, 2002).

**Effect on Disinfection:** Depending on the pretreatment process, partial or complete disinfection can be achieved by pretreatment processes due to the disintegration of the pathogenic microorganisms as well (Müller et. al., 2004).

Thermal pretreatment is known to be the best pretreatment method in terms of disinfecting the sludge (Müller, 2001).

There are many kinds of pretreatment methods which are mechanical (ultrasound, homogenizer, mill, and others), physical (thermal treatment, microwave, freezing and thawing), chemical (usage of ozone, acids, alkali and other chemicals), biological hydrolysis with or without enzyme addition and combined methods (such as thermochemical) (Müller, 2001).

This research investigates the combination of a chemical method, alkaline pretreatment and a physical method, microwave pretreatment. Therefore in the following sections, information about different pretreatment methods is given. Alkaline, thermal, thermochemical and microwave pretreatment methods are described in more details towards the end of the literature survey.

### 2.3.1 Mechanical Pretreatment of Sludge

In mechanical pretreatments, energy is applied as pressure, translational and rotational energy to the sludge. Microbial cells can resist the applied energy as long as applied tension is lower than the strength of the cell wall (Müller, 2001). As a result with the principles of shearing or exploding cells, bound water and soluble COD are released (Panter, 2002).

Most commonly used mechanical methods are as follows:

- Ultrasonic pretreatment
- Lysate Centrifuge
- Stirred ball mill
- High pressure homogenizer

#### 2.3.1.1 Ultrasonic Pretreatment

Ultrasonic sludge disintegration depends on the formation of the cavitation bubbles. Sonication initiates cavitation bubbles formation and bubbles collapse when they reach a critical size. These collapses lead to high temperatures in the system (Show et al. 2006). Ultrasonic frequencies range between 20 kHz and 10 MHz but low frequencies from 20 to 40 kHz are proposed for cavitation bubble formation and an effective disintegration of sludge (Tiehm et al., 1997).

Show et al. (2006) operated four continuous anaerobic reactors. Pretreatment reactors were fed with the pretreated sludges having different sonication intensities of 32, 56 and 92 $W/cm^2$. Different organic loadings of 3.6, 7.2 and 14.5 g COD/L.d were examined by decreasing HRT after steady state. It was found that highest sonication intensity led to highest COD removal and methane production whatever the organic loading was. Moreover the highest improvements were achieved with the highest organic loading rate over control whatever the intensity was. Compared to control reactor at 3.6 g COD/L.d 5%, 7% and 11% more COD removal was achieved with the intensities of 32, 56 and 92 $W/cm^2$ but at 14.5 g COD/L.d, COD removal efficiencies were increased by 32%, 57% and 59% over control, respectively. Average daily gas productions were increased by 45-202%, 184-220%, 115-205% with the intensities of 32, 56 and 92 $W/cm^2$ for different organic loadings.

Tiehm et. al. (1997) operated five semi-continuous anaerobic reactors at different residence times. Ultrasonic pretreatment was applied for 64 seconds at 3.6 kW and frequency of 31 kHz. At 22 days of residence time VS reductions were 45.8% and 50.3% for control and disintegrated sludge, respectively. The highest biogas production was achieved at shortest residence time of 8 days with 2.2 times of control.

#### 2.3.1.2 Lysate Centrifuge

The destruction of the sludge cells takes place using a special beater (lysate ring) integrated into the centrifugal thickener and it dissipates the kinetic energy provided by the centrifuge. Under these conditions microbial cells can not resist to the applied energy and disintegrate (Lysatec Official Website).

The first full-scale experiment was carried out in Central Wastewater Treatment Plant of Prague (1,200,000 PE). The average daily biogas production was increased from 30,000 $m^3$/d to 38,000$m^3$/d. Another installation of lysate centrifuge was in WWTP in Czech Republic. Biogas production was increased by 26% in WWTP (Dohányos et. al., 2003).

#### 2.3.1.3 Stirred Ball Mill

The principle of this pretreatment is the stressing microorganisms between agitated grinding beads. With a stirrer agitation is achieved which will pass on kinetic energy to small beads and force them to collide with each other. Different velocities of grinding beads and the shear forces lead to the disruption of microbial cells (Strünkman et al., 2006).

Baier and Schmidheiny (1997) examined the effect of stirred ball mill pretreatment on disintegration and biodegradation. With anaerobic batch digesters, VS degradation was enhanced from 38% to 57% and biogas production was increased by 10% with pretreated WAS after 500 hours. In terms of COD solubilization, smaller balls (<0.25 mm) and higher velocities (>10m/s) led to better effects.

#### 2.3.1.4 High Pressure Homogenizer

The principle of the pretreatment method is pressurizing the sludge up to some hundred bars and then reducing the pressure back to the environmental pressure again. As in the ultrasonic pretreatment, high pressure homogenizer lead to cavitation bubbles formation and increased sludge temperatures to over 40°C (Strünkmann et. al., 2006).

Lehne et. al. (2001) compared the mechanical disintegration methods of ultrasonic homogenizer, a high pressure homogenizer and a stirred ball mill. High solid contents led to operational problems with the homogenizer. On the other hand high pressure homogenizer and stirred ball mill used less energy than ultrasonic pretreatment.

Full scale application of high pressure homogenizer combined with alkaline pretreatment named as MicroSludge is given in Section 2.3.5.1 in details.

### 2.3.2 Chemical Pretreatment of Sludge

Chemical disintegration of sludge can be achieved by using agents such as acids, alkaline, advanced oxidation by Fenton’s reagent and ozonation. Alkaline pretreatment that the research concentrated on is illustrated in section 2.3.5.1.

#### 2.3.2.1 Acidic Pretreatment

Acidic conditions make microbial cells loose their activities and disruption of the cell walls. In acidic pretreatment, value of pH plays an important not only for the degree of disintegration but dewaterability of sludge as well. pH range of 2.6-3.6, near isoelectric point, minimizes the repulsive forces and therefore minimum dissociation constants are achieved in this range. Therefore water content of sludge is reduced and sludge aggregates can be easily packed. As a result dewaterability is improved (Neyens et. al., 2004).

Krepro process is a pilot scale application of combination of acidic and thermal pretreatment methods which is applied after digestion in Helsingborg, Sweden. Sludge after dewatering is acidic pretreated with sulfuric acid to pH between 1 and 2. After that sludge is exposed to thermal pretreatment at the temperature of 140°C for about 30-40 minutes. Solubilization reaches up to 40%. Ferric salts and alkali are also applied in order to precipitate ferric phosphate which is used as fertilizer. After that water phase is returned to the influent where soluble organic matter is used as carbon source for denitrification and iron acts as a coagulant (Ødegaard, 2003; Neyens and Baeyens, 2003).

#### 2.3.2.2 Advanced oxidation by Fenton's Reagent

Combination of $H_2O_2$ by Fe(II) salts leads to Fenton's reaction which leads to dissociation of the oxidant and creation of hydroxyl radicals that are very effective and destroy the organic compounds.

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\bullet} + OH^{-}$$

With Fenton reagent high depolymerization rates can be achieved at ambient temperatures. Moreover dewaterability can be improved as well (Neyens et. al., 2004).

#### 2.3.2.3 Ozonation

Ozonation is a chemical pretreatment method in which chemicals are not needed and there is not any increase in the salt concentration. The principle of ozonation is the partial oxidation and hydrolysis of organic matter (Müller, 2001).

Weemaes et. al. (2000) studied ozonation as a pretreatment process before anaerobic digestion. It was found that 0.1 g $O_3$/g COD, reduced total COD by 16±6% before anaerobic digestion and soluble COD was increased from 0.06±0.05 g/L to 2.3±0.3 g/L. During anaerobic batch digestion initial methane production rate was increased from 8.3-15.1 mL $CH_4$/g COD.d to 22.8-32.5 mL $CH_4$/g COD.d.

### 2.3.3 Physical Pretreatment of Sludge

Disintegration of sludge depends on the destruction of microbial cell walls by either applying heat and increasing the temperature or by freezing the sludge. Thermal pretreatment and thermochemical pretreatments are illustrated in section 2.3.5.2 and microwave irradiation is explained in section 2.3.5.3.

#### 2.3.3.1 Freezing and Thawing

First freezing and then thawing the sludge transform the floc structure into a more compact form and floc structure is irreversibly changed (Müller 2001). Chu et al. (1999) applied the pretreatment as first freezing sludge up to around –20 ºC. Then frozen sludge is immersed into 25ºC water bath for a several hours and let it thawed.

Sanin et al. (1994) proposed that a freeze/thaw pretreatment is an effective method in terms of reducing the pathogenic level in municipal sludges as well. According to the US Sludge Regulations, freeze-thaw conditioned sludge can be regarded as Class B. Chu et. al. (1999) also declared that for an efficient bacteria removal, freezing should not be rapid.

It was also suggested that this treatment technique reduces the bound water content of sludge; therefore dewaterability of the sludge is enhanced. Although freezing and thawing is very feasible in cold regions where natural freezing is possible, the mechanical freezing would be very expensive in warmer regions (Müller, 2001).

### 2.3.4 Biological Pretreatment of Sludge

Biological pretreatment of sludge can be achieved by autolytic processes or by addition of external enzymes. By enzymatic pretreatment even a high strength bacteria of gram-positive can be disintegrated (Müller, 2001).

Barjenbruch and Kopplow (2003) studied enzymatic pretreatment by using the enzyme *carbohydrase*. It was found that enzymatic pretreatment had no effect on the reduction of foaming problem. Although the effect of disintegration was lower for enzymatic pretreatment than thermal pretreatments at 80, 90 and 121°C and ultrasonic pretreatment, it was found that enzymatic pretreatment improved dewaterability of sludge.

### 2.3.5 Review of Literature Findings on the Pretreatment Methods Used in This Work

#### 2.3.5.1 Alkaline Pretreatment

Kim et. al. (2003) explained alkaline pretreatment of sludge as saponification of uronic acids and acetyl esters, neutralization of different acids that were formed from the particular materials degradation and reactions happening with free carboxylic groups which all lead to an increased COD solubilization.

Alkaline pretreatment is an effective pretreatment method that was examined by many researchers so far. However alkaline solubilization is most commonly studied with combined pretreatments such as thermochemical or combination with mechanical pretreatment since the efficiency of pretreatment is enhanced with combined methods.

Tanaka et. al. (1997) studied a range of 0.05-1.5 g NaOH/g VSS as alkaline pretreatment. It was found that VSS solubilization increased as the alkaline dose increased up to 0.6 g NaOH/g VSS and became constant around 15% above the dose of 0.6 g NaOH/g VSS. When the dose was 1 g NaOH/g VSS, 50% more methane production was achieved in 8 day of anaerobic digestion.

Valo et. al. (2004) examined chemical pretreatment by using KOH with doses of 1.68 g/L and 3.65g/L to reach the pH values of 10 and 12. It was found that after 1 hour, soluble COD was stable and reached 9.3% for pH 10 and 30.7% for pH 12.

Lin et. al. (1997) set up four 1 L anaerobic semi-continuous reactors and they were named as A, B, C and D. Reactor A was fed with 1% TS raw WAS, reactor

B was fed with 1% TS WAS pretreated with 20 meq/L NaOH, reactors C was fed with 1% TS WAS pretreated with 40 meq/L NaOH and reactor D was fed with 2% TS WAS pretreated with 20 meq/L NaOH. Pretreatments were achieved by adding NaOH and mixing for 24 hours. All reactors were operated with HRTs of 20, 13, 10 and 7.5 days. COD removal rates of reactor A was 21-39%, for B 39-47%, for C 37-51% and for D 37-52% for different HRT values. The highest COD removal improvements were achieved at lowest HRT of 7.5 day with all pretreatments since at low HRT control reactor hydrolysis step was more limited. When reactors C and D were compared, it was found that increasing the sludge concentration was more effective than increasing NaOH dose in terms of organic removal. The improvements in methane productions of B, C and D were 29-102%, 42-116% and 106-287%, respectively. The highest methane production was achieved with reactor D when organic loading was the highest.

Penaud et. al. (1999) investigated different NaOH doses (0 to 26.1 g NaOH/L) of alkaline pretreatment. It was found that COD solubilization reached 63% when 4.6 g NaOH/L was applied. Doses higher than 4.6 g NaOH/L led to slower increases in COD solubilization. The highest biodegradability rates were achieved with the alkaline doses of 4-5 g NaOH/L. Biodegradability rates increased from 22 to 58%. On the other hand when the dose was 26.1 g NaOH/L, biodegradability rate was below 5% which was explained by the inhibition of the system because of the large amounts of chemicals applied. Alkaline pretreatment doses were also combined with thermal pretreatment at 140°C for 30 minutes. When alkaline dose was lower than 5 g NaOH/L, biodegradability rates were higher for the heated samples compared to non-heated ones.

Kim et. al. (2003) studied alkaline pretreatments at pH 12 with different alkaline agents which were NaOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$. SCOD/TCOD was increased from 8.1% (control) to 39.8% (NaOH), 36.6% (KOH), 10.8% ($Mg(OH)_2$) and 15.3% ($Ca(OH)_2$). It was found that dibasic alkaline agents led to less solubilization than monobasic ones. The reason was explained by the partial solubilization of the dibasic alkaline agents. For NaOH, different alkaline doses were applied and the effect on COD solubilization was observed. It was found that for doses higher than 7g/L NaOH, there was no significant increase in the rate of COD solubilization. Therefore for anaerobic batch reactors, dose of 7g/L NaOH was studied. It was found that VS destruction was increased from 20.5% (control) to 29.8% with the dose of 7g/L NaOH alkaline pretreated WAS.

Chen et. al (2007) studied the effect of different pH on the releases of SCOD, protein, carbohydrate, nitrogen and phosphorus of WAS. 2M NaOH and 2M HCl was added to the identical reactors including WAS. Reactors were mechanically mixed. It was found that SCOD releases with alkaline pretreatments were higher than that of acidic pretreatments. The highest COD solubilization was achieved with the highest pH value of 11. After 20 days SCOD/TCOD of control was 13.8% while it was 68.3% and 22.1% for pH-11 and pH-4.0 reactors. The same trend was observed with the carbohydrate and protein releases as in the case of SCOD. It was found that soluble proteins and carbohydrates were the major components of SCOD and the highest releases were achieved with the alkaline conditions than acidic. Studied highest pH value of 11 gave the maximum releases of 938.33 mg/L and 119.29 mg/L concentrations of protein and carbohydrate, respectively on the second day. $PO_4^{3-}$-P and $NH_4^+$-N concentrations of the alkaline and acidic pretreated WAS did not follow the same trend of SCOD, carbohydrate and protein releases. $PO_4^{3-}$-P and $NH_4^+$-N concentrations were higher in acidic conditions than basic conditions and the result was explained by the toxicity at high pHs that inhibited the activities of hydrolytic enzymes.

Another study that compares the effect of acidic and basic pH conditions was undertaken by De Franchi (2005). In the study, 5N HCl and 5N NaOH were applied on primary sludge and WAS. Before anaerobic digestion, effects of pretreatments were examined for different temperatures of 4, 22 and 37°C for durations of 1, 2, 4, 6 and 8 days. For different pretreatment temperatures of 4, 22 and 37°C with respect to time, alkaline pretreatment led to more COD solubilization compared to acidic pretreatment for both primary and WAS and solubilization was higher in WAS than primary sludge. Then, 6 anaerobic reactors having the operation volume of 8L were set for the SRT values of 10 and then 20 days. Reactors were fed with a mixture of primary sludge and WAS in mass ratio 1:1. Reactors 1 and 6 were controls and fed with untreated primary and WAS. Reactors 2 and 4 were fed with primary sludge pretreated with HCl and WAS pretreated with NaOH. Reactors 3 and 5 were fed with primary sludge pretreated with NaOH and WAS pretreated with HCl. Reactors 3 and 5 gave the maximum VSS and COD removals for both SRTs. Average VSS removal efficiencies of control reactors were about 38% and 45% for SRTs of 10 and 20 days. Average VSS removal efficiency of the reactors of 2 and 4 were 44% and 50% and average solids removal efficiency of the reactors 3 and 5 were 46% and 53% for SRTs of 10 and 20 days, respectively. For COD removal efficiencies, control reactors achieved about 38% and 45% COD reductions for SRTs of 10 and 20 days. Reactors 2 and 4 achieved about 44% and 47% COD reductions for SRTs of 10 and 20 days and reactors 3 and 5 achieved about 45% and 51% COD reductions for SRTs of 10 and 20 days, respectively.

Alkaline pretreatment has full scale applications in the world. MicroSludge technology is a full scale application of combination of alkaline solubilization with a mechanical method of high pressure homogenizer. The first commercial demonstration was in 2004 near Vancouver, BC and the second demonstration was in 2006 in Los Angles. In the system first WAS is thickened about 5-10% TS content. Then thickened WAS is alkaline pretreated with NaOH in a conditioning tank for 1 hour. pH of WAS is increased from 7 to 9. After that mechanical disruption is applied with high pressure homogenizer in which WAS is forced up to 12,000 psi and then suddenly lowered to 50 psi. The sudden drop in the pressure causes extreme shear forces in the system that disintegrate cell cytoplasm into solution. During mechanical disruption, temperature is increased up to 20-25°C therefore energy cost of preheating sludge before anaerobic digestion is also reduced. More VS reductions are achieved as compared to conventional technology. As a result, the process provides valuable methane production for WWTP and due to reduction in sludge mass it provides savings in the transportation and disposal costs of sludge (MicroSludge Official Website).

#### 2.3.5.2 Thermal and Thermochemical Pretreatment

Thermal pretreatment is the application of heat to destroy cell walls which is generally applied in the range of 60°C to 180°C (Müller, 2001). Experiments conducted about thermal hydrolysis showed that for municipal sewage sludge the highest hydrolysis yield was achieved at 165 and 180°C. However for industrial WAS, the highest hydrolysis rate was achieved at temperatures 150 and 165°C. The reason was the more pure biomass content of industrial WAS than municipal WAS (Kepp et. al., 2000).

However, during thermal hydrolysis elevated temperatures more than 200°C can lead to formation of hardly biodegradable compounds due to Maillard reactions (Müller, 2001). Maillard reactions occur between with amino acids and reducing sugars at elevated temperatures. These reactions reduce the solubility of proteins and sugar and lead to polymerization. (Müller, 2001; Eskicioglu et. al., 2007).

Although thermal pretreatment is a studied and an applied method so far, thermochemical methods have also been investigated to further improve the efficiency of anaerobic digestion. Thermochemical pretreatments are the combination of thermal pretreatment with either acids or alkaline to enhance the solubilization of microbial cells.

Tanaka et. al. (1997) studied thermal, chemical and thermochemical pretreatment methods for combined WAS. For the thermal pretreatments VSS solubilization was around 15% between 115 and 150°C. As the temperature increased, solubilization further increased to above 160°C and reached up to 30% at 180°C. Methane production results according to BMP test showed the same behavior. 40% increase was achieved in between 115 and 150°C and increased further above 160°C and 90% improvement in methane production was achieved with 180°C (1 hour heating). For thermochemical pretreatments, it was found that the VSS solubilization rate increased until the alkaline dose of 0.25 g NaOH/g VSS. But this improvement was no longer improved above the temperature of 130°C with 5 minute heating. Combined pretreatment dose of 0.3 g NaOH/g VSS and 130°C with a 5 minute heating yielded a solubilization of 45% and methane production was 2.2 times of control.

Barjenbruch and Kopplow (2003) studied the pretreatment methods of mechanical disintegration by using high pressure homogenizer, enzymatic pretreatment by using the enzyme *carbohydrase* and thermal pretreatment at the temperatures of 80, 90 and 121°C for 60 minutes in an autoclave. It was observed that for thermal pretreatments at high temperature, ECP were disintegrated to a high degree which effectively stopped the foaming problem. Continuous anaerobic reactors were set to observe the effect of pretreatments. Reactors were fed with 60% surplus sludge and 40% primary sludge. With thermal pretreatment the increase in methane production was between 15-22%. In terms of improving the dewaterability, 90°C was better than 121°C pretreatment. It was found Excherichia coli was higher in primary sludge which was $7 \times 10^7$ CFU/10 g SS (suspended solids). However in surplus sludge, it was $2 \times 10^7$ CFU/10 g SS. With thermal pretreatments, E.coli was reduced to lower than $10^3$ CFU/10 g SS at all examined temperatures. On the other hand, after digestion E.coli amount of pretreated and non-pretreated digested sludges was the same. The reason was explained by the high concentrations E.coli in the primary sludge that was mixed with the pretreated surplus sludge.

Valo et. al. (2004) studied thermal pretreatment at 130, 150 and 170°C for durations of 15, 30 and 60 minutes. It was found that WAS was strongly solubilized at 15 minutes and as the treatment time increased, COD solubilization slightly increased. SCOD increased from 2.7% (control) to 25.3%, 43.9% and 59.5% at temperatures 130, 150 and 170°C, respectively. For thermochemical pretreatments, 130 and 170ºC were examined with the combinations of pH 10 and 12. KOH addition led to a significant increase in soluble COD at pH 10 for both temperatures of 130 and 170°C. Up to pH 10, there was a significant increase in COD solubilizations at both temperatures. However as the pH increased to 12, solubilization slightly increased at 130ºC and was stable at 170ºC. In continuous reactors two conditions were studied which were 170°C (alone) and 130°C with pH 10. The highest TCOD, TS and VS removal was achieved with the thermal pretreatment of 170°C. On the other hand the highest biogas production was achieved with 130°C with pH 10. The reason was that same organic loading was not applied to the pretreatment reactors. Since VS content of 170°C pretreated WAS was reduced, lower organic loading was applied to 170°C pretreatment reactor than applied to 130°C with pH 10 pretreatment reactor. Moreover alkaline application to WAS before anaerobic digestion led to an increase in feed TS concentration. Although both pretreatment methods improved the dewaterability, it was not possible to compare two methods efficiently, since influent organic loadings were different for each system.

Vlyssides and Karlis (2004) studied temperature range of 50-90°C by adding lime. A total of 20 experimental set ups were done with the temperatures of 50, 60, 70, 80, and 90°C with pH at 8, 9, 10 and 11. It was found that there was a linear correlation with pH and temperature increases and soluble COD increase. Combination of pH-11 alkaline pretreatment with the thermal pretreatment at 90°C followed by anaerobic batch digestion at thermophilic conditions led to 46% VSS reduction and methane yield was 0.28 L/g $VSS_{in}$ whereas it was 0.07 L/g $VSS_{in}$ for the combination of pH-8 with 50°C.

Weemaes and Verstraete (1998) cited to Smith and Göransson (1992) that thermo-chemical pretreatment of sludge was studied at low and high pH values. For thermal basic conditions, $Ca(OH)_2$ and NaOH were examined at the temperature of 120-160°C. Addition of NaOH gave a higher solubilization than $Ca(OH)_2$ up to 40-60%.

Kim et. al. (2003) investigated thermal, chemical, ultrasonic and thermochemical pretreatment of WAS. With 121°C thermal pretreatment for 30 minutes, SCOD/TCOD of WAS was increased from 8.1% to 17.6%. For thermochemical pretreatment of WAS, first alkaline pretreatment was applied then WAS was exposed to 121°C 30 minute thermal pretreatment. The effect of different NaOH doses on the COD solubilization was investigated for combined pretreatment. It was found that when NaOH dose was changed from 0 to 21 g/L, SCOD/TCOD increased from 17.6% to 86.5%. Maximum solubilization for thermochemical pretreatment was achieved with the dose of 9 g/L NaOH. However for anaerobic batch digestion, for thermochemical pretreatment, the optimum dose of 7 g/L NaOH was selected which gave a COD solubilization of 85.4%. With digestion, VS reduction of non-pretreated WAS was 20.5%, whereas 32.1% and 46.1% VS reductions were achieved with thermal and thermochemical pretreated WAS, respectively. Among all the studied pretreatment methods the maximum methane production was achieved with the thermochemical pretreated WAS with more than 34.3% increase in methane production.

Doğan et. al. (2007) studied the effect of thermal, thermochemical and acidic pretreatment of WAS on anaerobic digestion with anaerobic batch reactors. For thermochemical pretreatment, WAS was heated and mixed in a water bath for two hours at 80°C with the addition of 0.75 g NaOH/g VSS. Thermal pretreatment of WAS by autoclave at 121°C for 15 minutes led to 8.7% and 5.4% improvements in total gas and methane productions. However, 30.8% and 24.8% more total gas and methane productions were observed with thermochemically pretreated WAS over control at the end of a 37 day of digestion. No significant improvement in anaerobic digestion was achieved with acidic pretreatment of WAS.

There are many patented thermal pretreatment systems such as Cambi, Biothelys and Zimpro Process and these systems are now installed in full scale in WWTPs.

Cambi process which found many applications in the world is a thermal pretreatment of sludge before anaerobic digestion. There are full scale applications of Cambi process in Norway, Ireland, England, and Denmark and Sweden.

The first full scale thermal hydrolysis pretreatment unit Cambi process was established in Hamar, Norway. The plant has been in operation since 1995. The capacity of the treatment plant is 125,000 person equivalents where it serves for 50,000 people. Sludge that is going to be hydrolyzed with thermal pretreatment consists of one third primary, one third secondary and one third tertiary sludge. Before thermal pretreatment mixed sludge is dewatered by centrifuge to 15-20% DS, then pumped to the hydrolysis unit. Thermal hydrolysis temperature is changed from 165 to 180°C with the duration of 30 minutes. With pretreatment, higher DS content is introduced to anaerobic digestion than conventional system which saves digester volume more than 50%. 17 days of anaerobic digestion leads to the degree of COD conversion of about 60%. Solids reduction is increased by 23% and the mass reduction becomes higher over 50% due to a better dewaterability. All produced sludge is used in agriculture because of the disinfection of sludge due to high temperatures, stability of sludge under storage, no odor problem, and its easiness of spreading (Kepp et. al., 2000).

Pickworth et. al. (2006) summarized the reasons for choosing a Cambi pretreatment process as follows,

- Complete sterilization of all known pathogens and Class A sludge production
- Eliminating foaming problem by killing all foam producing organisms
- Improving the biogas production and sludge destruction
- Sludge dewaterability up to 34%DS
- At least 3 Megawatts of energy production
- Automatic and enclosed systems
- Digesters can be fed up to 12% DS

Another patented thermal hydrolysis pretreatment system is Biothelys process which is composed of two or three thermal hydrolysis batch reactors working in parallel. The first Biothelys process was installed in Saumur in France. The aim of the process was to hydrolyze organic solids before mesophilic anaerobic digestion to improve volatile matter removal and biogas production.

WWTP of Saumur has a capacity to treat 11,000 $m^3$/d wastewater. Wastewater is biologically treated in extended aeration system. After that produced sludge is centrifuged at a dryness of about 15% and sent to thermal hydrolysis process. Thermal hydrolysis is applied in 2 batch reactors at a temperature of 160°C for about 30 minutes. After cooling the pretreated sludge, sludge is sent to mesophilic anaerobic digester with HRT of 15 days. In digester more than 45%

volatile matter reduction is achieved. The produced biogas during digestion not only meets the energy demand of the thermal hydrolysis process and other energy requirements of the treatment plant as well. After digestion the digested extended aeration biological sludge is free of pathogens, odorless and has a good fertilizing value (Chauzy et. al., 2007).

Zimpro Process is a thermal sludge treatment process that was found in early 1960s. The principle of the process is applying wet air oxidation at elevated temperatures (190-250°C) under pressure to reduce COD. The process is also very effective in terms of reducing the human viruses and pathogenic bacteria. Moreover with this process greatly enhanced dewaterabilities are achieved. Therefore deposition of sludge in landfill is minimized. There exists a Zimpro process at the Sand Island Wastewater Treatment Plant, Honolulu, HI (Luck, 1999; Maugans and Ellis, 2002).

#### 2.3.5.3 Microwave Pretreatment

Microwave irradiation is associated with electromagnetic irradiation in the frequency range of 300 MHz–300 GHz that is equivalent to a wavelength range of 1 m to 1 mm (Banik et. al., 2003). Electromagnetic spectrum is given in Figure 2.3. Domestic and industrial microwave ovens generally operate at a frequency of 2.45 GHz that is equivalent to a wavelength of 12.2 cm and energy of $1.02\times10^{-5}$ eV (Jacob et al., 1995).

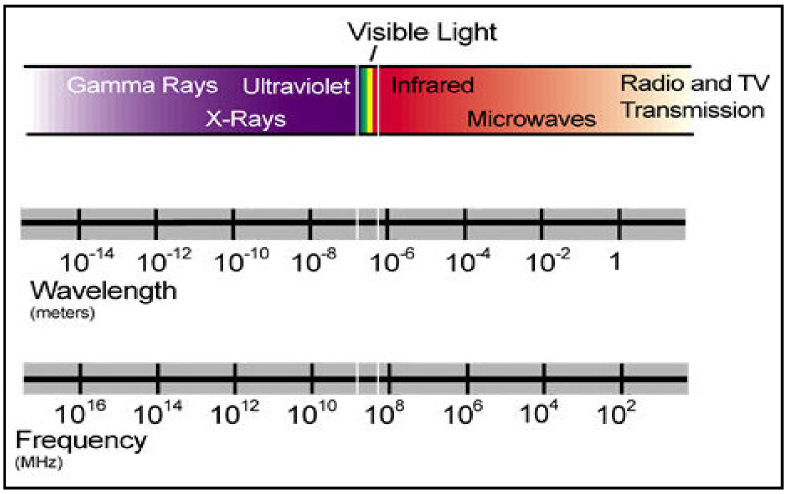

Figure 2. 3 Parts of electromagnetic spectrum

Since all materials cannot be heated by microwave, according to microwave absorption characteristics, materials can be classified into three groups as conductors, insulators and absorbers given in Figure 2.4 (Jones et. al., 2002).

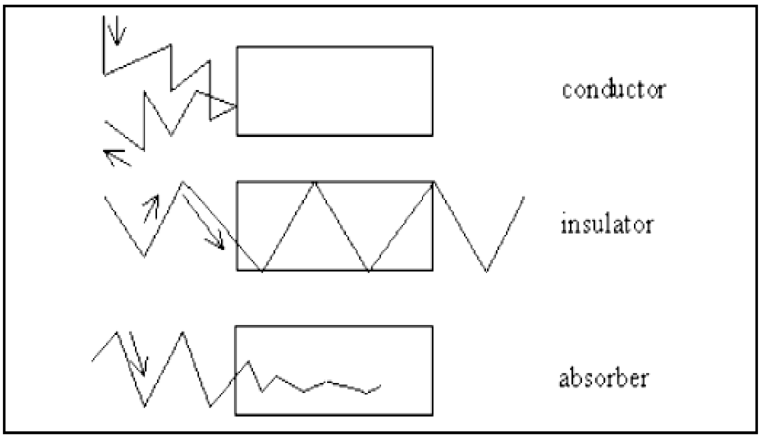

Figure 2. 4 Microwave absorption characteristics for conductor, insulator and absorber (Jones et. al., 2002)

The principle of the microwave application relies on the movements of the presence of dipole molecules (such as water, some lipids and many proteins) in the substance being irradiated (Pino-Jelcic et. al., 2006). With the microwave beams dipolar molecules start to rotate in order to align themselves with the poles of the electromagnetic field. The motions of the dipole molecules create friction and therefore friction leads to heat formation in the system (University of Colorado at Boulder Official Website).

Microwave irradiation has many applications in environmental engineering. Most commonly used areas are contaminated soil remediation, waste processing, minerals processing, activated carbon regeneration, contaminated soil vitrification, volatile organic compounds (VOC) treatment and recovery, waste sludge processing, mineral ore grinding and carbon in pulp gold recovery (Jones et. al., 2002).

Because of the dielectric properties and high water content, sewage sludge is an absorber that microwave irradiation can be applied on (Wojciechowska, 2005). Microwaves applied on sewage sludge lead to evaporation of water due frictional heat. Besides water molecules inside the pathogens, other microorganisms will also try to escape from the heat therefore an expansion and explosion of the microbial cells occur (Acquisto et. al., 2006). When microwave is used as a pretreatment method, explosion of microbial cells will lead to release of extracellular and intracellular materials and disintegrate complex organic molecules into biodegradable smaller structures which will all improve the anaerobic digestion. Although drying and sterilization of sewage sludge by microwave irradiation to achieve an environmentally safe disposal have been studied so far, microwave irradiation as a pretreatment process is a very new technology.

Microwave effects mainly depend on the heat formation however recent studies have found and suggested that variations and transformations of molecular structures are also due to athermal effects of microwaves (Banik et. al., 2003). Athermal effect implies the impact that is not related to increased temperature in the system (Hong et. al., 2004).

#### 2.3.5.3.1 Sludge Pretreatment with Microwave Irradiation before Anaerobic Digestion

Park et. al. (2004) investigated the effect of microwave pretreatment of secondary sludge on anaerobic digestion. In the experiment microwave oven with frequency of 2450 MHz and power of 700 W was used. Different irradiation times of 3, 5, 7, 9, 11 and 15 minutes were examined in order to understand the disintegration degree of organics. It was found that SCOD/TCOD increased up to 22% as the exposure time increased. However after 7 minutes the increase in COD release was not significant. With a 7 minutes microwave irradiation final temperature was 91.2°C, SCOD/TCOD increased from 0.02 (control) to 0.19 and $Ca^{+2}$ increased from 83.8 (control) to 95.2 mg/L. Therefore 7 minute of microwave irradiation was studied in mesophilic bioreactors with 5L working volume. 15, 12, 10 and 8 days of HRT were sequentially tried in anaerobic reactors. In terms of biogas production, for HRT values of 8, 10, 12 and 15 days, respectively, 240±11, 183±9, 147±8 and 117±7 mL/L/d biogas productions were achieved for MW pretreated sludge. On the other hand, in control reactors having HRT of 10 and 15 days 134±12 and 94±7 mL/L/d biogas was produced, respectively. When HRT was 15 days, about 30% more methane production and 63.8% and 12.6% relative improvements were achieved in TCOD and VS reductions, respectively. Effluent supernatants SCOD, $NH_4^+$, $PO_4^{3-}$ were also analyzed for each HRT. When HRT was 15 days, SCOD, $NH_4^+$, $PO_4^{3-}$ concentrations were 516 mg/L, 461 mg/L and 35 mg/L for the pretreated digested sludge, respectively while concentrations were 414 mg/L, 388 mg/L and 28 mg/L for the untreated digested sludge, respectively.

Due to its athermal effects along with thermal effects MW application is compared to the conventional thermal applications in many studies.

Athermal effect of microwave irradiation was most commonly investigated by comparing the viability of the microbial cells after conventional and microwave heating at the same temperature in earlier studies. However later on, the difference between two pretreatment methods was investigated in terms of the degree of organics, sugar, protein releases and biogas yield potentials in anaerobic digestion.

Hong et. al. (2004) investigated the coliform destruction due to microwave irradiation and conventional heating. 2450 MHz-1kW microwave oven and a water bath was used for microwave and conventional heating applications, respectively. It was found that microwave irradiation took much less time to achieve the desired temperature than conventional heating and led to higher coliform destruction. 60 seconds of microwave irradiation destroyed coliforms almost completely whereas conventional heating needed 100°C and 4.8 minutes for complete destruction in water bath.

Eskicioglu et. al. (2006a) studied the MW and conventional heating (CH) pretreatment methods at 96°C on thickened WAS. MW was applied by a household microwave oven at 1250 W and 2450 MHz and CH was applied in a water bath. MW irradiation took 5 minutes, whereas CH took 80 minutes to reach the desired final temperature of 96°C. Since the exposure time of CH was higher than MW irradiation, SCOD/TCOD ratio increased from 0.06 (control) to 0.15 and 0.27 with MW and CH pretreatments, respectively. Moreover in the soluble phase after pretreatments, it was found that the release of sugar was more in CH than that of MW pretreatment. On the other hand protein and TVFA releases of MW pretreated sample were higher than that of CH pretreated sample. It was explained by the extended duration in the water bath for CH led to release of more COD and sugar and denaturation of soluble proteins to ammonia and loss of TVFA. Therefore because of this reason, in BMP studies, more biogas was achieved with the CH pretreatment than achieved with MW irradiation. Although CH seems like more effective than microwave pretreatment, it was not reliable to compare these two pretreatment methods due to the large difference between the exposure times of the pretreatment methods.

In the lights of these findings Eskicioglu et. al. (2007) studied the athermal effects of microwave irradiation by comparing the CH and MW irradiation with the same temperature ramp rate. Thickened WAS was MW irradiated with 1250W-2450 MHz microwave oven and CH was applied with water bath up to 50, 75 and 96°C at identical temperature ramp rates. In terms of COD solubilization, no major difference was achieved between MW and CH pretreated sludges. Moreover at 50°C, CH led to more COD solubilization than MW irradiation. SCOD/TCOD was 0.05 for control and it was 0.14 and 0.15 for MW and CH pretreated sludge samples at 50°C. Therefore COD solubilizations after pretreatments did not indicate athermal effect of microwave. However it was found that MW irradiation led to more sugar and protein release than CH. Moreover MW irradiation released more ammonia than CH at any applied temperature. BMP test was also conducted to compare the pretreatment methods. During that test, acclimated and non-acclimated inoculum including reactors were studied. For acclimation, 5L anaerobic semi-continuous reactor was operated for 7 months with SRT of 20 days and fed with MW irradiated thickened WAS. It was found that the highest biogas productions were achieved with the acclimated reactors. Among pretreatment methods at different temperatures of MW and CH, the maximum biogas production was achieved with 96°C MW irradiated TWAS which produced 16±4% more biogas than the control reactor after 15 day of digestion. At the end of a 27 day digestion period, the difference became smaller and improvement was reduced to 14±4%. The reason was that after a certain period, difficult to degrade organics in control reactor continued to be degraded. As a result of this study, more protein, sugar and ammonia releases, moreover higher biogas productions due to microwave irradiation indicated athermal effect of microwave heating.

Pino-Jelcic et. al. (2006) compared CH and MW irradiation in terms of improvements in anaerobic digestion. In the study primary and secondary sludge was mixed at the same volumetric ratio of 1:1. CH was applied by using a hot plate and a 1L metallic bowl with tap water with an overhead stirrer for around 16 minutes to reach a temperature of 60-65°C. For MW irradiation 1kW-2450 MHz household microwave oven was used for duration of 110 seconds to reach a temperature of 60-65°C. Three 6 L anaerobic digesters effective volume of 4 L were set up at 35±0.5°C. Methane yield for microwave pretreated sludge was 374±60 mL $CH_4$/g VS, whereas for conventionally heated sludge and control, it was 352±58 and 326±53 mL $CH_4$/g VS, respectively. Moreover, microwave pretreated digested sludge had a better dewaterability than control and conventionally heated digested sludge.

Wojciechowska (2005) examined the dewaterability of sludge after MW and CH as a conditioning method. Different kinds of sludge samples which were primary, mixed and digested sludge were examined. Microwave conditioning was carried out in 2450 MHz-550W microwave generator. Contact time was 30, 90, 120, 180 and 240 sec. Dewaterability analyses were done after the sample was cooled to 20±0.5°C. According to specific resistance to filtration (SRF) test, microwave pretreatment improved dewaterability especially for the primary sludge. Except 240 seconds of exposure to microwave, as the duration time increased, SRF decreased, therefore dewaterability was improved. Moreover it was found that the average SRF values of conventionally heated sludge were distinctly higher than SRF values achieved with microwave. Therefore it was concluded that there are also athermal effects of microwave to improve sludge dewaterability.

Studies on the athermal effect of MW irradiation showed that, MW irradiation should be preferred rather than CH in terms of more biogas productions in anaerobic digestion and sterilization of sludge in a shorter period of time and at lower temperatures.

Moreover since microwave heating reaches to the desired temperature quicker than conventional heating, the process consumes less energy (Eskicioglu et.al. 2006b).

The document of Techcommentary Industrial Microwave Heating Applications (1993) summarizes other advantages of microwave pretreatment as following,

- Microwave heating can be easily maintained and can be operated automatically.
- Heating equipment of microwave occupies 20-35% of the floor area required by conventional heating equipment.

#### 2.3.5.3.2 Sterilization with Microwave Irradiation

Besides the improvement of the anaerobic digestion in terms of more biogas production and sludge minimization, microwave pretreatment can also lead to reduction in the pathogenic level of the digested sludge.

Studies about inactivation of microorganisms showed that microwave heating can damage many microorganisms, such as *Escherichia coli*, *Streptococcus faecalis*, *Clostridium perfringens*, *Staphylococcus aureus*, *Salmonella*, and *Listeria* spp (Woo et. al., 2000).

Woo et. al. (2000) studied the effect of microwave irradiation on the viability of *Escherichia coli*, a gram-negative bacterial strain, and *Bacillus subtilis*, a gram-positive strain. 600 W of microwave power was applied on cell suspensions. It was found that the maximum reductions in the microbial activities were achieved when microwave temperature was increased from 50° to 60°C. *E. coli* was reduced from $1.1\text{x}10^8$ to $2.5\text{x}10^5$ CFU/mL and *B. subtilis* was reduced from $3.3\text{x}10^6$ to $1.6\text{x}10^4$ CFU/mL. It was found that at higher temperatures; the rate of reductions in the viabilities was reduced compared to irradiation at 60°C.

According to studies of Pino-Jelcic et. al. (2006), it was also found that MW pretreatment pathogen inactivation efficiency was higher than CH. For *Salmonella* spp., disinfection was so effective that 85% of microwave pretreated samples did not show the growth of any colonies.

As it was mentioned before sewage sludge water content plays an important role for the absorption of microwave beams. As a result presence of water is also important for sterilization applications with microwave irradiation. Vela and Wu (1979) examined the effect of water in the inactivation of microorganisms by microwave irradiation at 2450 MHz-1.5kW. Same soil samples were prepared as moisturized and non-moisturized before microwave irradiation. It was found that for the wet sample, the temperature of the system and microbial activity was different from the dry sample. Microwave energy was absorbed more than 98% in the wet sample. However no bacterial damage was achieved in dry samples.

The first operation of microwave as a sterilization unit was installed in Fredericktown, Ohio. Dewatered sludge (>7%) moves through the system in a thin layer of a conveyor belt. Microwave generators with a power of 75-100W create heat greater than 80°C for 6-14 minutes. The process leads to dried sludge with 75-90% solids and Class A quality sludge (Acquisto et. al., 2006).

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 Sludge Samples Used During the Study

### 3.1.1 Wastewater Treatment Plant of Middle East Technical University

In the preliminary studies Part 1, wastewater was taken from wastewater treatment plant of Middle East Technical University (Figure 3.1). Treatment plant treats wastewater arising from the university housing and a big portion of wastewater originating from departments and the buildings. The plant consists of a vacuum rotating membrane bioreactor involving two tanks. In the first tank aeration is applied for biological treatment whereas the aim of the second tank is to apply filtration. During this research WAS was collected from the aeration tank of the treatment plant.

Figure 3. 1 METU, MBR treatment plant

### 3.1.2 Ankara Central Wastewater Treatment Plant

Ankara Central Wastewater Treatment Plant that serves 4,000,000 people (Figure 3.2). About 15% of input wastewater is industrial from Ostim and İvedik Organized Industrial Zones. Treatment plant has a preliminary and primary treatment followed by aerobic activated sludge unit. In the preliminary treatment station, solid objects, grit and floating matters are removed by coarse and fine screens. In the primary sedimentation tanks, settleable solids are removed and BOD load of wastewater is reduced. Biological treatment of wastewater is achieved with aerobic activated sludge unit with retention time of 4 hours. Following a thickening process, produced primary and waste activated sludge are sent to mesophilic anaerobic digesters with sludge retention time of about 24 days. After digestion, digested sludge is thickened again and sent to belt filter unit. Daily sludge production of the treatment plant is about 190 tons/day with 25% TS content after dewatering. Finally sludge cakes are transported with trucks and disposed to Çadırtepe Landfill site.

During this research WAS was collected from the return line of secondary sedimentation tank and anaerobically digested sludge (ADS) used as inoculum was sampled from one of the mesophilic anaerobic digesters.

Figure 3. 2 Ankara Central Wastewater Treatment Plant

### 3.2 Preliminary Studies

The aim of this part was to examine the disintegration effects of different pretreatment methods of alkaline, microwave and combination of the two methods. Soluble chemical oxygen demand (SCOD) and turbidity analyses were conducted since increases in SCOD and turbidity indicate the degree of disintegration. Moreover capillary suction time (CST) analysis was conducted in Part 2, 3 and 4 in order to have an idea about the effect of pretreatment methods on the dewaterabilities of sludges. Here also the CST test was indented to indicate the floc break-up as an indirect method at the end of pretreatment methods. In

Part 1, CST analysis was not conducted since the capillary suction timer did not exist in the laboratory of the department.

In preliminary studies Part 1 and Part 2, solid NaOH was used for the alkaline pretreatments. In Parts 3 and 4, alkaline pretreatment was applied with solubilized NaOH to reach the target pH value.

### 3.2.1 Preliminary Studies Part 1

In the first part activated sludge (AS) was taken from the treatment plant of Middle East Technical University Membrane Bioreactor. MLSS and MLVSS values of AS were 5363 and 4136 mg/L, respectively.

Tanaka et. al. (1997) studied the dose of alkaline in the range of 0.05-1.5 g NaOH/g VSS and suggested the range of 0.5-0.6 g NaOH/g VSS since higher doses did not improve VSS solubilization dramatically. In this part of the study, high alkaline doses were examined to observe whether the solubilization could be improved or not. Therefore doses of 0.8 g NaOH/g VSS and 1.2 g NaOH/g VSS were studied. In order to satisfy the alkaline dosing, based on MLVSS values 1 g and 1.5 g of solid NaOH were added to 300 mL WAS in beakers. Alkaline pretreatment was achieved by mixing the sludge samples on magnetic stirrers for 15 minutes. Initial and final pH values after 15 minutes of alkaline pretreatment are given in Table 3.1. After pretreatments SCOD and turbidity of control and pretreated sludges were examined. SCOD analysis for both control and pretreated WAS was conducted with the supernatant of sludge which was centrifuged for 15 minutes at 3500 rpm.

Table 3. 1 Initial and final pH values for applied chemical doses (Part 1)

|  | *pH initial* | *pH final* |
|---|---|---|
| 0.8 g NaOH/g VSS | 7.59 | 12.64 |
| 1.2 g NaOH/g VSS | 7.61 | 12.78 |

### 3.2.2 Preliminary Studies Part 2

In this part low alkaline doses, MW pretreatment alone and combination of microwave with one dose of alkaline pretreatment were carried out. For alkaline pretreatments 0.05, 0.24 and 0.35 g NaOH/g VSS alkaline doses were examined. Addition to these, MW+0.24 g NaOH/g VSS was selected to investigate combined pretreatment effects.

WAS was taken from Ankara Central Wastewater Treatment Plant. Before applying pretreatments, concentration of WAS was increased by settling and removing the supernatant of sludge. Studied MLSS and MLVSS values of WAS were 6550 and 5300 mg/L, respectively and TCOD was 12,412.5 mg/L. Therefore, according to MLVSS values 0.1, 0.5 and 0.75 g of solid NaOH was added to 400 mL WAS involving beakers. After 15 minutes of alkaline pretreatments, SCOD, turbidity and CST of control and pretreated sludges were examined. Different from Part 1, SCOD was measured after filtering supernatants of pretreated and control sludges from 0.45 µm pore size filters. Initial and final pH values after alkaline pretreatment are given in Table 3.2.

Table 3. 2 Initial and final pH values for applied chemical doses (Part 2)

| | ***pH initial*** | ***pH final*** |
|---|---|---|
| 0.05 g NaOH/g VSS | 7.26 | 9.50 |
| 0.24 g NaOH/g VSS | 7.26 | 12.01~12.00 |
| 0.35 g NaOH/g VSS | 7.35 | 12.49~12.50 |

MW irradiation was achieved with Berghof, MWS-2 Microwave System (Figure 3.3), having a maximum temperature of 220°C, maximum power of 1000 W, maximum pressure of 40 bars and the frequency of 2450 MHz. In the system there are 10 teflon vessels with a capacity of 60 mL. Temperature in the vessels was recorded by the infrared radiation of the samples and it was recorded on a digital screen in every 15 seconds on the microwave oven. For MW pretreatment maximum temperature of 160°C was decided. The reason for choosing a temperature of about 160°C was that for conventional heating the highest hydrolysis rates were achieved with the temperature range of 165 and 180°C (Kepp et. al., 2000). It was not possible to reach 160°C instantly microwave in use. Besides, a sharp increase in temperature caused the disks of the sample vessels to rupture which leads to possible sample losses. Therefore different temperatures, durations and power values were developed for a three step microwave program. Temperature, duration and power of MW steps and temperature profile are given in Appendix A, Table A.1 and Figure A.1. As a result of the three stage temperature profile of the microwave pretreatment the temperature in the system were: for the first 2 minutes temperature was lower than 100 °C, the following 8 minutes, the average temperature was 148 °C. For the final 6 minutes the average temperature was 171°C. For the last 14 minutes of application, the weighted average of temperatures was 160°C.

Figure 3. 3 Berghof, MWS-2 microwave system

For MW pretreatment alone 20 mL WAS was irradiated in each vessel with a total 200 mL of sludge treated in each MW batch. For the combined pretreatment (alkaline + MW), 200 mL of 0.24 g NaOH/g VSS alkaline pretreated sludge was exposed to microwave pretreatment with the same microwave program applied for the MW pretreatment alone.

### 3.2.3 Preliminary Studies Part 3

The aim of Part 3 was to examine alkaline pretreatment of WAS at pH 10, 11, 12 and 12.5, MW pretreatment alone and the combination of alkaline pretreatments with MW. As the study progressed, it was thought that different sludge samples may have different buffering capacities. Therefore the study was decided to be based on pH values rather than alkaline doses added per gram of VSS. Also, different from Part 1 and Part 2, solubilized 2N NaOH was used in the alkaline pretreatment instead of solid NaOH. In this part too, sludge sample from Ankara Central WWTP was used.

WAS sampling and concentrating was as explained in Part 2. MLSS and MLVSS values were 9825 and 7325 mg/L, respectively with TCOD value of 11,325 mg/L. Alkaline pretreatment was achieved with the addition of 2N NaOH to 400 mL WAS while sludge was mixed on a magnetic stirrer. Different from Part 1 and Part 2, alkaline pretreatment duration was extended to 30 minutes in order to achieve a more homogenous distribution of alkaline agent. With the 2N NaOH application the target pH was achieved instantaneously. But since the pH of the WAS dropped slightly with time, application of NaOH was continued for the whole 30 minutes to keep the pH at the desired value. The desired pH values were kept within ±0.1 fluctuations. Applied chemical doses, initial and final pH values are given in the Table 3.3.

Table 3. 3 Initial and final pH values and applied chemical doses (Part 3)

| **Initial pH** | **Final pH** | **Dose (mL/400 mL WAS)** |
|---|---|---|
| 7.42 | 10.09 ~ 10.00 | 1.95 |
| 7.56 | 11.00 | 3.50 |
| 7.75 | 12.06 ~ 12.00 | 5.50 |
| 7.72 | 12.50 | 8.50 |

For MW pretreatment alone, 200 mL of raw WAS was exposed to MW pretreatment with the same program explained in Section 3.2.2.

For the combination of alkaline and microwave pretreatments, 200 mL of 400 mL alkaline pretreated sludges were exposed to microwave pretreatment with the same MW program explained in Section 3.2.2. Combinations of two pretreatment methods were named as MW+pH-10, MW+pH-11, MW+pH-12 and MW+pH-12.5.

After pretreatments, specific oxygen uptake rate (SOUR), SCOD (<0.45 µm), turbidity and CST of control and pretreated sludges were examined. SOUR was applied for the first time in Section 3.2.3. The aim of SOUR test was to observe the inactivation of microorganisms after applied pretreatment methods and to compare activities of microorganisms in pretreated sampled with non-pretreated control samples.

### 3.2.4 Preliminary Studies Part 4

From the results of 3 preliminary experiments; alkaline pretreatment at pH-10, pH-12, MW (only) and combined pretreatments of MW+pH-10 and MW+pH-12 were chosen as pretreatment methods to be observed with anaerobic batch reactors. Before setting up anaerobic batch reactors, selected pretreatment methods were examined once more in terms of soluble COD, carbohydrate and protein releases in order to relate the released soluble COD component with the biogas production.

WAS sampling and concentrating was conducted as explained in Section 3.2.2. MLSS and MLVSS of WAS was 5355 mg/L and 4340 mg/L. 2N NaOH was applied to 500 mL of WAS for 30 minutes with the same procedure applied in Section 3.2.3. Applied chemical doses, initial and final pH values after 30 minutes of pretreatments are given in the Table 3.4.

Table 3. 4 Initial and final pH values and applied chemical doses (Part 4)

| Initial pH | Final pH | Dose (mL/500 mL WAS) |
|---|---|---|
| 7.71 | 10.01 ~ 10.00 | 2.05 |
| 7.92 | 12.01 ~ 12.00 | 6.10 |

MW pretreatment alone was also studied for 200 mL of WAS with the applied MW program before. For the combination of alkaline and microwave pretreatments, 200 mL of 500 mL alkaline pretreated sludge was exposed to microwave pretreatment with the same program explained in Section 3.2.2.

## 3.3 Anaerobic Batch Reactors

Alkaline pretreatment at pH-10, pH-12, MW (only) and combined pretreatments of MW+pH-10 and MW+pH-12 were studied as pretreatment methods with anaerobic batch reactors. ADS (seed) and WAS (food) sampling and concentrating was as explained in Section 3.2.2. MLSS and MLVSS values were 5225 mg/L, 4325 mg/L for WAS and 13065 mg/L, 7265 mg/L for ADS, respectively.

Alkaline pretreatment was applied for the pH values of 10 and 12. Different from preliminary studies, two different normality of NaOH was applied to WAS in order not to affect the sludge volume. pH-10 was adjusted with 2N NaOH and pH-12 was adjusted with 5N NaOH. 500 mL WAS was exposed to alkaline pretreatment with the same procedure applied in Part 3. Applied chemical doses, initial and final pH values are given in the Table 3.5.

Table 3. 5 Initial and final pH values and applied chemical doses before anaerobic batch digestion

| **Initial pH** | **Final pH** | **Dose (mL/500 mL WAS)** |
|---|---|---|
| 8.20 | 10.04 ~ 10.00 | 2.30 (2N NaOH) |
| 7.92 | 12.05 ~ 12.00 | 2.40 (5N NaOH) |

200 mL of WAS was exposed to microwave pretreatment with the same procedure applied in previous sections in order to achieve MW (only) pretreatment. For the combined pretreatments 200 mL of alkaline pretreated WAS was exposed to microwave pretreatment and named as MW+pH-10 and MW+pH-12. After pretreatments, in order to make reactors suitable for anaerobic digestion, pH of all pretreated sludge was neutralized to 7, by applying few mL's of 1N and 2N HCl.

WAS and ADS were fed to 250 mL bottles at a food to microorganism ratio of 0.5 as in the case of Tanaka et. al. (1997).

$$\frac{\mathrm{F}}{\mathrm{M}}=\frac{\mathrm{WAS}}{\mathrm{ADS}}=\frac{4325\ \mathrm{mg/L}\times 46\ \mathrm{mL}}{7265\ \mathrm{mg/L}\times 54\ \mathrm{mL}}=0.507 \qquad 3.1$$

To satisfy F/M ratio as 0.5, 46 mL of WAS and 54 mL of ADS were added to the reactors (Figure 3.4). Finally 20 mL of basal medium (Table 3.6) was added to the reactors to provide nutrients and adjust pH during the digestion period. This way, approximately half of the reactor volume remained empty as headspace for the gas production.

Control reactors were set up with the same methodology; the only difference being the WAS used in the control reactors had not gone through any pretreatment. Triplicate reactors were prepared for the pretreatments and duplicate reactors were prepared for the control reactors which were prepared with raw WAS. One of the reactors for each group was filled with 10 mL more than the actual case again with F/M ratio of 0.5 (50 mL WAS, 58 mL ADS and 20 mL basal medium were added). These higher volume reactors were used to analyze initial MLSS and MLVSS values of each pretreatment and control group. After analyses, volume of all reactors became identical as 120 mL.

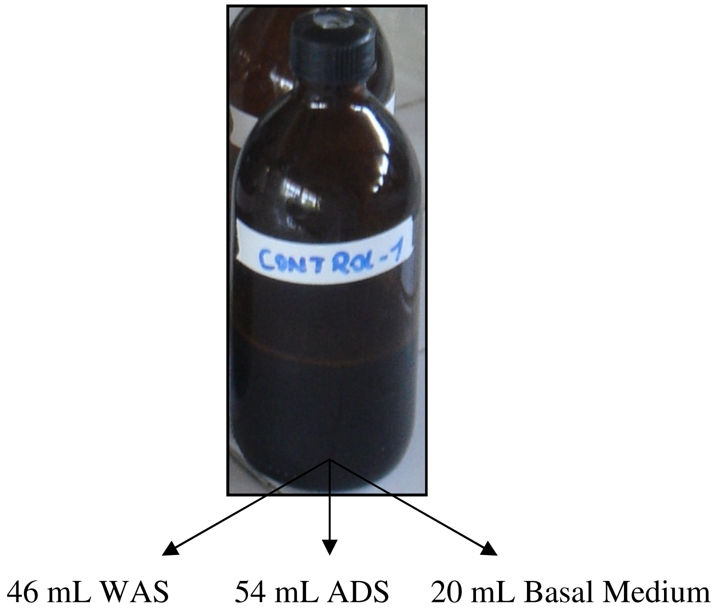

Figure 3. 4 Components of anaerobic batch reactors

Table 3. 6 Basal medium components

| | |
|---|---|
| $KH_2PO_4$ = 2.58 g/L | $MnCl_2.4H_2O$ = 0.3 mg/L |
| $Na_2HPO_4.7H_2O$ = 4.788 g/L | $CuSO4.5H_2O$ = 556.8 mg/L |
| $NaHCO_3$ = 0.6 g/L | $NaEDTA.2H_2O$ = 2847.31 mg/L |
| $NH_4CL$ = 1.8 g/L | $ZnCl_2$ = 0.3 g/L |
| $MgCl_2.6\ H_2O$ = 0.78 g/L | $Na_2(Mo)O_4.2H_2O$ = 0.48 g/L |
| $CaCl_2.2\ H_2O$ = 0.72 g/L | $CoCl_2.6H_2O$ = 299.93 mg/L |
| $FeSO_4.7\ H_2O$ = 16.8 g/L | $NiCl_2.6H_2O$ = 549.6 mg/L |
| $H_3BO_3$ = 0.3 mg/L | HCl = 6 mL/L (concentrated) |
| $Al_2(SO_4)_3.\ 18\ H_2O$ = 718.62 mg/L | |

Then, all reactors were purged with $N_2$ gas for five minutes to remove oxygen from the system. After capping the reactors with rubber stoppers, all reactors were incubated in 37°C without application of mixing.

During the digestion period, at predetermined time intervals, total gas productions and gas compositions of the reactors were analyzed. Anaerobic batch reactors were opened at the end of a 49 day of digestion period since the biogas productions were ceased. After opening the reactors pH, MLSS, MLVSS, CST of digested sludges and SCOD and turbidity of supernatants were analyzed.

pH of digested sludges were analyzed just after opening the reactors in order to see whether the optimum pH range for anaerobic digestion had been satisfied.

MLSS and MLVSS of digested sludges were analyzed in order make a rough estimation in the sludge reduction of reactors.

CST analysis was conducted for each system in order to compare the dewaterabilities of digested sludges and detect the effect of pretreatments on dewaterability of digested sludges.

Finally SCOD and turbidity of digested sludges were examined to observe whether the pretreatment processes led to excess SCOD and turbidity values in the digested sludges compared to untreated digested sludges.

## 3.4 Anaerobic Semi-Continuous Reactors

According to promising results achieved in preliminary studies and anaerobic batch reactors, MW+pH-12 pretreatment was performed in anaerobic semi-continuous reactors. ADS and WAS sampling and concentrating sludge was explained in Section 3.2.2. MLSS, MLVSS values of raw WAS, pretreated WAS and ADS are given in Table 3.7.

Table 3. 7 MLSS and MLVSS values of raw and pretreated WAS and ADS

| Parameter | Raw WAS | Pretreated WAS (MW+pH-12) | ADS |
|---|---|---|---|
| MLSS (mg/L) | 5697 | 3230 | 11400 |
| MLVSS (mg/L) | 4535 | 2400 | 6530 |

Pretreatment procedure was as the same applied in the preliminary studies. First alkaline pretreatment was applied in order to increase pH to 12. Then sludge was exposed to MW pretreatment. Two beakers each having a volume of 1350 mL of WAS was exposed to alkaline pretreatment with 5N NaOH for 30 minutes. Therefore totally 2700 mL of WAS was alkaline pretreated. Applied chemical doses for each beaker are given in the Table 3.8.

Table 3. 8 Initial and final pH values and applied chemical doses before anaerobic semi-continuous reactors

| Initial pH | Final pH | Dose (mL/1350 mL WAS) |
|---|---|---|
| 7.24 | 12.05 ~ 12.00 | 5.60 |
| 7.30 | 12.06 ~ 12.00 | 5.70 |

As the combined pretreatment was completed, concentrated HCl was added to pretreated WAS in order to reduce pH to about 7.25 to make pH suitable for anaerobic digestion. As given in Table 3.7, it was found that pretreated WAS had lover MLSS and MLVSS values than control since solubilized organic fraction of WAS was increased and some organic fraction was lost during pretreatment due to elevated temperature. Anaerobic semi-continuous reactors, having pretreated sludge were set according to these final MLVSS values of WAS after pretreatment.

Anaerobic semi-continuous system consists of four reactor sets; two identical control and two pretreatment reactors. Each set consists of a 3 L anaerobic reactor and a 4L graduated glass gas collector connected to the anaerobic reactor from the top by soft piping. Before filling up the reactors, all the connections and parts were examined for the leak-proof condition. The gas collectors were filled with brine solution at the beginning of reactor set up. As the gas was produced, the solution level was pushed down and the measured volume was recorded as gas produced.

Two liter reactor volumes were filled with liquid and the contents were adjusted to set F/M at 0.5. To be able to achieve this, 830 mL of raw WAS as food and 1170 mL ADS as seed were added in control reactors; 1150 mL pretreated WAS and 850 mL ADS were added in pretreatment reactors Basal medium was not added to anaerobic semi-continuous reactors thinking that sludge to be daily fed to these reactors would contain enough nutrients and buffer. Thus 2 L of 3L reactor volume was filled with WAS and ADS and 1 L was remained as empty. After filling reactors, each reactor was purged with $N_2$ gas for five minutes to remove oxygen from the system. After that, the reactors were connected to the gas collectors in such a way that there was no air intrusion into the system. Reactors were put on magnetic stirrers and constantly stirred. Anaerobic semi-continuous reactors were run for 92 days in hot room with the temperature of 37°C. Photographs of reactors are given in Figures 3.5 and 3.6.

Figure 3. 5 Anaerobic semi-continuous system involving a reactor and gas collector

Figure 3. 6 Control and pretreatment anaerobic semi-continuous reactors

After setting up each reactor, 20 mL of mixed sludge was drained from the reactors from the sampling ports in order to analyze initial TCOD, MLSS and MLVSS values of control and pretreatment reactors (Table 3.9). It was analyzed that initial TCOD of pretreatment reactors were higher than those of control reactors as it was expected because of the higher organic loadings to the pretreatment reactors while adjusting F/M ratio. It was observed that initial TCOD, MLSS and MLVSS values of control reactors were similar. However initial TCOD, MLSS and MLVSS concentrations of pretreatment reactor-2 were lower than its replicate. This could be most probably because of the non-homogenous sampling and filling the pretreatment reactor-2. In order to eliminate the differences between the reactors, they were not drained and fed for 1 week of an acclimation period. At the end of 1 week, gas productions in each reactor ceased and active systems became stable for each one. After that draining and feeding of the reactors initiated.

Table 3. 9 Semi-Continuous Reactor Set-Up and Operational Conditions

| **Reactor** | **TCOD (mg/L)** | **MLSS (mg/L)** | **MLVSS (mg/L)** | **SRT (days)** | **OLR (gVS/L.d)** |
|---|---|---|---|---|---|
| Control 1 | 9238 | 7540 | 5030 | 15 | 0.50±0.01 |
| Control 2 | 9453 | 7000 | 4730 | 15 | 0.50±0.01 |
| Pretreatment 1 | 11248 | 8690 | 5480 | 15 | 0.50±0.01 |
| Pretreatment 2 | 10273 | 6810 | 4370 | 15 | 0.50±0.01 |

During the acclimation period, daily gas production and gas composition were analyzed. After each gas composition analysis water level in gas collectors were vacuumed to the top level of the gas collectors with a vacuum pump with a care of no air intrusion to the gas collectors.

### 3.4.1 Solids Retention Time (SRT)

After one week of acclimation period, daily draining and feeding of the anaerobic semi-continuous reactors were started. WAS was collected from Ankara Central Wastewater Treatment Plant weekly or in some conditions, once in two weeks. Solids retention time (SRT) was set as 15 days for each reactor. In order to satisfy SRT of 15 days, 132 mL of digested mixed reactor contents was drained and feed WAS was fed to the reactors with 60 mL injector from the sampling port of reactors every day. Control reactors were fed with raw WAS and pretreatment reactors were fed with pretreated WAS.

$$\text{SRT} = \frac{\text{Sludge volume inside the reactor (mL)}}{\text{Wasted volume of sludge (mL/d)}} = \frac{1980\text{ mL}}{132\text{ mL/d}} = 15 \quad \text{……………………..…3.2}$$

### 3.4.2 Organic Loading Rate (OLR)

Organic loading rate (OLR) was kept at 0.50±0.01 g VS/L.d for each reactor. WAS taken from Ankara Central Wastewater Treatment Plant was concentrated until the required VS concentration was reached. Feed VS concentration to the reactors had to be about 7576 mg/L in order to achieve OLR as 0.5 g VS/L.d.

$$\text{OLR} = \frac{7576\, mg/L \times 132 mL/d}{2L} \times 10^{-6} = 0.50\, g\, VS/L.d \text{…...…………………..…3.3}$$

MW+pH-12 pretreatments were done as fresh WAS was taken from treatment plant weekly. Pretreatment was done with the same procedure applied in preliminary studies. After microwave pretreatment of alkaline pretreated WAS, pH was reduced from 12 to 10.2±0.2. Therefore pH of WAS was further neutralized by adding concentrated HCl. Pretreated and raw WAS was stored at 4°C before feeding to the reactors. Before feedings raw and pretreated WAS pH values were checked again, and if required adjusted to 7.3±0.2 by adding acid or base.

### 3.4.3 Reactor Operation

For control and pretreatment reactors, feed TS, VS and TCOD concentrations are given in the Table 3.10. As it seen from table, feed VS and TCOD concentrations were intentionally kept the same for control and pretreatment reactors. This way, the same OLR was satisfied for all reactors. However, feed TS concentration of pretreatment reactors was higher than that of controls. The reason was that, after applying combination of alkaline and microwave pretreatment, TS concentration of WAS was increased due to the alkaline application. Moreover with MW addition, some organic fraction of WAS was lost due to elevated temperatures during microwave pretreatment. Therefore in order to satisfy approximately the same amounts of VS loading to pretreatment and control reactors, approximately 15% more TS was fed to the pretreatment reactors in the 132 mL of the feeds.

Table 3. 10 Feed TS, VS and TCOD concentrations of control and pretreatment reactors

| | **Feed TS (mg/L)** | **Feed VS (mg/L)** | **Feed TCOD (mg/L)** |
|---|---|---|---|
| Control Reactors | 10954.0±454.8 | 7575.7±136.9 | 11733.6±655.9 |
| Pretreatment Reactors | 12598.9±396.5 | 7626.5±123.2 | 12256.4±595.7 |

Anaerobic semi-continuous reactors were run for 92 days including the acclimation week. A number of parameters were analyzed at predetermined time intervals. Table 3.11 gives a summary of these parameters, their measurement frequencies and purpose.

Table 3. 11 Parameters analyzed in anaerobic semi-continuous reactors

| **Parameter** | **Measurement Frequency** | **Measurement Purpose** |
|---|---|---|
| Total gas volume | Every day | Monitor the condition of reactors |
| Gas composition | Twice a week | Monitor the condition of reactors |
| TS, VS | Twice a week | To assess sludge reduction |
| TCOD | Twice a week | To assess sludge reduction |
| MLSS, MLVSS | Once a week | To assess sludge reduction |
| pH | Twice a week | Monitor the condition of reactors |
| SCOD | Twice a week | To check the effluent quality from digesters |
| CST | Twice a week | To assess sludge dewaterability |
| Heavy Metals | At reactor termination | To assess sludge quality |
| $NH_3$-N | At reactor termination | To check the effluent quality from digesters |

| | | |
|---|---|---|
| $PO_4$-P | At reactor termination | To check the effluent quality from digesters |
| Carbohydrates | At reactor termination | To observe the amount of increases in concentrations due to the pretreatment |
| Proteins | At reactor termination | To observe the amount of increases in concentrations due to the pretreatment |
| Turbidity | At reactor termination | To check the effluent quality from digesters |

## 3.5 Methods of Analyses Conducted during Preliminary Studies, Anaerobic Batch Reactors and Anaerobic Semi-Continuous Reactors

### 3.5.1 Soluble Chemical Oxygen Demand (SCOD) and Total Chemical Oxygen Demand (TCOD)

In Part 1 of the preliminary studies SCOD analysis was done without filtration of the supernatant of sludge. Sludge samples were centrifuged for 15 minutes at 3500 rpm with Rotofix 32A Hettich Centrifuge and supernatants were analyzed for SCOD. Closed reflux colorimetric method was applied for COD analysis by using Hach DR2000 spectrophotometer at 620 nm.

For the rest of the SCOD analysis, sludge sample supernatants were filtrated through filters with 0.45 µm pore size. Filtrate was collected in test tubes. Closed reflux colorimetric method was applied for COD analysis by using Hach DR2000 spectrophotometer at 620 nm.

For total COD analysis, 1 mL of homogenously mixed sludge sample was taken and it was diluted to 10 mL with distilled water. After that closed reflux colorimetric method was applied for COD analysis by using Hach DR2000 spectrophotometer at 620 nm.

### 3.5.2 Turbidity

For turbidity analysis first sludge samples were settled for 2 hours in 100 mL beakers. After settlement supernatants were taken and analyzed with Hach Turbidimeter 2100N. The unit of the turbidity was expressed as Nephelometric Turbidity Units (NTU).

### 3.5.3 Capillary Suction Time (CST)

In order to examine dewaterability of sludge capillary suction time (CST) test was carried out. The aim of the CST analysis in the preliminary studies was to observe the floc break up as an indirect method and observe dewaterabilities of pretreated and non-pretreated sludges. CST analysis was also conducted after anaerobic batch digestion and anaerobic semi-continuous digestion. The more reliable results about dewaterabilities achieved at that point since dewatering is applied after digestion of sludge.

The experiment was done according to Method 2710G (APHA, AWWA, WEF, 2005). Type 304 M Triton Electronics Capillary Suction Timer was used in the experiment. Sludge sample was placed in a small cylinder of the instrument on a Whatman 17 chromatography paper sheet. There existed a digital display which indicated the time required for liquid to travel a certain distance. Lower the travel time, shorter is the CST and better the dewaterability of sludge.

### 3.5.4 Specific Oxygen Uptake Rate (SOUR)

Dissolved Oxygen was measured by YSI Model 51B Oxygen Meter according to Method 2710B (APHA, AWWA, WEF, 2005). The aim of this experiment was to investigate the inactivation of aerobic microbial cells of WAS samples after pretreatments and also compare the results with non-pretreated WAS sample. A low or no oxygen uptake rate can be linked to the high rates of inactivation of aerobic microbial cells and hence WAS and therefore the effectiveness of the pretreatment method. For the experiment sample was saturated with oxygen, put into the flask with oxygen probe and the head of the flask was sealed with no head space. While the flask was mixed on a magnetic stirrer, dissolved oxygen concentration was measured with respect to time. Then a graph of DO concentration with respect to time was prepared and the rate was calculated from the initial part of the graph.

### 3.5.5 Soluble Carbohydrate

Soluble carbohydrate and proteins were analyzed after pretreatment to understand the fractions contributing to the released organics (soluble COD). Soluble carbohydrate and protein analyses were also conducted in the last part of this study in anaerobic semi-continuous reactors. The aim was to observe the amount of increases in concentrations in digested sludges due to the pretreatment.

For soluble carbohydrate analysis first control and pretreated sludge samples were filtered through 0.45 µm and soluble phases were collected in the test tubes. Soluble carbohydrate was assessed by Dubois Method (Dubois et al., 1956) by using glucose solution as a standard.

For the experiment, 2 mL of samples were added into the test tubes. After that 50 µL phenol and 5 mL sulphuric acid were added. Phenol was prepared as 80% w/w. After adding all, mixtures were waited for 10 minutes. Then all tubes were vortexed and they were put in 35°C incubator for 15 minutes. The procedure was applied for samples and glucose standards as triplicate. Sample measurements were done with 490 nm of absorbance with Pharmacia LKB Novaspec II Spectrophotometer. After absorbance measurement, calibration curve was drawn according to the glucose standard. Then, soluble carbohydrate concentrations of samples were measured according to the calibration curve by intersecting the absorbance of samples on the curve. Calibration curves that were used throughout this research are given in Appendix B, Figures B.1 and B.3.

### 3.5.6 Soluble Protein

For soluble protein analysis first control and pretreated sludge samples were filtered through 0.45 µm. and filtrates were collected in test tubes. Soluble protein was assessed by Lowry Method (Lowry et al., 1951) by using bovine serum albumin (BSA) solution as a standard.

In the method there exist four reagents. Reagent A consists of 2% w/v sodium carbonate which was dissolved in 0.1 N NaOH. Reagent B consists of 1% w/v sodium potassium tartarate and 0.5 % w/v cupric sulphate that were dissolved in 100 mL deionized water. Reagent C was prepared by mixing 1 mL of Reagent B and 49 mL of Reagent A. Finally Reagent D was prepared by mixing 10 mL of deionized water and 10 mL Folin-Ciocalteu's phenol and then vortexing the mixture.

For the experiment 600 µL of samples were put into test tubes. After that 3 mL Reagent C was added and waited for 10 minutes. Finally 0.3 mL Reagent D was added to each test tube and vortexed just after the addition. Before analysis test tubes were kept at room temperature for 30 minutes. The procedure was applied for samples and BSA standard as triplicate. Sample and standard measurements were done with 750 nm of absorbance with Pharmacia LKB Novaspec II Spectrophotometer. In order to find out sample soluble protein concentrations first calibration curve was drawn according to BSA standard. Soluble protein concentrations were determined according to the drawn curve. During protein analysis a new calibration curve was prepared for each analysis done at different times. Calibration curves that were used throughout this research are given in Appendix B, Figures B.2 and B.4.

### 3.5.7 Total Gas Production

#### 3.5.7.1 Anaerobic Batch Reactors

In aerobic batch reactors, total gas production was analyzed by the mechanism, which simply worked as an open-tube manometer. Hose of the system was filled with water and one end of the system was opened to the atmosphere whereas other end was connected to a needle for piercing the rubber stoppers of the reactors to sample the gas. Graduation interval was 0.1 mL and gas volume was measured from the rise in the water level between two arms. This apparatus is given in Figure 3.7.

Figure 3. 7 Gas volume analysis apparatus for anaerobic batch reactors

#### 3.5.7.2 Anaerobic Semi-Continuous Reactors

In anaerobic semi-continuous reactors, daily gas production was directly read from the gas collectors that were connected to the reactors. Gas collectors were graduated 10 mL intervals and filled with brine solution in order to prevent the solubilization of produced gas into water. Brine solution was prepared as 10% NaCl w/v and 2% $H_2SO_4$ v/v. Daily gas productions were measured from the water level difference in the graduated cylinders between any two consecutive days.

### 3.5.8 Gas Composition

Gas composition was analyzed with gas chromatography (GC) with Thermal Conductivity Detector (TCD) (Agilent Technologies 6890N) in both experiments of anaerobic batch reactors and anaerobic semi-continuous reactors. A 30.0 m x 530 μm x 40.0 μm nominal HP-Plot Q capillary column was used for the gas composition analysis. The column temperature was maintained at 45°C for 1 minute, then programmed to reach 65°C at a rate of 10°C/min with a carrier gas (He) flow rate of 3 mL/min (average velocity of 29 cm/sec). In analysis, nitrogen peak came out at 2.1 minute, then methane peak came out at 2.3 minute and finally carbon dioxide peak came out at 2.9 minutes. For the injection, 1mL Gas Tight SGE Syringe was used. For the gas composition analysis, 0.3 mL of gas was removed from the reactors (from the rubber stoppers); 0.1 mL of the removed gas was given to the atmosphere in order to clean the injector and the rest 0.2 mL was injected to the GC. The analysis was conducted twice for each reactor.

In anaerobic batch reactors, for methane gas volume calculation for each reactor, average methane content analyzed with GC was multiplied with the total gas volume produced that day and 130 mL which was the headspace of anaerobic batch reactors was multiplied with the difference of the methane contents of that day's analysis and the previous one. Therefore wasted methane and the methane volume produced between two analyses inside the reactors were found. These values were summed up and the amount of methane production date from the last analysis was found. For cumulative methane production, methane gas volumes calculated with this procedure were summed up with respect to analysis dates.

For anaerobic semi-continuous reactors, actual methane content of the reactors were analyzed after calibrating the GC with a calibration gas in which nitrogen (9.86%), methane (50.74%) and carbon dioxide (39.40%) contents were contained. Methane volumes of the systems were calculated by multiplying the gas production of that day with the average actual methane content of that reactor.

### 3.5.9 $NH_3$-N

$NH_3$-N analysis was done according to Method 4500B-C (APHA, AWWA, WEF, 2005) by titrimetric methods.

Before analysis, sludge samples were centrifuged for 15 minutes with 3500 rpm with Rotofix 32A Hettich Centrifuge. Then supernatants were taken and filtered through 0.45µm. 25 mL of filtrate was diluted to 250 mL in distillation flask. Duplicate samples were prepared while one beaker was prepared as blank consisting 250 mL distilled water. pH of each flask was checked with pH papers and 1N NaOH was added in order to raise the pH around 9.5. After that 12.5 mL borate buffer was added to each beaker in order to keep the pH at desired value. In order to adsorb $NH_3$, erlenmeyer flasks were prepared for each system consisted of 25 mL boric acid (which was prepared as 2%) and a few droplets of indicator.

For the distillation, heaters were turned on and about 150-175 mL of distillate was collected in the boric acid solutions after around 30 minutes. Purple color turned into green indicated distillate $NH_3$-N being in the samples. After collecting the adequate amounts of sample in the erlenmeyer flasks, heaters were turned off.

Green colored erlenmeyer flasks were (~150 mL) were diluted to 250 mL before titration. Finally titration was done with 0.02N $H_2SO_4$ (prepared by dissolving 2.8 mL of $H_2SO_4$ to 1L). Titration was continued until green color was turned in to the initial purple color. Totally added acid amount was recorded and $NH_3$-N concentration was calculated according to the following equation.

$$NH_3\text{-N (mg/L)} = \frac{(S-B)\times0.02\times14000}{25} \quad \text{……………………………………..………3.4}$$

Where,

S is the volume of $H_2SO_4$ titrated for sample; B is the volume of $H_2SO_4$ titrated for blank (mL), 0.02 is the normality of $H_2SO_4$ and 14000 is the conversion factor. Finally, 25 is the amount of sample that was used in the experiment (mL).

### 3.5.10 Soluble $PO_4$-P

Soluble $PO_4$-P analysis was done according to Method 4500P-B-E (APHA, AWWA, WEF, 2005) with persulfate method. Before analysis, sludges were centrifuged for 15 minutes with 3500 rpm with Rotofix 32A Hettich Centrifuge. Then supernatants were taken and filtered through 0.45μm filter papers. Analyses were conducted on the filtrates.

50 mL of filtrate was put into 100 mL beakers. After that 1mL of 11N $H_2SO_4$ and 0.4 g ammonium persulfate was added to each beaker. 11N $H_2SO_4$ was prepared by dissolving 308 mL of $H_2SO_4$ (98%) to 1L of distilled water. One beaker was prepared for blank with 50 mL of distilled water. After digesting the samples in pressure cooker, 8 mL of composite reagent was added to each beaker.

After adding composite reagent, beakers were allowed to stand for 10 minutes. Transparent color of the beakers was turned to blue color. Dark blue color indicated high concentration of $PO_4$-P. Before reading the concentrations, since the color of beakers were dark blue, 1/50 dilution was done for each sample. After that the measurements were done as duplicate at 880 nm by Colepalmer Spectrophotometer.

Calibration curve was achieved with 0.1, 0.3, 0.5, 0.75 and 1 mg/L standards. $PO_4$-P concentrations of sludge samples were analyzed according to the calibration curve given in Appendix B, Figure B.5.

### 3.5.11 Heavy Metal

Heavy metal contents of digested sludges were analyzed according to a microwave digestion method developed by Özsoy (2006). In order to extract heavy metals from sludges, microwave digestion was carried out by adding a number of different acids. After digestion, Ni, Cd, Zn, Pb, Cr, Cu, Ca and Mg were analyzed by Perkin Elmer AAnalyst 400 Flame Atomic Absorption Spectrometry with electrode discharge lamps and Hg analysis was done by Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometry with cold vapor hydride system.

Dried sludge samples were exposed to microwave digestion in 2 steps. In order to dry sludge, first sludge samples were centrifuged for 15 minutes at 3500 rpm by Rotofix 32A Hettich Centrifuge. Centrifuged samples supernatants were dumped and sludges at the bottom of the centrifuge tubes were collected and dried at 105°C for 24 hours. For 2 step of microwave digestion, the same instrument that was used for pretreatment of sludge was used.

In the first step 0.5 g of dried sludge were put into the microwave Teflon vessel. Then 2 mL nitric acid (65%), 6 mL hydrochloric acid (37%) and 0.5 mL hydrofluoric acid (40%) were added. Triplicate vessels were prepared for each sludge sample and duplicate for the blank containing only acid combinations.

After step 1, Teflon vessels were allowed to stand and cooled to room temperature. After that Teflon vessels were opened and 5 mL saturated boric acid solution was added to each vessel and microwave digestion step 2 was applied. Step 1 and 2 of microwave digestion are given in Table 3.12.

Table 3. 12 Time, temperature and power of microwave digestion stages for two steps

| Program Stages | Time (min) | Temperature (°C) | Power (W) |
|---|---|---|---|
| STEP 1 | | | |
| Stage 1 | 5 | 140 | 750 |
| Stage 2 | 5 | 160 | 850 |
| Stage 3 | 20 | 175 | 900 |
| STEP 2 | | | |
| Stage 1 | 15 | 160 | 800 |
| Stage 2 | 15 | 100 | 400 |

After digestion solutions were boiled until the final volume was reduced to near dryness. Then, they were diluted to 50 mL and filtered through 0.45 µm filters to prevent the negative impact of particles larger than 0.45 µm on atomic adsorption instrument.

With this procedure, Ni, Cd, Zn, Pb, Cr, Cu, Ca and Mg were analyzed. However for Hg analysis another microwave digestion with the same steps were followed. But this time 0.2 g of dried sludge was used and no boiling after digestion was carried out since a portion of Hg could be lost during boiling. After digestion final samples were directly diluted to 50 mL and they were filtered through 0.45 µm filters. Then Hg analysis was done.

Heavy metal concentration calculation was done according to the equation given below.

$$\text{Heavy Metal (mg/kg)} = \frac{\mathrm{C} \times 0.05 \times 1000}{\mathrm{M}} \times \mathrm{DF} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

Where,
C is the amount read by the atomic adsorption (mg/L)
0.05 is the volume of the diluted sample (L)
1000 is the conversion factor (g/kg)
M is the amount of dried sludge (g)
DF is the dilution factor if any dilution was done before atomic adsorption.

### 3.5.12 Total Solids (TS) and Volatile Solids (VS)

TS was done according to Method 2540B (APHA, AWWA, WEF, 2005) and VS was done according to Method 2540E (APHA, AWWA, WEF, 2005).

### 3.5.13 Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS)

MLSS and MLVSS were done according to Methods 2540D and 2540E (APHA, AWWA, WEF, 2005).

### 3.5.14 pH

pH was a important parameter not only for the alkaline and combined pretreatments but also for the adjustment of pH for anaerobic reactors. It was measured by CyberScan PC 510 pH meter/conductivity meter.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Preliminary Studies Part 1

In the fist part of the study, a certain amount of solid NaOH was added into sludge with respect to an attempt to fix the pH in the sample. It was found that alkaline pretreatments of 0.8 and 1.2 g NaOH/g VSS led to approximately the same final pH of WAS (Table 3.1). Similar findings were reported by De Franchi (2005). It was stated that either primary or WAS, pH of 12.5 was achieved after the addition of 3 mL of 5N NaOH to 100 mL sludge. After that point, increasing the alkaline dosage led to a slow increase in pH.

It was found that higher dose of 1.2 g NaOH/g VSS alkaline pretreatment did not lead to further COD solubilization (Figure 4.1). On the contrary, SCOD value of 1.2 g NaOH/g VSS pretreated WAS was lower than that of 0.8 g NaOH/g VSS pretreated WAS. SCOD of pretreated sludge was increased from 36 mg/L (control) to 2377.5 mg/L and 1987.5 mg/L with the pretreatments of 0.8 and 1.2 g NaOH/g VSS, respectively. Similarly, Tanaka et. al. (1997) reported a decline in VSS solubilization with the dose of 0.8 g NaOH/g VSS compared to 0.7 g NaOH/g VSS. Like SCOD, higher dose alkaline pretreatment led to a lower turbidity value of WAS. Turbidity was increased from 13.78 NTU (control) to 2473.00 and 782.67 NTU with the pretreatments of 0.8 and 1.2 g NaOH/g VSS, respectively.

Considering the final pH values achieved with alkaline pretreatments and according to literature, similar findings in SCOD were achieved for both alkaline doses of pretreated WAS. Lower SCOD and turbidity results at higher dose can be explained by the 15 minutes of alkaline pretreatment duration that might not be adequate for the high alkaline dosage to be homogenously distributed in WAS.

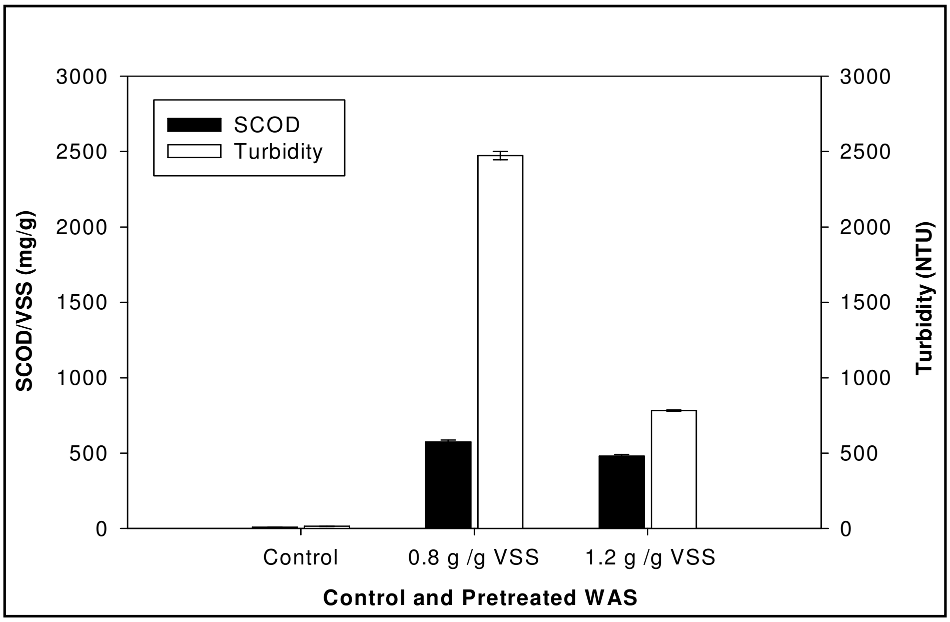

Figure 4. 1 SCOD/VSS and turbidity of control and pretreated WAS (Part 1)

## 4.2 Preliminary Studies Part 2

In this part, lower alkaline doses were tested to observe if the pH can be lowered. In the first part it was found that 0.8 g NaOH/g VSS led to final pH value of 12.64 and in this experiment 0.35 g NaOH/g VSS led to final pH of 12.5 (Table 3.2). Alkaline doses of 0.24 and 0.05 g NaOH/g VSS led to final pH values of 12 and 9.5. Therefore by comparing the results obtained in Parts 1 and 2, it can be said that doses higher than 0.35 g NaOH/g VSS do not lead to a dramatic increase in pH.

In this part, the methods (MW + alkaline) were also combined for the first time. Results showed that SCOD/TCOD increased from 0.006 (control) to 0.03, 0.18, 0.15, 0.10 and 0.36 with the pretreatments of 0.05, 0.24 and 0.35 g NaOH/g VSS, MW (only) and MW+0.24 g NaOH/g VSS, respectively. SCOD release normalized with MLVSS is given in Figure 4.2.

Although final pH reached to 12.5 with 0.35 g NaOH/g VSS alkaline pretreatment, it was found that higher alkaline dose pretreatment led to a lower COD solubilization than 0.24 g NaOH/g VSS. SCOD was increased from 78 mg/L to 2182 mg/L and 1824.5 mg/L with alkaline pretreatments of 0.24 g NaOH/g VSS and 0.35 g NaOH/g VSS, respectively. Similar results were observed in this research in Part 1 and in the studies of Tanaka et. al. (1997). As expected, alkaline pretreatment at lowest dose of 0.05 g NaOH/g VSS which gave a final pH of 9.5 was so poor that led to a minor increase in SCOD release. SCOD was increased from 78 mg/L to 333.8 mg/L at pH 9.5. Among all pretreatment methods, for the pretreatment time applied, highest SCOD value was achieved with the combination of microwave and alkaline pretreatment with the dose of 0.24 g NaOH/g VSS at pH-12. SCOD was increased from 78 mg/L to 4449 mg/L with combined pretreatment. The improvement in COD release was higher than the addition of increases of individual pretreatments which indicated the synergistic effect of combined pretreatment.

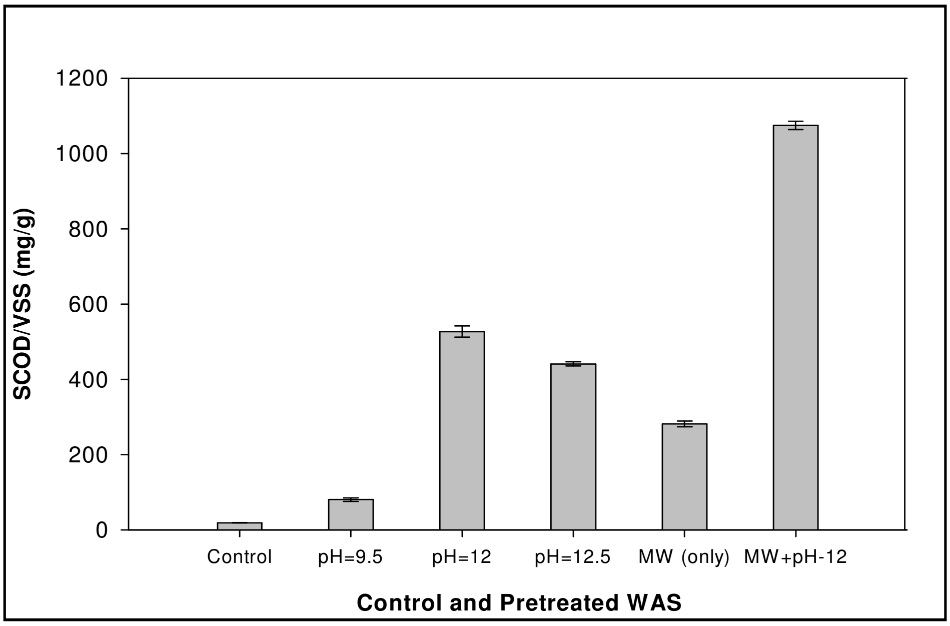

Figure 4. 2 SCOD/VSS of control and pretreated WAS (Part 2)

Following pretreatments, the turbidity of supernatants and CST value of sludge samples were also measured. The actual purpose here was not necessarily assessing the dewaterability of sludge, but rather to get an indirect idea about the particle break-up in sludge following disintegration. It was found that for the alkaline pretreatment, highest turbidity and the worse dewaterability of sludge were achieved with 0.24 g NaOH/g VSS pretreatment which were 2229.3 NTU and 1746.8 seconds, respectively (Figure 4.3). Deterioration in the dewaterability with alkaline pretreatment was an expected result since WAS had a viscous structure after alkaline pretreatment especially for higher doses. On the other hand highest alkaline dose of 0.35 g NaOH/g VSS had a lower CST and turbidity values than 0.24 g NaOH/g VSS. As for SCOD, lower CST and turbidity values can be explained by the improper solubilization of high dose of solid NaOH in sludge within 15 minutes.

MW pretreatment alone had a better dewaterability result than high alkaline dose pretreatments. This is possibly due to the well-known conditioning effect of thermal treatments which is valid for microwave application as well. It was found that among the all studied pretreatment methods, combination of 0.24 g NaOH/g VSS pretreatment with microwave had the lowest CST value. Therefore it was concluded that the adverse effect of alkaline pretreatment on dewaterability was overcome by the combination of microwave with alkaline pretreatment and there too, the effect was synergistic. In terms of turbidity, no major difference was observed between MW (only) and MW+pH-12 pretreatments.

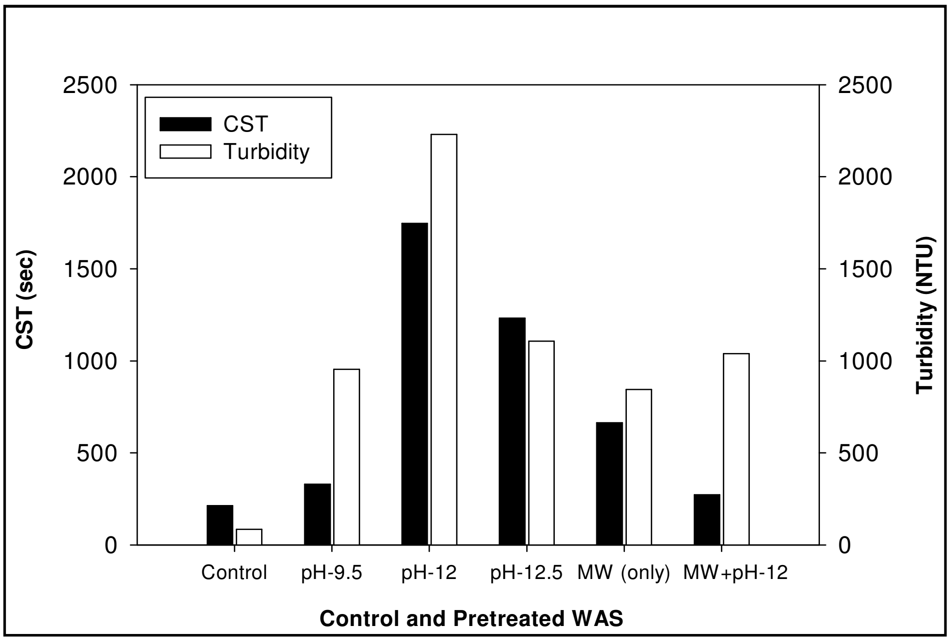

Figure 4. 3 CST and turbidity of control and pretreated WAS (Part 2)

As a result of preliminary studies Part 2, it was concluded that by the combined pretreatment method a significant synergy was created for sludge disintegration measured by SCOD values. Moreover deteriorated dewaterability due to alkaline pretreatment was improved as well.

Since lower SCOD, CST and turbidity values were achieved at the highest doses of alkaline pretreatment in Parts 1 and 2, it was decided to study alkaline pretreatment with NaOH in liquid form in further experiments and with the duration of 30 min instead of 15 min. Therefore, after this experiment, in alkaline pretreatment, the main objective was to achieve the target pH using liquid NaOH.

## 4.3 Preliminary Studies Part 3

In this set of experiments along with using liquid NaOH and 30 min interaction time, the desired pH values were taken as reference. For this purpose pH-10, pH-11, pH-12, pH-12.5 and MW pretreatment and the combinations of these were studied. In addition to the previously studied parameters oxygen consumption rate of sludge samples were also measured to check the microbial activity after pretreatments.

### 4.3.1 Specific Oxygen Uptake Rate (SOUR)

After MW (only) and all alkaline pretreatments, SOUR of pretreated and control sludge were examined in order to make a comparison and to develop an understanding of the effect of pretreatment method on microbial activity. The absence of microbial activity does not necessarily indicate the cell rupture or hydrolysis of the macromolecules on the cell wall; but it is still a good indicator for the effectiveness of pretreatment method when used together with the SCOD increase data.

Oxygen consumption values with respect to time are given in Figure 4.4. As expected oxygen consumption of control sludge which was not pretreated was faster than all pretreated WAS samples. For alkaline pretreatment, it was observed that as the pH increased oxygen consumption rate decreased, for which pH-12 and 12.5 pretreatments had approximately the same effect on inactivation of WAS. However, with the microwave pretreatment, no oxygen consumption was observed which means complete inactivation of WAS. Therefore, it was concluded that for each pH of alkaline pretreatment, combination of microwave with alkaline pretreatment will also lead to complete inactivation of microbial cells. Therefore, SOUR tests were not conducted for combined pretreatments.

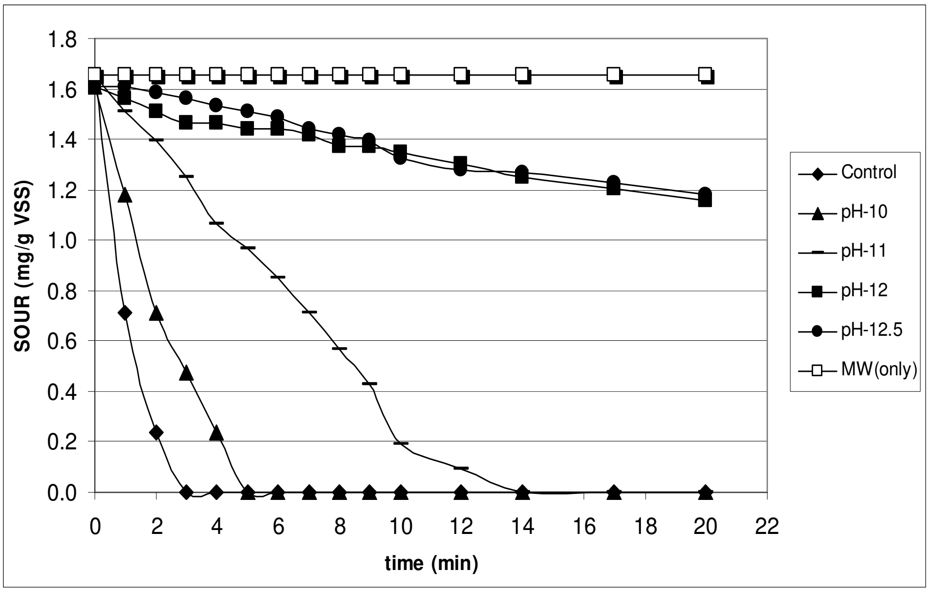

Figure 4. 4 Specific oxygen uptake rate of control, microwave and alkaline pretreated WAS

### 4.3.2 SCOD

COD releases normalized with MLVSS are given in Figure 4.5. For alkaline pretreatment, as expected it was found that increase in pH resulted in more solubilization of organics. SCOD values increased from 61.5 mg/L (control) to 1077.0 mg/L, 1901.5 mg/L, 2291.0 mg/L and 3239.0 mg/L for the alkaline pretreatments at pH-10, 11, 12 and 12.5 respectively. In terms of SCOD/TCOD, the ratio increased from 0.005 (control) to 0.10, 0.17, 0.20 and 0.29 at pH-10, 11, 12 and 12.5, respectively.

Valo et. al. (2004) found the COD releases of 9.3% for pH 10 and 30.7% for pH 12 with 1 hour KOH addition of alkaline pretreatment. So finding of this study is in agreement with findings of Valo et. al. (2004). Chen et. al. (2007) also stated that the increase in pH led to higher SCOD concentrations. The highest SCOD was achieved with the highest pH of 11 where SCOD was 1242 mg/L and 7939 mg/L for control and pretreated WAS at pH-11 on the 8th day of pretreatment duration. Increase in SCOD with alkaline pretreatment was also stated by De Franchi (2005). It was found that pretreatment of WAS with 5N NaOH at pH-12.5 at 37°C led to an increase in soluble COD from 2217 mg/L to 10427 mg/L after 1 day and in the 8th day SCOD was 11618 mg/L for alkaline pretreated WAS. Although in the study of De Franchi (2005), sludge samples were filtered through 0.45μm before SCOD analysis, SCOD of control WAS was too high to be compared with the results found in this study.

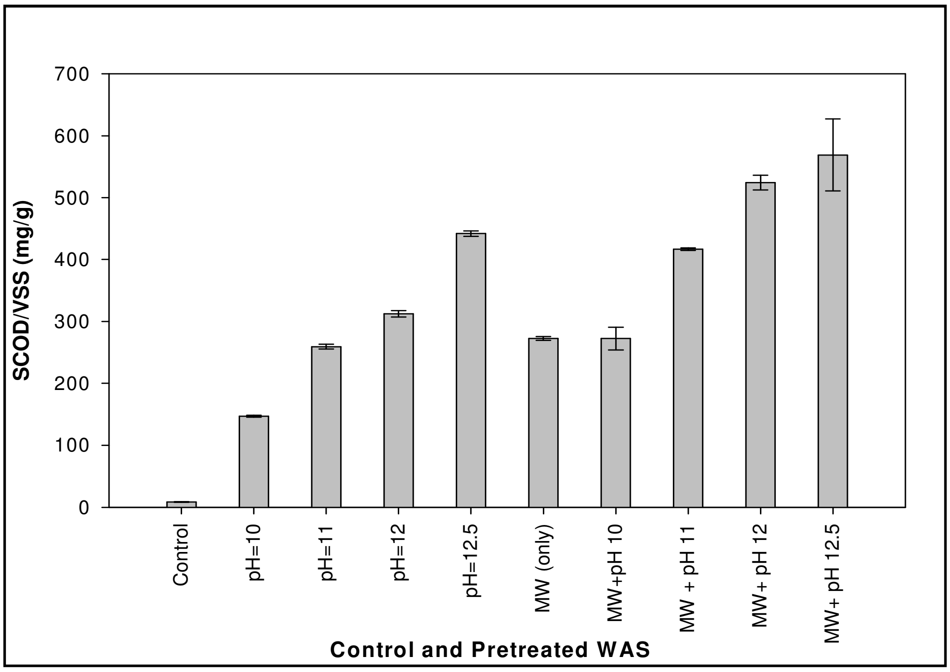

Figure 4. 5 SCOD/VSS of control and pretreated WAS (Part 3)

For the microwave pretreatment alone, it was found that SCOD after pretreatment was approximately the same as in pH-11 alkaline pretreatment; where SCOD increased from 61.5 mg/L (control) to 1998.0 mg/L. In terms of SCOD/TCOD, the ratio increased from 0.005 (control) to 0.18 with microwave pretreatment alone. Eskicioglu et. al. (2006a) reported that SCOD/TCOD was increased from 0.06 (control) to 0.15 with MW pretreatment at 96°C. Park et. al. (2004) found that SCOD/TCOD increased from 0.02 (control) to 0.19 with MW pretreatment at 91.2°C and 0.21 at boiling temperature. Therefore, findings of this study are in line with the results of previous work in terms of the amount of soluble COD release. It should be noted that, MW irradiation at 160°C resulted in loss of some organic materials and this possibly led to a lower SCOD/TCOD ratio after pretreatment. Eskicioglu et. al. (2006b) stated that SCOD/TCOD values were higher at MW-75°C than MW-96°C which was explained by the loss of organic materials at high temperature.

When the two pretreatment methods were combined it was observed that, with the increase in pH, SCOD values increased as well. SCOD increased from 61.5 mg/L (control) to 1997.0 mg/L, 3056.0 mg/L, 3844.0 mg/L and 4170.0 mg/L with the pretreatments MW+pH-10, MW+pH-11, MW+pH-12 and MW+pH-12.5, respectively. In terms of SCOD/TCOD, the ratio increased from 0.005 (control) to 0.18, 0.27, 0.34 and 0.37 with the pretreatments MW+pH-10, MW+pH-11, MW+pH-12 and MW+pH-12.5, respectively. It was observed that the percent soluble COD release values were well above the releases achieved by each individual method. Only when MW application was combined with pH-10 pretreatment, SCOD/TCOD was at the level of released by MW only. When the pH increased to 11 then to 12 and 12.5 together with MW application, the releases increased well above the release accomplished by each method. However, it was not possible to achieve the synergistic effect observed in Part 2 of the preliminary studies in terms of SCOD values in this part of the study. For example when pH was 11, soluble COD ratio was 17% of total COD; when only MW was applied, the percentage was 18; when two methods were combined, this amount became 0.27 (instead of one on one addition of 35% which is simply obtained by summing the percentages of two methods). Although lower SCOD values were achieved with combined pretreatment than by the addition of individual pretreatments in this part, and this was a little disappointing, still the increases over the individual method’s achievements are considered remarkable. This effect was observed to become more pronounced when the pH was 12 and alkaline pretreatment was applied with MW; the observed soluble COD release (34%) was having the closest value to the number obtained by simply summing up the releases of the two methods (38%).

### 4.3.3 CST and Turbidity

Following pretreatments, turbidities of supernatants and CST values of sludge samples were also measured. It was found that as pH increased, because of the viscous structure of WAS, dewaterability of WAS was deteriorated as it was shown by the increase in the CST values (Figure 4.6). CST was 60.60 sec. for control and it was 257.97 sec., 937.50 sec., 1536.65 sec. and 1742.70 sec. at pH 10, 11, 12 and 12.5 pretreatments, respectively. As in the case of SCOD, turbidity was increased too with the increase in pH, especially for pH-12 alkaline pretreatment. Turbidity of control was 55.87 NTU where it was 255.67, 954.67, 2760.00 and 1330.00 NTU at pH 10, 11, 12 and 12.5. Altogether these data indicate that at high pH values some floc break-up occurs.

Microwave pretreatment alone and pH-11 alkaline pretreatment gave similar COD releases. However, a better dewaterability property was achieved with microwave pretreated sludge as compared to pH-11 alkaline pretreatment. CST of MW pretreated WAS was 292.30 seconds. Turbidity of MW pretreated sludge was 1193.33 NTU which was somewhere between turbidity of pH-11 and 12.5.

For the combined pretreatments, CST values were 775.25 sec., 549.00 sec., 436.75 sec. and 448.20 sec. for MW+pH-10, MW+pH-11, MW+pH-12 and MW+pH-12.5 pretreated WAS, respectively. As a result it was found that due to the conditioning effect of microwave pretreatment, the main disadvantage of alkaline pretreatment (poor dewaterability) was overcome when combined with microwave pretreatment as it was observed in Part 2. For each combined pretreatment, there was not a major difference between the turbidity values which was about 1300 NTU.

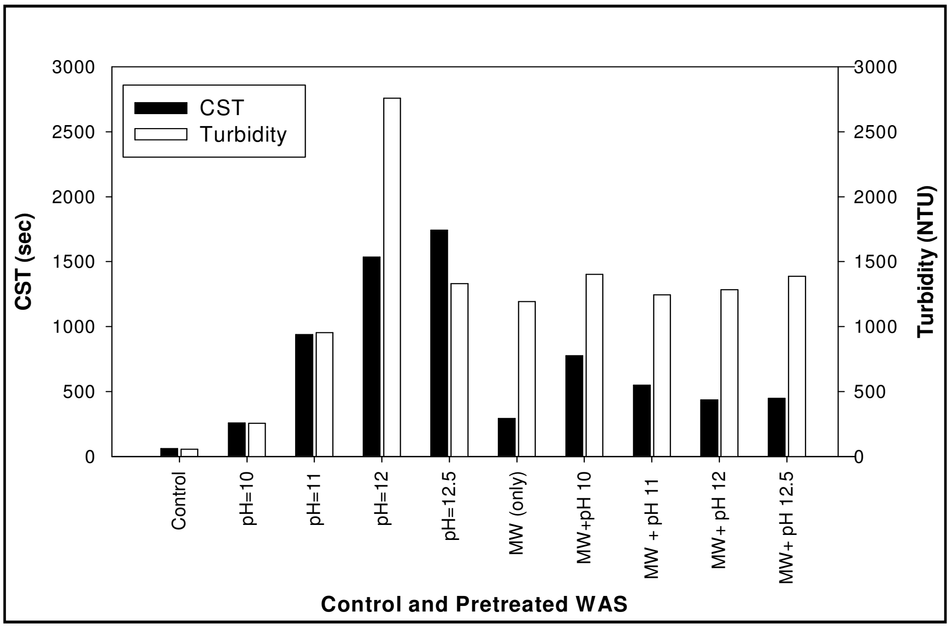

Figure 4. 6 CST and turbidity of control and pretreated WAS

Among the studied pretreatment methods, pH-10, pH-12, MW (only), MW+pH-10 and MW+pH-12 were chosen for the second part for anaerobic biodegradability analysis. Since MW and MW+pH-10 resulted in the same amount of SCOD release, pH-10 is decided to be investigated intentionally in the second part, in order to observe any difference in biogas production and improvements of the combined method. Also since with the combined pretreatments, there was not a large difference between SCOD/TCOD values of MW+pH-12 and MW+pH-12.5, pH-12 was chosen instead of pH-12.5 in separate and combined applications.

Before setting up the reactors, COD, soluble carbohydrate and protein releases of the selected pretreatment methods were again examined with the same sludge samples collected at the same time of construction of batch reactors which are given in Part 4.

## 4.4 Preliminary Studies Part 4

### 4.4.1 SCOD

In Figure 4.7 COD releases of control, pH-10, pH-12, MW (only), MW+pH-10 and MW+pH-12 pretreated WAS normalized with MLVSS are given. When SCOD/VSS values were compared, the same trend was achieved as in the preliminary studies Part 3. Lowest COD release was achieved with alkaline pretreatment of pH-10, whereas combined pretreatment at pH-12 gave the maximum COD release. Moreover again MW (only) (with the same pH of control) and MW+pH-10 pretreatments led to approximately the same COD releases.

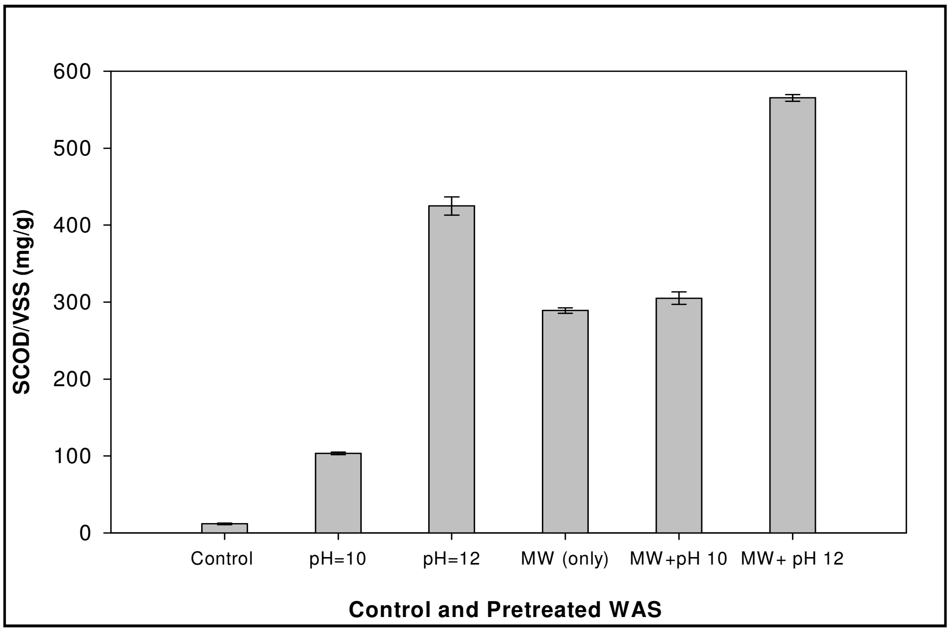

Figure 4. 7 SCOD/VSS of control and pretreated WAS (Part 4)

### 4.4.2 Soluble Carbohydrate and Protein Releases after Pretreatments

Soluble COD, carbohydrate and protein concentrations of control and pretreated WAS are given in Figure 4.8. The calibration curve used in the concentration analyses of carbohydrate and protein are given in Appendix B, Figures B.1 and B.2.

For the alkaline pretreatments, it was found that releases of carbohydrate and protein at pH-12 were about twice of that pH-10. Soluble carbohydrate and protein concentrations of control were 8.1 and 17.4 mg/L. Carbohydrate and protein concentrations increased up to 37.7 and 223.9 mg/L with pH-10 pretreatment and increased up to 76.7 and 503.5 mg/L with pH-12 pretreatment, respectively.

Chen et. al. (2007) examined SCOD, carbohydrate and protein releases at acidic and basic conditions after filtering samples from 1.2 µm pore size filters. For the alkaline solubilization, pH 8, 9, 10 and 11 were examined. It was found that as the pH increased SCOD, carbohydrate and protein releases increased as well. pH-11 gave the maximum releases of 938.33 mg/L and 119.29 mg/L concentrations of protein and carbohydrate on the second day of alkaline solubilization while concentrations were 112.25 mg/L and 30.11 mg/L for pH-7 respectively. Since samples were filtered through 1.2 µm pore size filters and the duration of alkaline pretreatment was longer, concentrations are higher than those found in this study. However the ratio between carbohydrate and protein releases is approximately the same with this study indicating that results of this study are in correlation with literature findings.

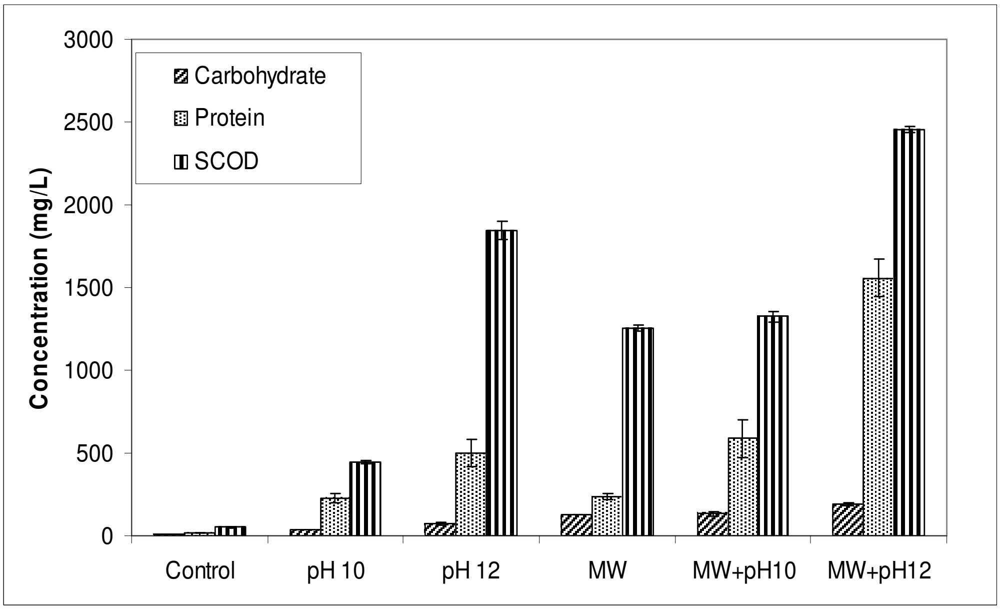

Figure 4. 8 Soluble carbohydrate, protein and COD concentrations of control and pretreated WAS

With MW pretreatment alone, soluble carbohydrate and protein concentrations increased from 8.1 and 17.4 mg/L to 125 and 234.4 mg/L. As it is seen from the Figure 4.8, MW pretreatment alone released approximately the same protein with pH-10 pretreatment, but released more carbohydrate than that was released at pH-10 and even more than that released at pH-12 pretreatments.

Eskicioglu et. al. (2006a) found that MW pretreatment at 96°C led to 140 and 150 mg/L soluble sugar and protein concentrations, respectively after ultrafiltration where control WAS had 96 and 127 mg/L of soluble sugar and protein concentrations. Therefore, it can be understood that a higher temperature of 160°C MW pretreatment improved the release of both carbohydrate and protein compared to control sludge.

It was found that for the combined pretreatments, soluble carbohydrate and protein concentrations increased from 8.1 and 17.4 mg/L to 134.8 and 586.8 mg/L with MW+pH-10 and increased to 190.5 and 1559 mg/L with MW+pH-12 pretreatments, respectively. Thus, among the all studied pretreatment methods, combination of microwave with pH-12 led to maximum carbohydrate and protein releases. It was found that, although SCOD and carbohydrate concentrations of MW (only) and MW+pH-10 were approximately the same, MW+pH-10 led to the release of more protein than MW pretreatment alone.

Moreover for combined pretreatments at each pH, release of protein was higher than sum of the protein releases of individual pretreatments indicating a very clear synergistic effect. So it can be said that alkaline pretreatment had weakened the cell walls and led to the release of more proteins when combined with microwave. Although concentration of carbohydrate was higher in combined pretreatments, the release of carbohydrate did not increase dramatically compared to individual pretreatment methods.

Effect of a thermochemical pretreatment on carbohydrate and protein releases was studied by Tanaka and Kamiyama (2002). It was found that autoclaving at 130°C for 5 minutes after 0.3 g NaOH/g VSS alkaline pretreatment led to just 4% increase in protein of WAS. On the other hand it was found that carbohydrate concentration of WAS was reduced about 30% after pretreatment.

## 4.5 Anaerobic Batch Reactors

### 4.5.1 Total Gas Production

Total gas productions of 49 day of anaerobic digestion are given in Figure 4.9. All of the results presented are the average values obtained from identical reactors. At the stage where the gas production ceased, there was not a difference between cumulative total gas productions of control and pH-10 reactor and there was little improvement achieved with pH-12 pretreatment which was only 3.4%. With alkaline pretreatment Valo et. al. (2004) achieved no significant improvement in biogas production at pH-12 in batch reactors. On the other hand, Penaud et. al. (1999) achieved about 40% improvement in biogas production when 5 g/L NaOH was applied to WAS in batch reactors.

With the MW pretreatment alone, 10.7% improvement was achieved in cumulative total gas production, however this improvement was reduced when MW was combined with pH-10 alkaline pretreatment which caused an improvement of only 8.4% over control. The maximum cumulative total gas production was achieved with MW+pH-12 pretreatment which produced 16.3% more gas than control. Total gas productions and standard deviations of anaerobic batch reactors are given in Appendix C, Table C.1.

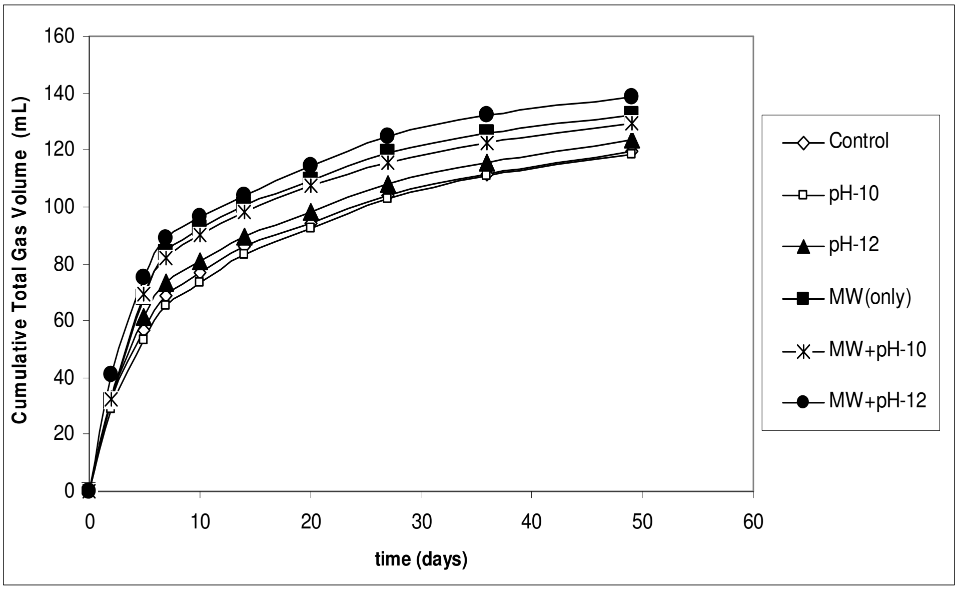

Figure 4. 9 Total gas productions for control and pretreated WAS with time

With mesophilic batch reactors, Eskicioglu et. al. (2007) achieved only 4% higher biogas production with MW-96°C pretreatment over control with non-acclimated inoculum. On the other hand with an acclimated inoculum 16±4% higher biogas was achieved after 15 day of anaerobic digestion. Although in this study inoculum was not acclimated, 16.9% more total gas production was achieved with MW pretreatment alone after 14 days of anaerobic digestion. In the length of time, the improvement was reduced to 10.7% since there occurred sufficient time for the degradation of hardly biodegradable organics in control reactors.

Eskicioglu et. al. (2008) observed 31±6% more biogas production with 175°C MW pretreated TWAS (3% TS) in mesophilic batch digestion. The difference between the biogas production improvements of two studies can be explained by the high TS content of WAS and also a much higher microwave pretreatment temperature that was used in the study of Eskicioglu et. al. (2008) since pretreatment led to more COD solubilization with more TS concentrated WAS.

In the second day of sampling, it was found that MW (only) and MW+pH-10 produced even less biogas than control. An inhibition in the initial biodegradation of microwave pretreated WAS was suspected. A similar finding was also stated by Eskicioglu et. al. (2006b). It was stated that microwave pretreated sludge produced less biogas than control in the early times of the anaerobic batch reactors but the rate of biogas production was accelerated in microwave pretreated reactors after a while. The initial inhibition was explained because of loosing some enzymes contributing the hydrolysis and biodegradability in anaerobic digestion with high temperature MW pretreatment (Eskicioglu et. al., 2007). However, the initial inhibition/delay period of MW and MW+pH-10 was not observed with MW+pH-12 pretreatment.

Climent et. al. (2007) examined the effect of microwave pretreatment of WAS on thermophilic anaerobic digestion with batch reactors. Microwaving sludge at 800W for duration of 180 to 300 seconds and microwaving at 400W for 240 to 600 seconds did not cause any improvement in biogas production.

Among the mechanical pretreatment methods, Baier and Schmidheiny (1997) observed 10% more biogas production in anaerobic batch reactors with stirred ball mill pretreatment of WAS after incubation for about 21 days which is about the same improvement achieved with MW pretreatment alone in this study but after 49 days of incubation.

### 4.5.2 Methane Production

Methane production results are given in Figure 4.10. Methane production results were not in one to one correlation with total biogas production results. Although there was not an improvement in total gas production with pH-10 pretreatment, 5.8% more methane production was achieved at this pH-10. Alkaline pretreatments at pH 10 and 12 led to approximately the same amounts of methane production. At pH-12 improvement in methane production was 5.4%. In the preliminary studies SCOD/TCOD values of pH-10 and pH-12 pretreatments were 0.10 and 0.20. However it was found that both alkaline pretreatments led to the similar improvements in methane production.

With MW pretreatment alone, 11.3% more methane production was achieved over control. For the combined pretreatments, both of them led to approximately the same methane production, with the highest improvement achieved in MW+pH-12 pretreatment as 18.9% increase compared to control where improvement was 17.4% in MW+pH-10 pretreatment. Methane contents and volumes and standard deviations of anaerobic batch reactors are given in Appendix C, Table C.2. In the preliminary studies, it was found that MW (only) and MW+pH-10 released same amount of COD. However in anaerobic batch reactors it was found that, MW+pH-10 pretreatment caused more methane production over MW pretreatment alone.

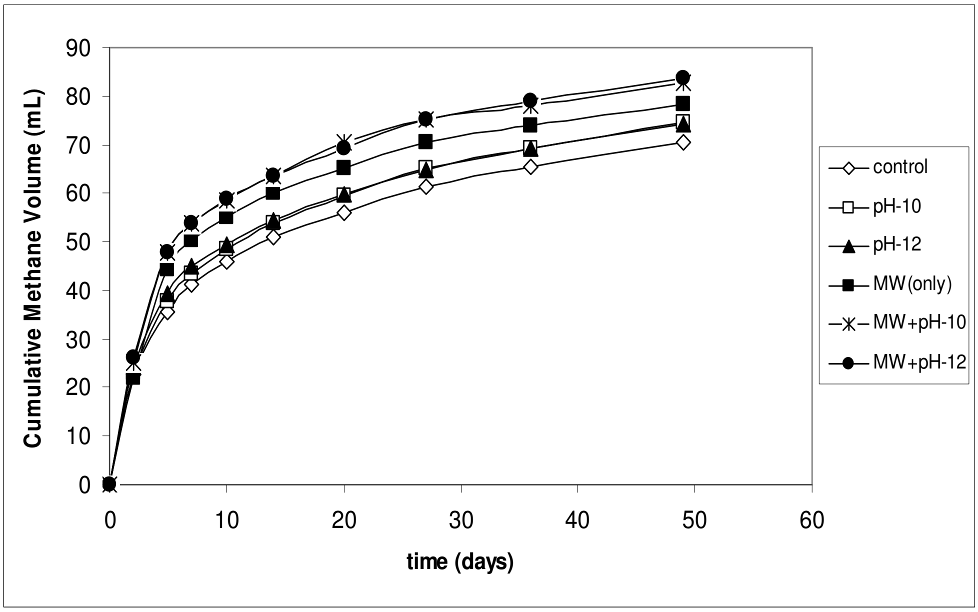

Figure 4. 10 Methane productions for control and pretreated WAS with time

In Table 4.1, cumulative methane yields of reactors at different times are given. As it is seen from the Table, lowest methane yield was achieved with the control reactor at all times. Among pretreatment methods, lowest yields were achieved with alkaline pretreatments, then followed MW pretreatment alone and the maximum yields were achieved with combined pretreatments. Although methane yields were similar for MW+pH-10 and MW+pH-12 pretreated WAS at 5th and 20th day, maximum yield was achieved with MW+pH-12 pretreated WAS at 49th day which was 46% higher than control.

Table 4. 1 Cumulative methane yield of batch reactors at different times

| **Reactor** | **Cumulative Methane Yield at times (L/g VSS loading)** | | |
|---|---|---|---|
| | **5 days** | **20 days** | **49 days** |
| **Control** | 0.069 | 0.108 | 0.135 |
| **pH-10** | 0.080 | 0.127 | 0.158 |
| **pH-12** | 0.087 | 0.131 | 0.163 |
| **MW (only)** | 0.099 | 0.146 | 0.176 |
| **MW+pH-10** | 0.111 | 0.163 | 0.190 |
| **MW+pH-12** | 0.112 | 0.162 | 0.197 |

Valo et. al. (2004) stated that added chemicals to thermal pretreatments limit the effect of pretreatment methods. On the contrary, it was not the case in this study. MW+pH-12 pretreatment led to 67.3% relatively more methane production than MW pretreatment alone.

After 49 day of a digestion period, gas productions ceased and anaerobic batch reactors were opened. MLSS, MLVSS, CST, Turbidity and SCOD of digested sludge were analyzed. Apart from analyzing the sludge quality, a preliminary assessment of sludge reduction was also aimed to be calculated from the results of this part of study.

After opening the reactors, pH of digested sludge for each reactor was 7.4±0.2 which was in the optimum range required for anaerobic digestion (Vesilind, 1979). Further analyses, conducted after anaerobic digestion, are given in the following sections.

### 4.5.3 MLSS and MLVSS Reductions

In Tables 4.2 and 4.3 initial and final MLSS and MLVSS values after anaerobic digestion of control and pretreated WAS are given.

As given in tables; at time 0, initial MLSS and MLVSS values of each pretreatment reactor were lower than that of control reactors and they were higher for alkaline pretreatments than MW (only) and combined pretreatments. These reductions implied that during pretreatment some fraction of the organic phase was solubilized and already oxidized before the anaerobic reactors were set. The very same sludge was divided into portions and put into pretreatment.

The one which did not go through pretreatment was called as control and control reactors were set using that. Others which went through different pretreatments, originally from the same sludge, were used to set the pretreated anaerobic reactors. Due to this fact, and the fact that no attempt was made to set MLSS and MLVSS values equal in all reactors at time zero, MLSS and MLVSS reductions of control and pretreatment reactors were calculated according to the initial MLSS and MLVSS values of control. The discussion below is based on this calculation. Therefore, one needs to keep in mind that the reductions include both the ones lost during pretreatment as well as during anaerobic digestion.

Lowest MLSS and MLVSS reductions were achieved with alkaline pretreatments whereas the highest reductions were achieved with MW pretreatment alone with 39% and 51.4% reductions in MLSS and MLVSS. For combined pretreatments the highest removals were recorded with MW+pH-12 pretreatment which reduced MLSS and MLVSS by 35.9% and 48.3%. These calculated reductions are taken as rough indicator of sludge quantity reduction.

Table 4. 2 Initial and final MLSS of control and pretreatment reactors

| | **MLSS initial (mg/L)** | **MLSS after digestion (mg/L)** | **% Reduction with respect to control at t=0** |
|---|---|---|---|
| Control | 8550 | 5885 | 31.16 |
| pH-10 | 7710 | 5715 | 33.15 |
| pH-12 | 7650 | 5670 | 33.68 |
| MW (only) | 7350 | 5215 | 39.00 |
| MW+pH-10 | 7180 | 5705 | 33.27 |
| MW+pH-12 | 7370 | 5485 | 35.85 |

Table 4. 3 Initial and final MLVSS of control and pretreatment reactors

| | **MLVSS initial (mg/L)** | **MLVSS after digestion (mg/L)** | **% Reduction with respect to control at t=0** |
|---|---|---|---|
| Control | 5190 | 3010 | 42.00 |
| pH-10 | 4690 | 2960 | 42.97 |
| pH-12 | 4540 | 2955 | 43.06 |
| MW (only) | 4440 | 2525 | 51.35 |
| MW+pH-10 | 4330 | 2830 | 45.47 |
| MW+pH-12 | 4260 | 2685 | 48.27 |

### 4.5.4 Soluble COD

SCOD of control and pretreated digested sludge are given in Figure 4.11. Except for pH-10, all pretreated digested sludge especially for combined pretreatments had a higher SCOD value than control. A maximum of about 24% increase was achieved in SCOD with the combined pretreatments. As Müller et. al. (2004) stated, the increase in SCOD in the effluent due to pretreatments is very minor when compared to the overall COD loading to the treatment plant. The higher efficiency reactor MW+pH-12 seemed to only increase soluble COD to about 320 mg/L whereas controls had it as 260 mg/L. This is thought to be not very significant.

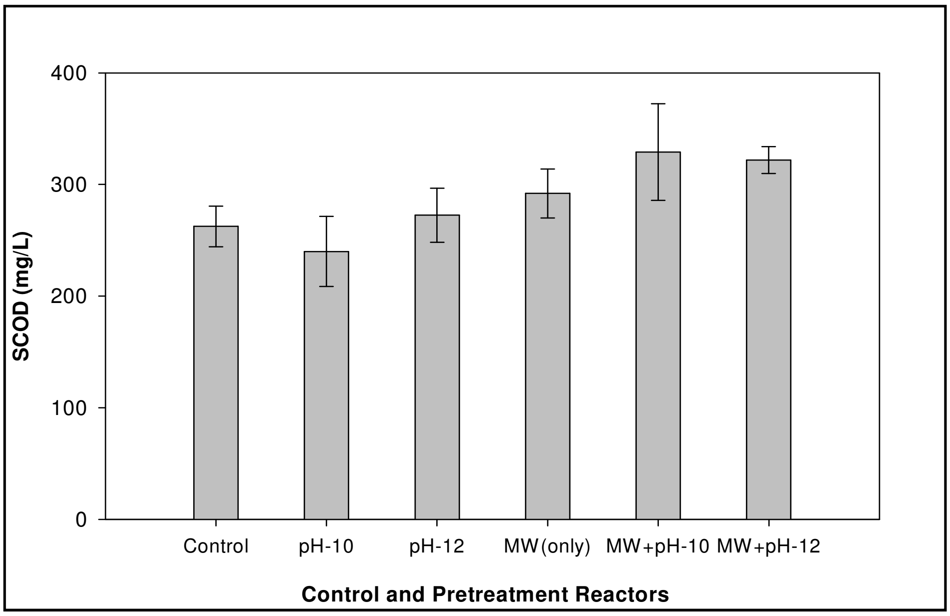

Figure 4. 11 SCOD of control and pretreated digested sludge

### 4.5.5 CST and Turbidity

Figure 4.12 represents CST and turbidity of all pretreated digested sludges. It was found that, MW (only) and MW+pH-12 pretreatments improved dewaterability. However other pretreatment methods had a higher CST value than control. But in general, there was not a large difference between the CST values of differently treated systems (Figure 4.11). Improvement of dewaterability with microwave pretreatment was also reported by Eskicioglu et. al. (2006b, 2008) and Pino-Jelcic et. al. (2006).

The highest turbidity was achieved with the combined pretreatments especially with MW+pH-12 pretreatment. This was an expected result because of the efficient disintegration of WAS before anaerobic digestion. For control turbidity was about 500 NTU where it was about 700 NTU for combined pretreatments.

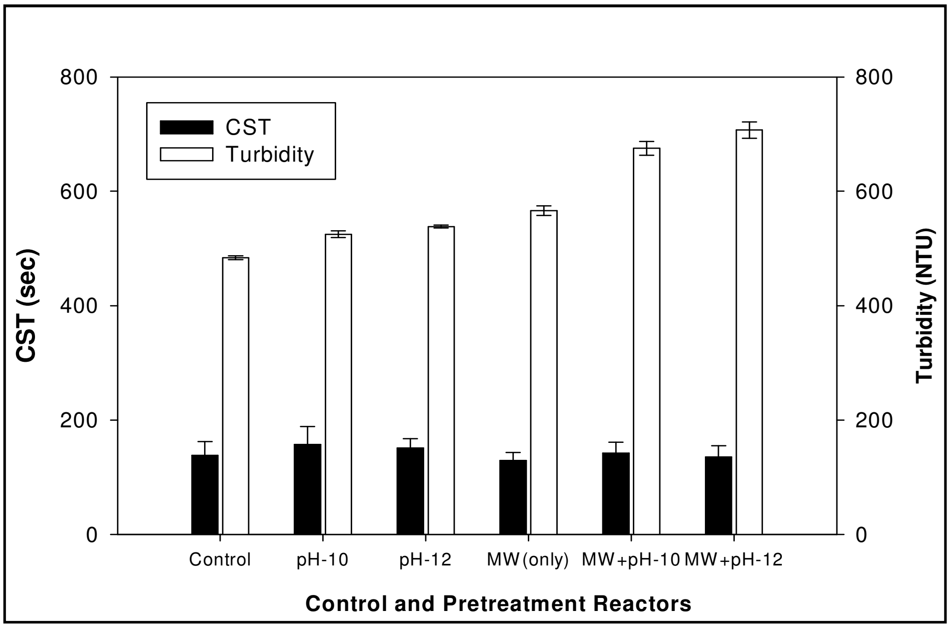

Figure 4. 12 CST and turbidity of control and pretreated digested sludge

The result of anaerobic batch reactors indicated that, the maximum gas and methane productions were achieved with MW+pH-12 pretreatment. Although the highest VSS removal efficiency was achieved with MW pretreatment alone, the removal efficiencies of MW (only) and MW+pH-12 were very close to each other. Moreover CST analyses indicated that MW+pH-12 improved dewaterability of digested sludge. Consequently, the final part of the study is designed to investigate the performance of MW+pH-12 as a pretreatment method in larger size anaerobically operated semi-continuous reactors.

## 4.6 Anaerobic Semi-Continuous Reactors

Anaerobic semi-continuous reactors were set up as explained in Section 3.4 and operated as detailed in Section 3.4.3.

With the experience gathered from the batch reactors, the semi-continuous reactors were set up at the same level of volatile solids both in control reactors and pretreatment reactors. Since the main target was to both increase the biogas as well as reduce the sludge as much as possible by pretreatment, volatile solids have been taken as reference and kept constant. In addition, the total COD of sludge fed to the digesters are also equal on a daily bases as shown in Table 3.10.

### 4.6.1 Daily Gas Production

Upon the set up of continuous reactors, one week acclimation period was provided. At the end of the acclimation period total gas productions were 2610, 2620, 3445 and 2995 mL for control-1, control-2, MW+pH-12-1 and MW+pH-12-2 reactors, respectively. After the 7th day during which no feeding was done, biogas productions of all reactors stopped. In accordance with 15 days SRT, 132 mL sludge was drained from the reactors and 132 mL of fresh sludge was added into each reactor and draining and feeding were started.

In Figure 4.13 daily biogas productions of control and pretreatment reactors are given. The graph represents the 92 day of daily gas production except the first week of acclimation period.

From Figure 4.13 it is seen that up to a certain time, there was a great variation in the daily gas productions of replicate reactors of each group. However in general trend, pretreatment reactors produced more gas than control reactors. At the day of 37, there occurred a sudden decrease in daily gas productions for each system (Figure 4.13). The reason is that the day before, there had been a power outage for one day in the Environmental Engineering Department of METU. Therefore in that day no draining and feeding was applied to reactors since reactors were not mixing and draining would not be homogenous. But after a period of time reactors became stable and after the day of 53, the daily gas productions of replicates did not fluctuate so much and the daily gas production of each reactor did not vary more than 10% and it was believed that steady state was achieved in all reactors.

Average daily gas productions of control and pretreatment reactors after steady state (after the day of 53) are given in Figure 4.14. After steady state, average daily gas productions were 248.4 mL/day for control and 356.4 mL/day for pretreatment reactors. Therefore by applying MW+pH-12 pretreatment before anaerobic digestion, a relative 43.5% improvement was achieved in daily gas production. Eskicioglu et. al. (2006b) achieved 30% more biogas production over control with MW-96°C pretreatment with the lowest HRT of 5 days. Park et. al. (2004) achieved about 25% more daily biogas production with MW-91.2°C pretreatment when HRT was 15 days. Therefore the result achieved in this study is in line with the results of previous work.

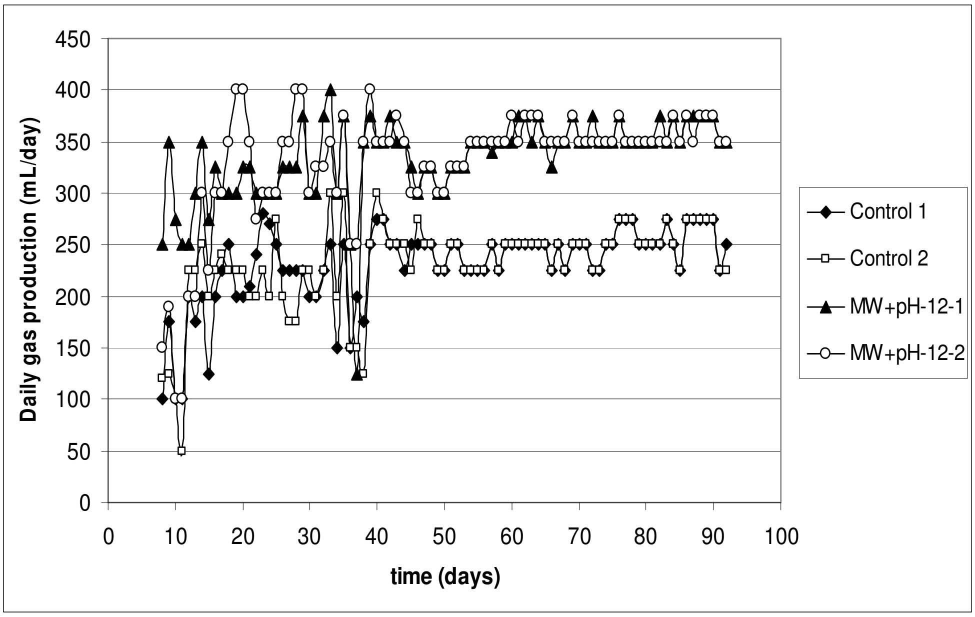

Figure 4. 13 Daily gas productions of control and pretreatment reactors

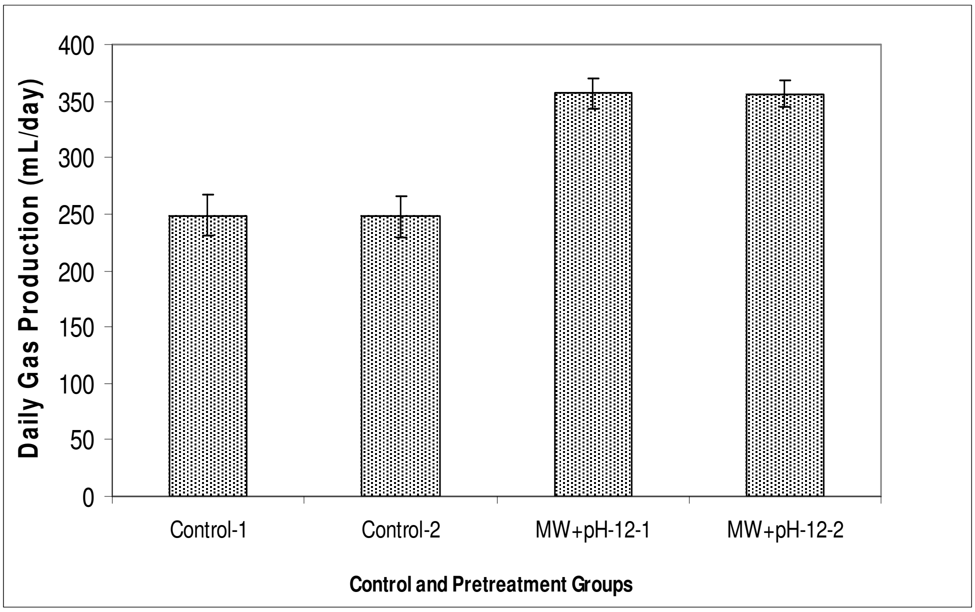

Figure 4. 14 Daily gas productions of control and pretreatment reactors after steady state

### 4.6.2 Daily Methane Production

Daily biogas production of each reactor after the day of 56 is given in Figure 4.15. As it is seen from the figure, daily methane productions of control reactors are identical however pretreatment reactors are not. The reason is that in early times of anaerobic semi-continuous reactor operation, during one of the feedings there had been air intrusion to pretreatment reactor-2 from its sampling port. Therefore the $N_2$ content of the reactor increased sharply. After air intrusion, methane content of this reactor increased as the progressed. However, methane content of pretreatment reactor-2 could not exactly reach the value of its identical reactor.

After steady state, average daily methane productions of controls were similar which were 144.53 and 142.45 L $CH_4$/ kg $VS_{in}$ for control-1 and control-2 reactors, respectively. Methane yield of MW+pH-12-1 reactor was 219.77 L $CH_4$/ kg $VS_{in}$, and 204.06 L $CH_4$/ kg $VS_{in}$ for MW+pH-12-2 reactor. Because of the air intrusion to pretreatment reactor-2, the methane yield improvement in pretreatment reactor-1 which was 53.2% is more reliable than that of pretreatment reactor-2. However, although there had been air intrusion to pretreatment reactor-2, the methane yield improvement of this reactor was 42.2%. After steady state average methane percents of the produced biogas were 58.5% for control reactors, 62.4% for pretreatment reactor-1 and 57.6% for pretreatment reactor-2. Methane contents of anaerobic semi-continuous reactors after steady state are given in Appendix C, Table C.3. When control reactors and pretreatment reactor-1 were compared, it is clear that MW+pH-12 pretreatment improves the methane content of produced biogas in anaerobic digesters. Similar results were reported by Park et. al. (2004). It was found that when SRT was 15 days microwave pretreated digested sludge methane content was higher that that of non-pretreated digested sludge.

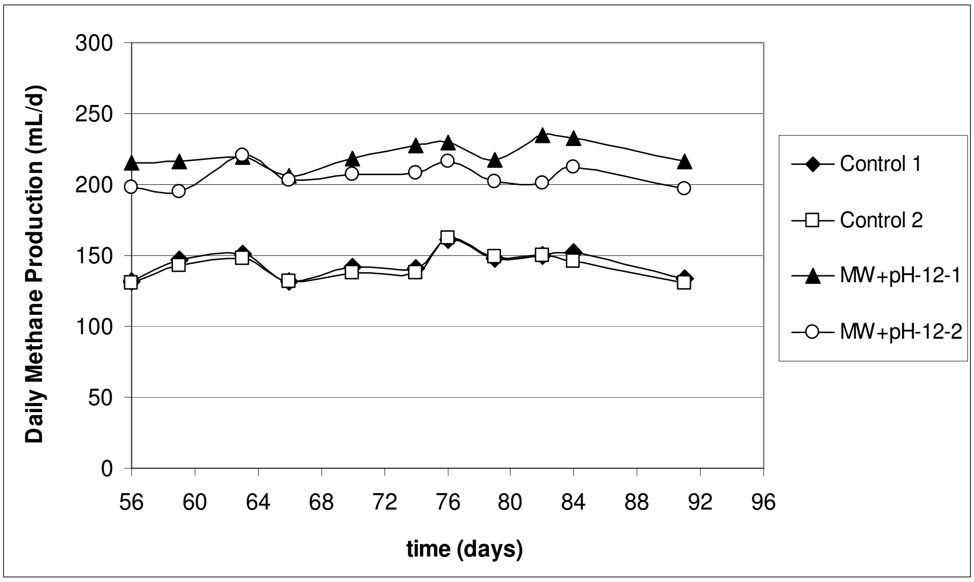

Figure 4. 15 Daily methane productions of control and pretreatment reactors

In terms of VS removal, control reactors had average methane production of 332.15 L $CH_4$/ kg $VS_{rm}$ and pretreatment reactor-1 had methane production of 373.76 L $CH_4$/ kg $VS_{rm}$. In the study of Park et. al. (2004), when SRT was 15 days, methane production was 242 and 314 L $CH_4$/ kg $VS_{rm}$ for control and pretreatment reactors, respectively.

### 4.6.3 pH

pH of the digested sludge were analyzed for all reactors from the drained digested sludge periodically. Digested sludge pH was about 7.5±0.3 for each reactor on the average which was in the optimum range required for anaerobic digestion (Figure 4.16).

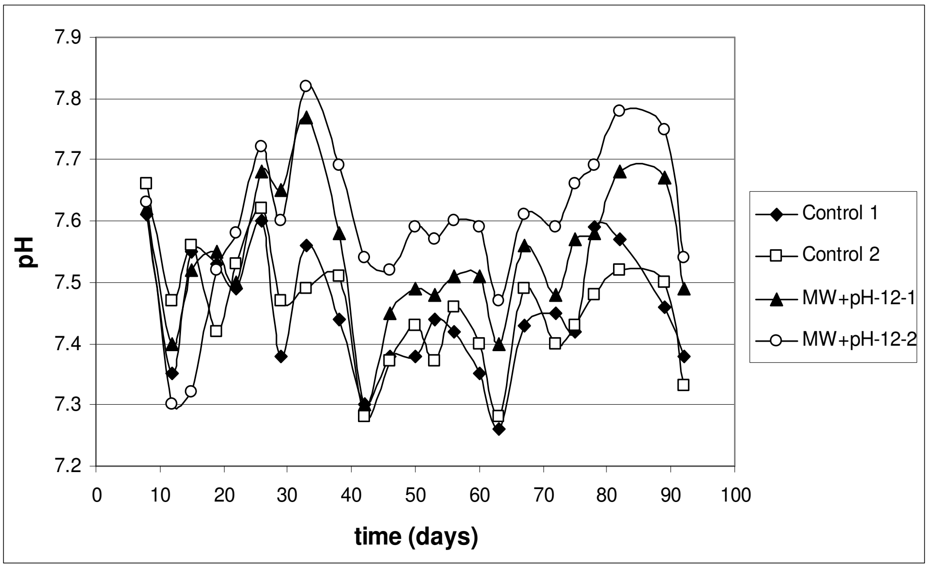

Figure 4. 16 pH of control and pretreatment reactors

### 4.6.4 TS Reductions

Effluent TS concentrations of each reactor were analyzed twice a week. From Figure 4.17, it is seen that TS concentrations of control and pretreatment reactors were approximately the same after steady state. Therefore, one might think that there is not much solids reduction difference between the control and pretreatment reactors. However, one should remember that the influent TS concentrations of pretreatment reactors were set as higher values that those of control reactors. Rather than TS, VS was taken as reference and reactors were fed at constant VS value. Therefore, this was a natural consequence of fixing the VS content of all reactors at the same level during feedings. For this reason, TS reduction achievement can be compared by using the initial and final TS values of each reactor separately. Effluent TS concentrations of each reactor after steady state are given in more details in Appendix D, Tables D.1 and D.2. This way, after steady state, average TS reduction was 35.7% and 44.6% for controls and the pretreatment reactors, respectively. Therefore an absolute 8.9% and a relative 24.9% more TS reduction was achieved with MW+pH-12. The improvement in TS reduction would be higher for lower SRT values. For example, Eskicioglu et. al. (2006b) achieved 29% more TS reduction with MW-96°C pretreated WAS when SRT was 5 days. The reason was that as SRT is reduced, organic loading to the reactors increase. As a result the hydrolysis step in the control reactors become more limited which affects the overall efficiency of anaerobic digestion.

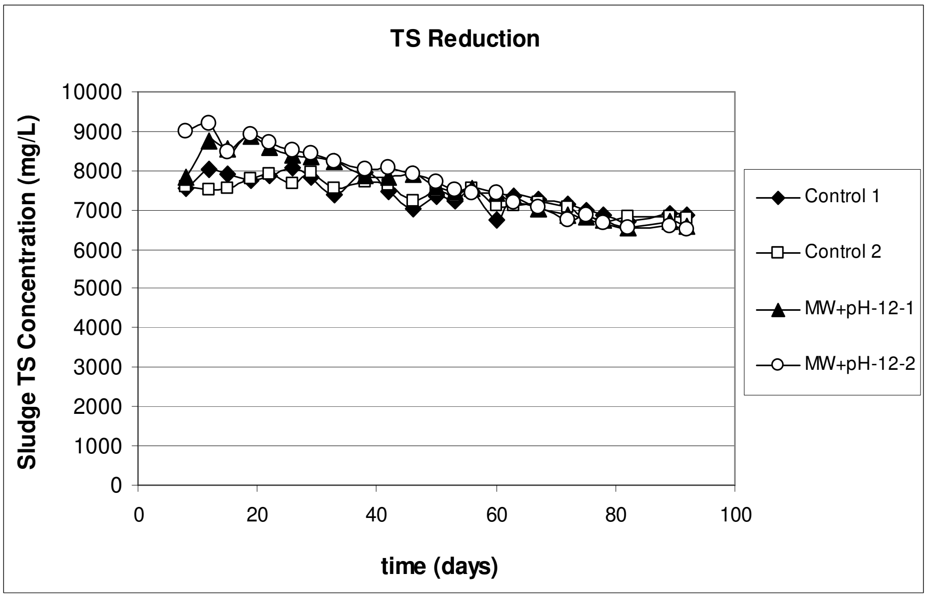

Figure 4. 17 Effluent TS concentrations of control and pretreatment reactors

### 4.6.5 VS Reductions

In Figure 4.18, effluent VS concentrations of all reactors are presented. After steady state effluent VS concentrations of the replicates did not vary more than 10%. Effluent VS concentrations of each reactor after steady state are given in

]

more details in Appendix D, Tables D.3 and D.4. It should be reminded that the same VS loading was applied to control and pretreatment reactors.

Chen et. al. (2007) citing to work of Parkin and Owen (1986) in which WAS led to 30-50% TCOD or VS degradation in 30 days if sludge is not appropriately solubilized. In this study, after steady state average VS reduction potential of control reactors was 43.2%, which is in the reported range. In the pretreatment reactors, average VS reduction was 58.5%. As a result by applying MW+pH-12 pretreatment, an absolute 15.3% and a relative improvement of 35.4% were achieved.

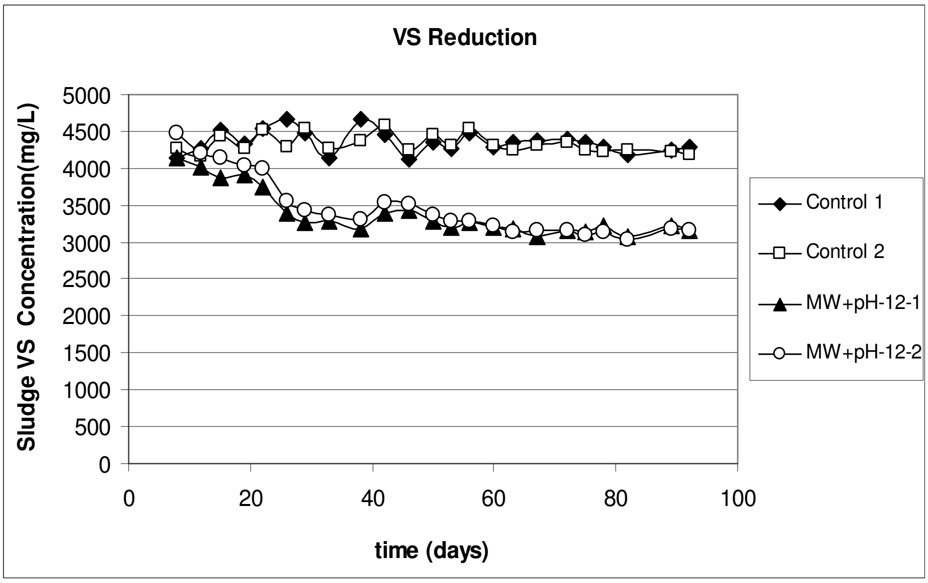

Figure 4. 18 Effluent VS concentrations of control and pretreatment reactors

For only microwave pretreatment at 96°C, Eskicioglu et al. (2006b) observed the maximum VS reduction with the lowest SRT of 5 days which was 23% higher than control. With the same sense, if SRT of the semi-continuous reactors in this study was lower than 15 days, then the relative improvement in VS reduction would be higher than 35.4%. A low improvement in VS reduction was reported by Park et. al. (2004) that MW-91.2°C pretreated sludge led to an improvement in VS reduction by 12.6% relatively when HRT was 15 days. Higher solids removal rates were reported by Navaneethan (2007) with ultrasonically pretreated WAS (190W, 45 seconds). 32.7% and 60.3% more TS and VS removals were reported with ultrasonically pretreated WAS compared to control WAS when SRT was 15 days.

### 4.6.6 TCOD Reductions

In Figure 4.19 effluent TCOD concentrations of each reactor are given. As it is seen from the figure, after steady state effluent TCOD concentrations did not vary more than 10% for each system. Considering the influent TCOD concentration of each reactor was approximately the same, more TCOD reduction was achieved with pretreatment reactors. Effluent TCOD concentrations of each reactor after steady state are given in more details in Appendix D, Tables D.5 and D.6. Average TCOD reductions were 44.1% and 57.6% for control and pretreatment reactors, respectively. As a result by applying a MW+pH-12 pretreatment, an absolute 13.5% and a relative 30.6% more TCOD reduction was achieved. For both control and pretreatment reactors, TCOD and VS reductions were in correlation which indicated the reliability of the observed results.

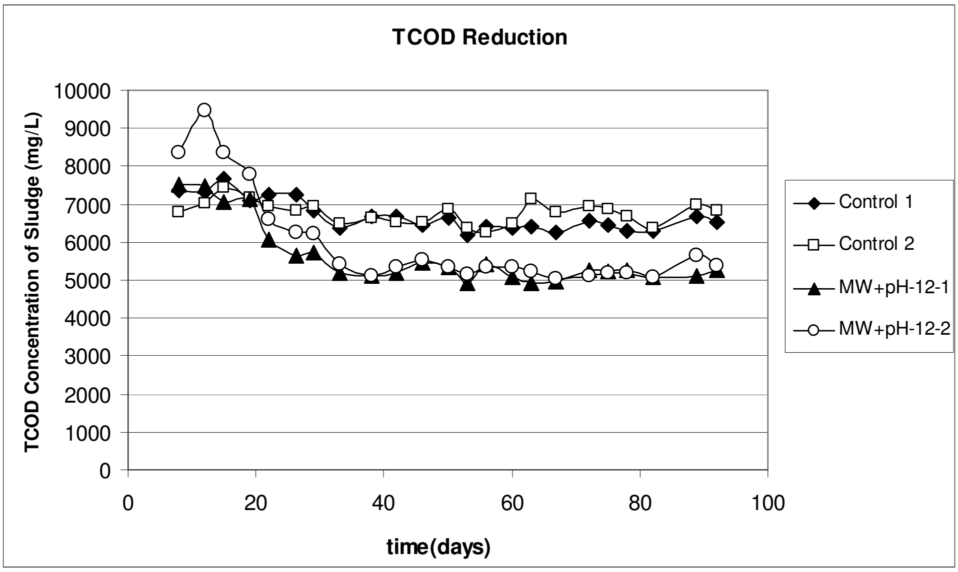

Figure 4. 19 Effluent TCOD concentrations of control and pretreatment reactors

Eskicioglu et. al. (2006b) achieved 16% improvement in TCOD reduction with MW-96°C pretreated WAS at the shortest SRT of 5 days. Tanaka and Kamiyama (2002) combined thermal and alkaline pretreatment (0.3 g NaOH/g VSS and autoclaving at 130°C for 5 minutes). It was found that COD removal efficiencies of the control reactor were 16, 31 and 38% with HRTs of 2, 6 and 8 days. On the other hand COD removal efficiencies were increased up to 33, 48 and 57% with the HRTs of 2, 6 and 8 days respectively.

De Franchi (2005) achieved the highest TCOD reductions in the anaerobic semi-continuous reactors that were fed with alkaline pretreated primary sludge and acidic pretreated WAS. Control reactors achieved about 38% and 45% TCOD reductions for SRTs of 10 and 20 days, respectively. However the pretreatment reactors achieved about 45% and 51% TCOD reductions for SRTs of 10 and 20 days. As a result about a relative improvement of 18% and 13% were achieved in TCOD reduction over control with the SRTs of 10 and 20 days, respectively.

### 4.6.7 MLSS and MLVSS Reductions

Sludge reduction potential of the digesters were estimated and compared according to the effluent TS and VS concentrations of drained digested sludges. But in addition to these, MLSS and MLVSS concentrations of digested sludges were analyzed as well. For both analyses, identical reactors followed the same trend (Figures 4.20 and 4.21). It was found that as VS concentrations, effluent MLSS and MLVSS concentrations of pretreated digested sludges were less than non-treated digested sludges. After steady state, 24.8% and 30.1% less MLSS and MLVSS concentrations were detected in the pretreated digested sludges compared to non-treated digested sludges

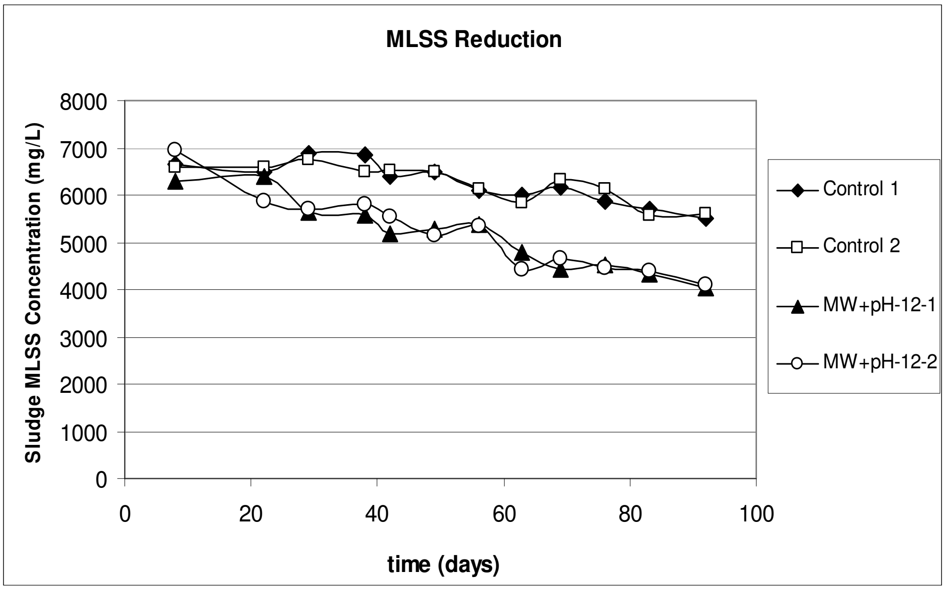

Figure 4. 20 Effluent MLSS concentrations of control and pretreatment reactors

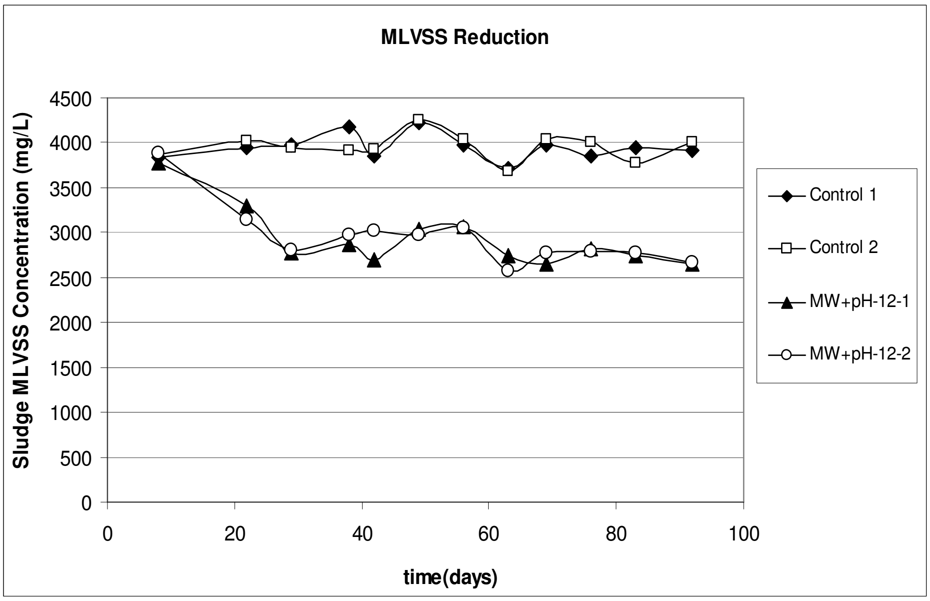

Figure 4. 21 Effluent MLVSS concentrations of control and pretreatment reactors

### 4.6.8 SCOD

In Figure 4.22, SCOD values of control and pretreatment reactors are given. As it is seen from the figure, early times of the anaerobic semi-continuous reactors, in some analyses extreme SCOD values were detected. The reason was investigated and it was found that an experimental error occurred because of the contamination originating from the filter apparatus to the filtrate while filtering the supernatant of digested sludge from 0.45 μm filter. Therefore all filter apparatus were soaked longer times in acidic water to completely remove the contamination from filter apparatus. This procedure was applied after each usage of the filter apparatus. In order to calculate the SCOD values of digested sludges of reactors, SCOD values analyzed after the day 72 were averaged since after that day, SCOD values of replicates varied less than the former data. SCOD values of digested sludge were 182.2±28.42 mg/L and 137.5±22.46 mg/L for control reactors 1 and 2, respectively and 258.1±30.13 mg/L and 303.3±58.55 mg/L for pretreatment reactors 1 and 2, respectively. As a result, about 76% increase in SCOD was achieved by applying a MW+pH-12 pretreatment.

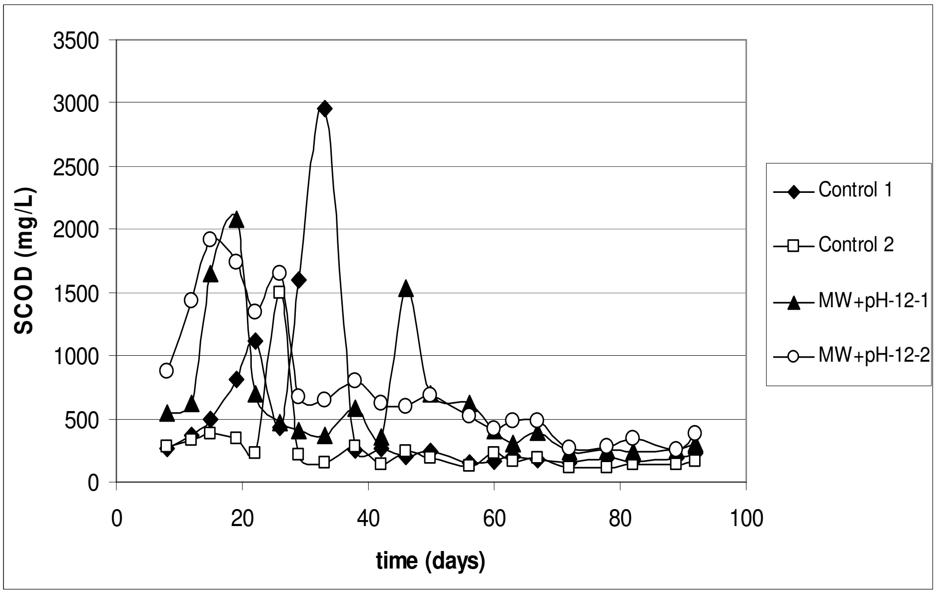

Figure 4. 22 SCOD concentrations of control and pretreatment anaerobic reactors

The increase in SCOD after anaerobic digestion with just microwave pretreatment was also reported by other researchers. Eskicioglu et. al. (2006b) stated that MW-96°C led to 5%, 29%, 80% increases in SCOD at SRTs of 20, 10 and 5 days. Park et. al. (2004) analyzed effluent SCOD of MW-91.2°C pretreated and non-treated digested sludge as 516 mg/L and 414 mg/L, respectively at SRT of 15 days.

The increase in SCOD after anaerobic digestion due to chemical pretreatment was also reported so far. De Franchi (2005) set anaerobic continuous reactors as a mixture of acidic pretreated primary sludge and alkaline pretreated WAS and also a mixture of alkaline pretreated primary sludge and acidic pretreated WAS.

SCOD concentrations of anaerobic reactors were about 1040 mg/L for control reactors and about 1350 mg/L for the pretreatment reactors when SRT was 10 days.

The usual practice is to return the digester supernatant to the head of the treatment plant in any plant involving anaerobic digestion. However, the further increase in SCOD in the effluent from the anaerobic digestion is a drawback of the pretreatment process. However as explained in anaerobic batch digesters, the increase in COD loading in the effluent will be minor in comparison to the overall wastewater load to the treatment plant. As a result there will not be an overloading problem in WWTP (Müller et. al., 2004).

### 4.6.9 CST

In Figure 4.23, CST of control and pretreatment reactors after steady state are given. Although there are variations of CST values for each analysis, on the average, pretreatment reactors had lower CST values than control reactors. After steady state, the average CST values of control 1 and control 2 reactors were 356.4 and 328.5 seconds. Pretreatment reactors had average CST values of 256.2 and 276.6 seconds. Although microwave pretreatment was combined with alkaline pretreatment which deteriorates dewaterability, as in the case of anaerobic batch digesters, dewaterability of digested sludge was improved by the combined method. By applying MW+pH-12 pretreatment, dewaterability was improved by 22%.

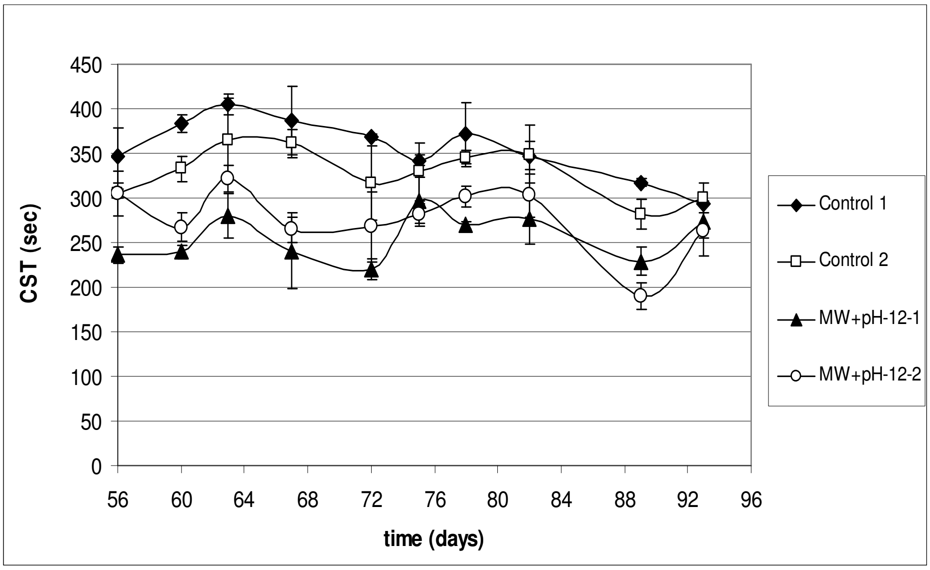

Figure 4. 23 CST of control and pretreatment reactors

Dewaterability improvement with just microwave application has been reported so far. Improvement of dewaterability with microwave as a conditioning method was reported by Wojciechowska (2005). For MW pretreatment alone Eskicioglu et. al. (2006b) stated that MW-96°C led to 39% improved dewaterability when SRT was 10 days. Pino-Jelcic et. al. (2006) also reported an 11.1±5.9% improvement in dewaterability with MW~65°C pretreatment after anaerobic digestion with mixed sludge at SRT of 25 days.

Reactors were shut down and opened at the end of 92 days and further analyses were conducted with anaerobically digested sludges. Supernatant turbidity, $NH_3$-N and $PO_4$-P concentrations and heavy metal concentrations of the digested sludge are given in the following sections.

### 4.6.10 Turbidity

In Figure 4.24 supernatant turbidity values of each reactor are given. As expected, turbidity values of the pretreated digested sludges were higher than control reactors. On the average pretreatment process increased the turbidity of effluent supernatant by 25.4%.

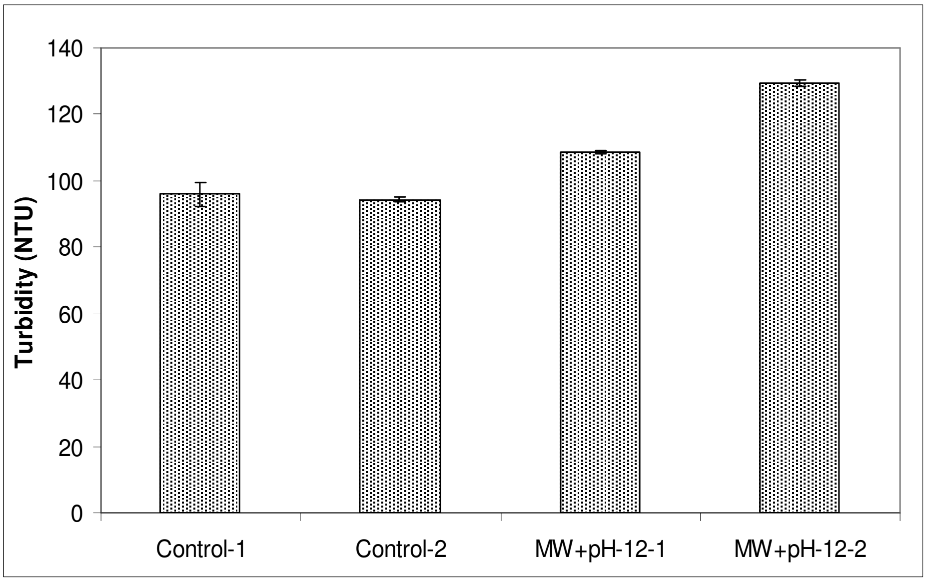

Figure 4. 24 Turbidity of control and pretreatment reactors

### 4.6.11 Supernatant $NH_3$-N

In Figure 4.25 supernatant $NH_3$-N concentrations of each reactor are given. As expected, because of the efficient disintegration of WAS before anaerobic digestion, $NH_3$-N concentration of pretreatment reactors were higher than control. $NH_3$-N concentrations were 330.4±48.2mg/L and 357.3±21.3 mg/L for the control 1 and 2 reactors, respectively and 412.2±17.9 mg/L and 465.4±17.3 mg/L for pretreatment reactors 1 and 2, respectively. Therefore MW+pH-12 pretreatment led to about 27.6% increase in supernatant $NH_3$-N concentration of digested sludge.

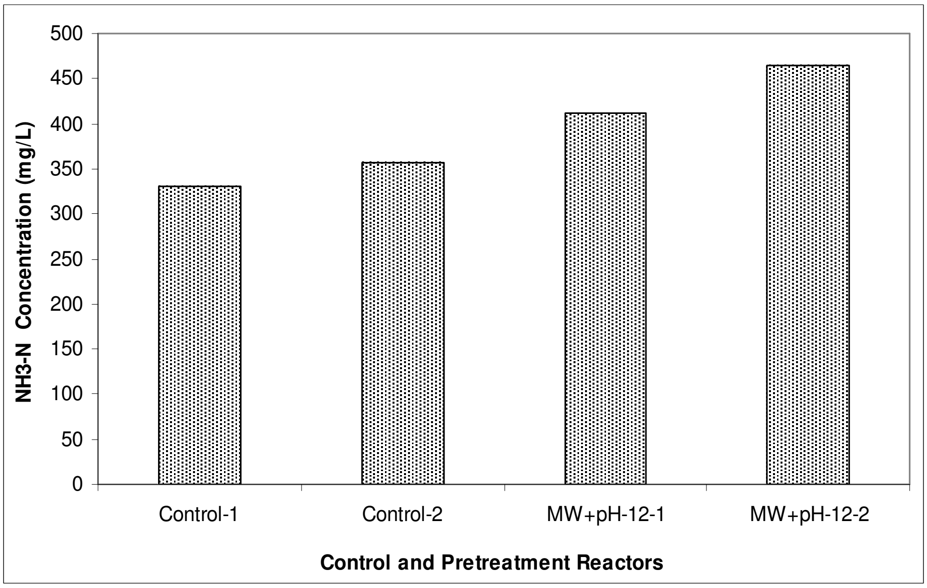

Figure 4. 25 Supernatant $NH_3$-N concentrations of control and pretreatment reactors

Park et. al. (2004) also observed an increased in $NH_4^+$ concentration in the effluent of MW-91.2°C pretreated digested sludge. $NH_4^+$ concentration was increased from 388 mg/L (control) to 461 mg/L HRT was 15 days. As a result about 19% increase in effluent $NH_4^+$ concentration which is similar to the result found in this study.

De Franchi (2005) examined effluent $NH_3$-N concentrations from anaerobic digester. Reactors fed with either alkaline or acidic pretreated WAS and primary sludge led to an increase in $NH_3$-N. When SRT was 10 days, average $NH_3$-N concentration of control reactors was about 1200 mg/L, where it was above 1320 mg/L for the pretreatment reactors. As a result 10% increase in $NH_3$-N concentration was achieved with the pretreatments. $NH_3$-N concentrations observed in the study of De Franchi (2005) are much higher than that of found in this study. However the behavior of pretreatment and control reactors were the same that pretreatment reactors had higher $NH_3$-N concentration.

### 4.6.12 Supernatant $PO_4$-P

Supernatant soluble $PO_4$-P concentrations of each reactor after digestion are given in Figure 4.26. According to the results, control and pretreatment reactors had approximately the same supernatant $PO_4$-P concentration. Control reactors average $PO_4$-P concentration was 29.4±0.2 mg/L and pretreatment reactors average $PO_4$-P concentration was 30.4±0.3 mg/L which was about 3.4% higher than control reactors. As a result no significant increase in effluent $PO_4$-P was observed. Müller et. al. (2004) also stated that pretreatment methods lead to inconsiderable increases in phosphorus concentrations. Park et. al. (2004) observed that $PO_4^{3-}$ concentration was increased from 28 mg/L to 35 mg/L with MW-91.2°C digested sludge when HRT was 15 days. Therefore the achieved results are in line with the previous work.

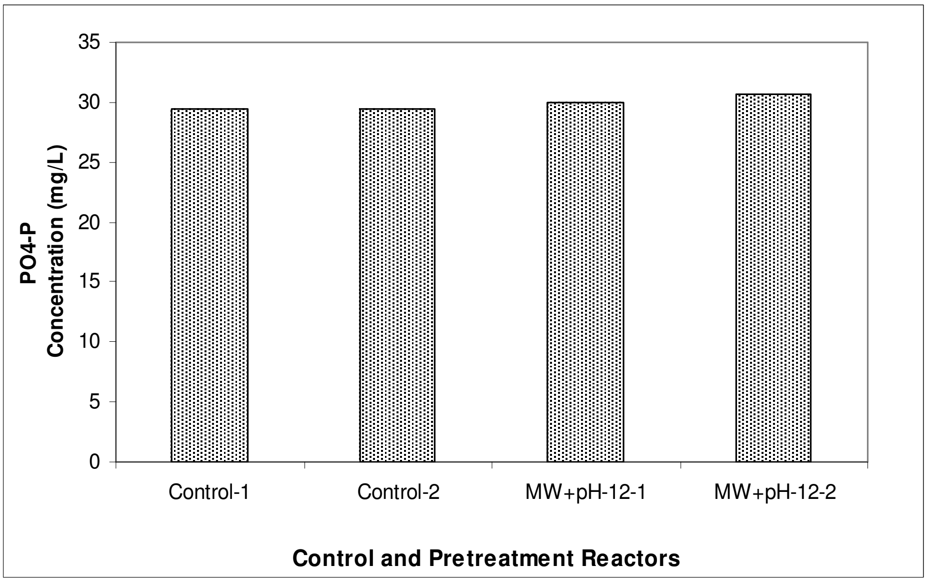

Figure 4. 26 Supernatant $PO_4$-P concentrations of control and pretreatment reactors

### 4.6.13 Soluble Carbohydrate- Protein

Soluble carbohydrate and protein concentrations of feed WAS and digested sludges are given in Figure 4.27. Calibration curves for glucose and protein are given in Appendix B, Figures B.3 and B.4. As it was found in the preliminary studies, MW+pH-12 pretreatment led to release of protein more than carbohydrate as represented in the feed pretreated WAS in Figure 4.27. Feed soluble carbohydrate and especially protein concentrations of pretreated WAS were higher than those of feed control WAS.

When effluent supernatant glucose and protein concentrations of control and pretreated digested sludges were analyzed, it was found that influent extreme concentrations of protein and high concentrations of carbohydrate were utilized and therefore decreased in pretreatment reactors. Effluent soluble carbohydrate and protein concentrations of pretreatment reactors were again higher than those of controls. On the other hand large differences between feed concentrations were reduced because of the effective utilization of soluble materials in pretreatment reactors. On the contrary, it was observed that effluent carbohydrate and protein concentrations of control reactors were higher than the concentrations of feed WAS of control reactors. This can be explained by the hydrolysis of non-pretreated control WAS during anaerobic digestion. Average soluble carbohydrate and protein concentrations were 12.3 mg/L and 42.39 mg/L for control reactors and 35.9 mg/L and 133.15 mg/L for pretreatment reactors, respectively.

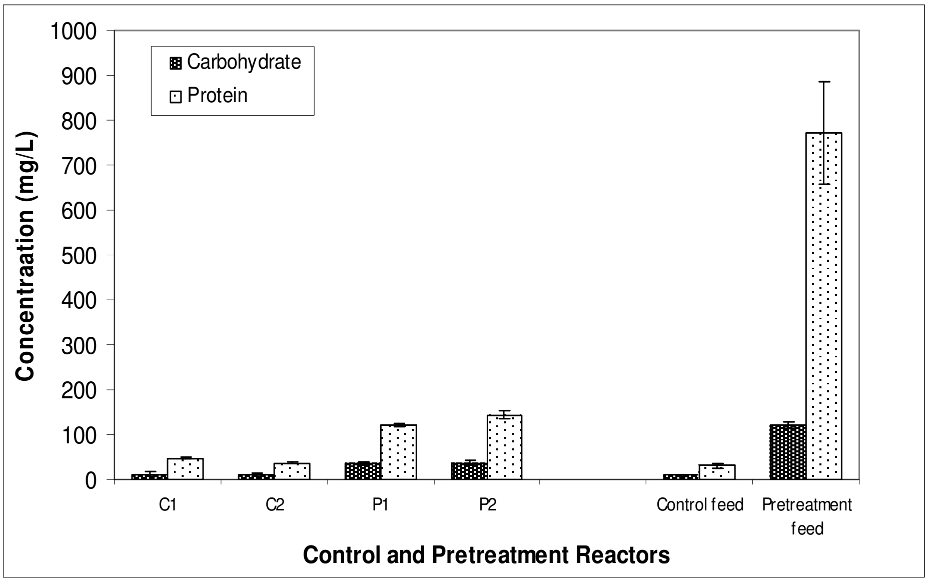

Figure 4. 27 Supernatant glucose and protein concentrations of control and pretreatment reactors

Wang et. al. (1999) examined supernatant protein and carbohydrate concentrations of the ultrasonically pretreated (200W, 30 minutes) and control WAS during anaerobic digestion periodically after ultra centrifuging. It was found that in the digestion time of 5 days, soluble carbohydrate and protein concentrations of control were about 75 and 200 mg/L and they were about 150 and 550 mg/L for ultrasonically pretreated digested sludge, respectively. As a result, in pretreated digested WAS higher carbohydrate and proteins were detected as found in this study.

### 4.6.14 Heavy Metals

When the sludge goes through pretreatment, there is concern of heavy metals concentrating even more due to the total mass reduction happening. If this happens it may cause sludge to become unuseful for agricultural applications. For this purpose heavy metal concentrations after pretreatment and digestion were measured in the sludges.

In Figure 4.28 heavy metal concentrations of control and pretreatment reactors are given. Except Zinc, all heavy metal concentrations of the identical reactors were approximately the same.

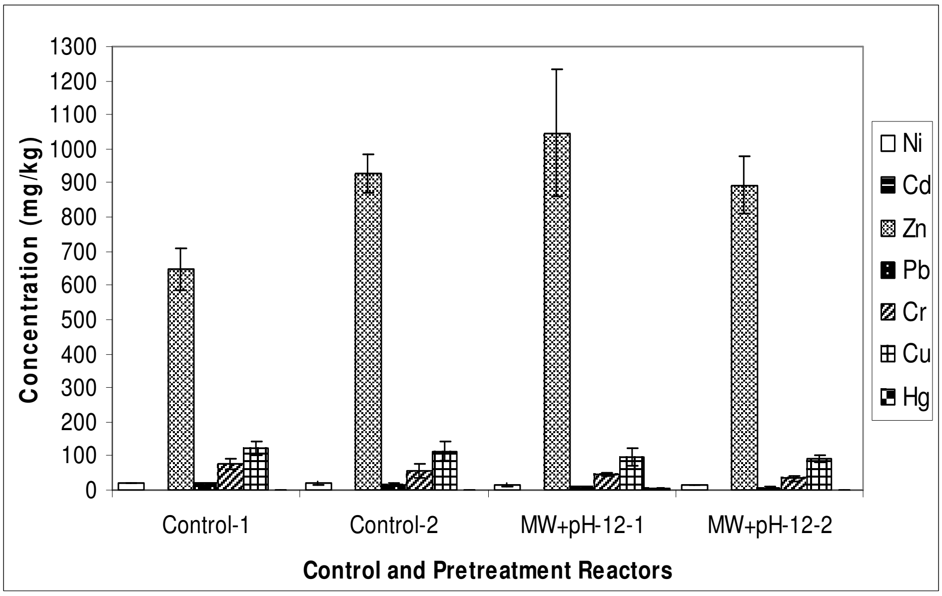

Figure 4. 28 Heavy metal concentrations of control and pretreatment reactors

Heavy metal concentrations of each reactor and maximum allowable concentrations of stabilized sludge that can be applied to the soil taken from the Soil Pollution Control Regulation are given in Appendix E, Table E.1. As a result of the heavy metal analysis, it was found that each heavy metal concentration of all reactors was lower than the limits given by the regulation.

Addition to the restricted heavy metals, calcium and magnesium concentrations of the control and pretreatment reactors were analyzed (Figure 4.29). It was found that calcium concentrations of the non-pretreated digested sludges were higher than pretreated digested sludge where magnesium concentrations of reactors were similar. Calcium and magnesium concentrations of control reactors were 11501 mg/kg and 2064.7 mg/kg, respectively and for pretreatment reactors concentrations were 9916 mg/kg and 2239.7 mg/kg, respectively.

The concentration of calcium being known as the main flocculating cation decreases in the pretreated samples indicating that the floc structure is degraded and calcium ions are released during the organic solubilization process in pretreatment of sludge. Therefore much less calcium can be found bound to the solids after pretreatment and digestion. Mg on the other hand is pretty much unaffected by this whole process.

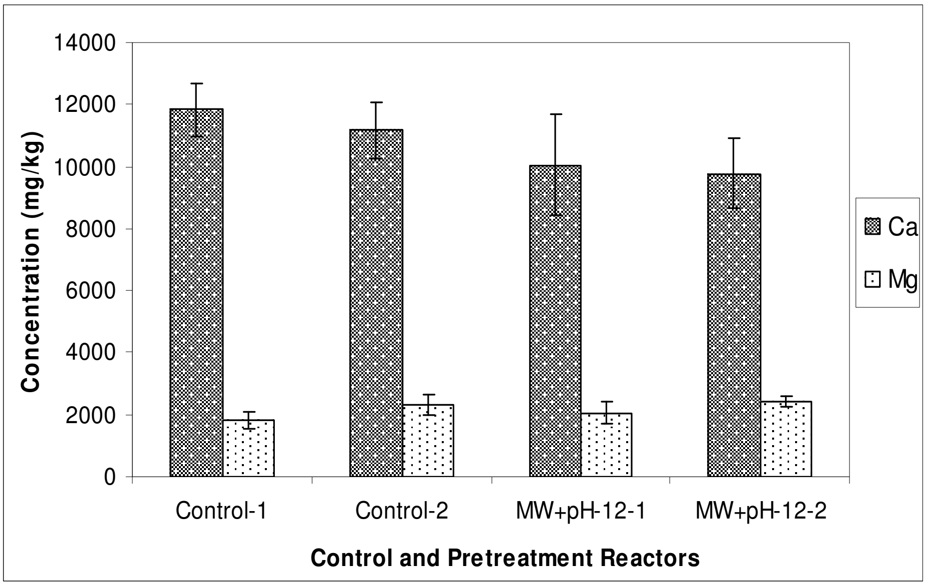

Figure 4. 29 Calcium and magnesium concentrations of control and pretreatment reactors

# CHAPTER 5

# COST CALCULATION

Cost calculation of combination of alkaline and microwave pretreatment unit was conducted by designing a fictitious WWTP. In the plant, there are 100 tons of dry primary and 100 tons of dry WAS production. In the sludge treatment flow scheme, WAS is put into alkaline pretreatment at pH 12 after thickening and then it is exposed to microwave irradiation. Finally thickened primary sludge and WAS are mixed in a volume ratio of 1:1 before anaerobic digestion and digested together.

## 5.1 Sludge Reduction Potential

Assumptions,

- Organic content of primary sludge is 65% and the degree of organic materials degradation of primary sludge in anaerobic digestion is 50% (Müller et. al., 2004 and information given by Ankara Central WWTP).

- Organic content of raw WAS is 75% (which was the case for WAS of Ankara Central WWTP) and the degree of organic materials degradation of WAS in anaerobic digestion is 43.2% which was the case for control anaerobic semi-continuous reactors that were conducted in this study.

- In the studies it was found that MW+pH-12 pretreatment reduced the organic content of WAS before anaerobic digestion from a value of 75% of organic material to a value of about 65% and then a further reduction is obtained in anaerobic digestion. However in the cost analysis instead of calculating the organic reduction of pretreated WAS in two steps, cost is calculated in one step and it is assumed that organic content of pretreated WAS is still 75% and the degree of organic materials degradation of pretreated WAS in anaerobic digestion is 58.5% which was the case for pretreatment anaerobic semi-continuous reactors that were conducted in this study.

***Without Pretreatment***

| **Primary Sludge** | **WAS** |
|---|---|
| 100 tons DS/day | 100 tons DS/day |
| ↓ 65% organic | ↓ 75% organic |
| 65 tons DS/day organic | 75 tons DS/day organic |
| ↓ 50% reduction | ↓ 43.2% reduction |
| 32.5 tons DS/day organic wasted | 42.6 tons DS/day organic wasted |
| + 35 tons DS/day inorganic wasted | + 25 tons DS/day inorganic wasted |
| 67.5 tons DS/day wasted | 67.6 tons DS/day wasted |

135.1 tons DS/day = 49,312 tons DS/year

*With Pretreatment*

| **Primary Sludge** | **WAS** |
|---|---|
| 100 tons DS/day | 100 tons DS/day |
| ↓ 65% organic | ↓ 75% organic |
| 65 tons DS/day organic | 75 tons DS/day organic |
| ↓ 50% reduction | ↓ 58.5% reduction |
| 32.5 tons DS/day organic wasted<br>+ 35 tons DS/day inorganic wasted | 31.13 tons DS/day organic wasted<br>+ 25 tons DS/day inorganic wasted |
| 67.5 tons DS/day wasted | 56.13 tons DS/day wasted |

123.63 tons DS/day = 45,125 tons DS/year

Therefore, each year 4187 tons DS will be less produced after anaerobic digestion which means 8.5% mass of sludge reduction in WWTP.

## 5.2 Reduction in the Transportation Cost

Assumptions

- In this study with MW+pH-12 pretreatment, improvement in dewaterability was achieved after anaerobic digestion. However in the cost analysis improvement in dewatering was not taken into consideration. The possibility of the increase in polymer demand (Müller et. al., 2004) was not considered as well. It is assumed that the final reduction in sludge mass after dewatering will be again 8.5%.

- After dewatering 540 tons of sludge (25% TS) is disposed from the WWTP daily without pretreatment.

- It is assumed that the landfill is 10 km far away from the WWTP. One truck has a capacity of 15 tons with its 350 L capacity of fuel oil tank. A truck with a full gas tank can travel 400 km. Cost of diesel fuel was taken as 3.2 YTL/L. It is assumed that 4 workers are responsible daily for the transportation of produced sludge and daily total cost of workers is 200 YTL/day. Values were decided according to the information given by Ankara Central WWTP.

***Without Pretreatment***

Since 540 tons of sludge should be disposed of daily, whole sludge can be transported with 36 trips to the landfill using one truck.

10 x 2 = 20 km distance, for one truck to go to the landfill and return back to the WWTP.

20 x 36 = 720 km, whole distance that one truck should take daily.

Since full capacity of the fuel oil tank is 350 L and truck can take 400 km distance;

For 720 km of distance $\frac{720\ km/d \times 350\ L}{400\ km} = 630$ L/day fuel oil is needed

Then daily fuel oil cost of truck will be,

630 L/day x 3.2 YTL/L = 2016 YTL/day

$$\underset{\text{Transport cost}}{\underset{\downarrow}{2016\ \text{YTL/day}}} + \underset{\text{Worker cost}}{\underset{\downarrow}{200\ \text{YTL/day}}} = 2216\ \text{YTL/day} = 808{,}840\ \text{YTL/year}$$

***With Pretreatment***

The reduction in the transportation cost due to pretreatment is assumed as 8.5% as in the reduction of the sludge mass.

As a result the savings in the transportation with MW+pH-12 pretreatment will be;

808,840 YTL/year x 0.085 = 68,751.4 YTL/year ≈ <u>69,000 YTL/year</u>

## 5.3 Reduction in Disposal Cost

Assumptions,

- Disposal cost of dried sludge to the landfill is 15-20 YTL/ton. (Information was given by MATAB (Manavgat Çevre Koruma Turizm Altyapı Tesisleri Yapma ve İşletme Birlikleri Başkanlığı)). Disposal cost of dried sludge was taken as 18 YTL/ton.

***Without Pretreatment***

540 ton/day x 18 YTL/ton = 9720 YTL/day = 3,547,800 YTL/year disposal cost of WWTP without pretreatment.

***With Pretreatment***

Disposal cost will be reduced by 8.5% with MW+pH-12 pretreatment as in the sludge mass and transport cost reductions.

As a result the savings in the transportation with pretreatment will be;

3,547,800 YTL/year x 0.085 = 301,563 YTL/year ≈ 302,000 YTL/year

## 5.4 Reduction in Energy Cost

Assumptions,

- Methane production potential of raw WAS is 143.49 L $CH_4$/kg VS which was found in the control anaerobic semi-continuous reactors. Methane production potential of pretreated WAS is 219.77 L $CH_4$/kg VS which was the methane potential of properly working anaerobic semi-continuous reactor that was fed with pretreated WAS.

- Methane production potential of primary sludge was assumed as 1.2 times of potential of raw WAS. (Gavala et. al. (2003) and Langhans and Hagenmeyer).

- It is assumed that without pretreatment, WWTP meets 80% of its energy demand including the operation of WWTP and the energy demands of the buildings of the plant and monthly electricity cost of the WWTP is 80,000 YTL/month. (The values were taken according to the information given by Ankara Central WWTP).

***Without Pretreatment***

Primary Sludge

Methane Prod. = 100 ton/day x $10^3$ kg/ton x 0.65 kg VS/kg x 172.19 L $CH_4$/kg VS x $10^{-3}$ $m^3$/L = 11,192.35 $m^3$ $CH_4$/day

Raw WAS

Methane Prod. = 100 ton/day x $10^3$ kg/ton x 0.75 kg VS/kg x 143.49 L $CH_4$/kg VS x $10^{-3}$ $m^3$/L = 10,761.75 $m^3$ $CH_4$/day

Total Methane Production = 11,192.35 $m^3$ $CH_4$/day + 10,761.75 $m^3$ $CH_4$/day
= 21,954.1 $m^3$ $CH_4$/day = 658,623 $m^3$ $CH_4$/month

If 658,623 $m^3$ $CH_4$/month meets 80% of electric demand of the WWTP then the total electricity demand of WWTP is,

658,623 $m^3$ $CH_4$/month x 100/80 = 823,278.75 $m^3$ $CH_4$/month

***With Pretreatment***

Primary Sludge

Methane Prod. = 100 ton/day x $10^3$ kg/ton x 0.65 kg VS/kg x 172.19 L $CH_4$/kg VS x $10^{-3}$ $m^3$/L = 11,192.35 $m^3$ $CH_4$/day

Pretreated WAS

Methane Prod. = 100 ton/day x $10^3$ kg/ton x 0.75 kg VS/kg x 219.77 L $CH_4$/kg VS x $10^{-3}$ $m^3$/L = 16,482.75 $m^3$ $CH_4$/day

Total Methane Production = 11,192.35 $m^3$ $CH_4$/day + 16,482.75 $m^3$ $CH_4$/day
= 27,675.10 $m^3$ $CH_4$/day = 830,253.00 $m^3$ $CH_4$/month

As a result WWTP can produce 830,253 $m^3$ $CH_4$/month which means that 100% electricity of WWTP will be met. Thus the profit in the electricity demand with MW+pH-12 pretreatment will be 80.000 YTL/month = 960,000 YTL/year

Moreover about 6974.25 $m^3$ $CH_4$/month is excess and can be used in the electricity demand of the microwave equipment. Since the calorific value of methane is 35.8kJ/L $CH_4$ (Bouallagui et. al., 2004). Then,

6.9 x $10^6$ L $CH_4$/month x 35.8 kJ/L $CH_4$ = 247.02 x $10^6$ kJ/month energy will be produced in excess.

As a result the total savings from the transport and disposal of sludge and from the electricity requirement of WWTP will be,

= 69,000 YTL/year + 302,000 YTL/year + 960,000 YTL/year
= 1,331,000 YTL/year

## 5.5 Alkaline Pretreatment

Alkaline pretreatment cost of the fictitious WWTP is calculated by referring to a full scale application of alkaline pretreatment as MicroSludge in Vancouver. In MicroSludge, alkaline pretreatment costs 6$/ton sludge in order to raise pH from 7 to 9. In this research in preliminary studies it was found that applied NaOH in order to make pH 12 is about 3 times of the dose applied for pH 10. Therefore the cost of alkaline pretreatment in fictitious WWTP was assumed as 20$/ton DS or 25YTL/ton DS. Since 100 tons dry solids of WAS should be alkaline pretreated,

100 ton/day x 25YTL/ton = 2500 YTL/day = 912,500 YTL/year

Cost of alkaline application storage tank was assumed as 500,000 YTL by assuming a concrete tank that has a capacity of 2000m$^3$ (Unit price of concrete and iron were taken from the official unit price website of Ministry of Public Works and Settlement).

## 5.6 Microwave Equipment

Assumptions,

- 100 tons of DS/day with a solid content of 5% produces 2000 m$^3$ of WAS/day that should be MW pretreated. According to the information given by microwave firms of Industrial Microwave Systems and AWI, power of the microwave equipment was selected as 400 kW (Industrial Microwave Systems and AWI Official Websites).

- Capital cost of the microwave equipments varies between 2000 and 5000$ per kilowatt of installed power (Techcommentary Industrial Microwave

Heating Applications, 1993). Moreover according to the capital cost range of microwave equipments given by the commissioners of microwave firms of Industrial Microwave Systems and AWI; capital cost of the microwave equipment was assumed as 1,000,000$. Including the installation cost of microwave equipment, the total cost was taken as 1,300,000 YTL.

- Maintenance, wearing and worker cost for the microwave equipment is assumed as 50,000 YTL/year (Techcomentary Industrial Microwave Heating Applications, 1993).

## 5.7 Microwave Energy Demand

Assumptions,

- It is assumed that microwave equipment works as a batch system that treats WAS every hour for 10 minutes with 400 kW. As a result MW equipment works 3 hours in a day (Values were decided according to the information and advices given by Industrial Microwave Systems and AWI.). Then,

400 kW / 3hr = 133.33 kWh = 4.79 x $10^5$ kJ daily energy requirement of microwave equipment.

It was found that with pretreatment there was 247.02 x $10^6$ kJ/month excess energy production which means 8.23 x $10^6$ kJ/day excess energy. As a result with the produced excess energy, the energy requirement of the microwave equipment is met so that there will not be an additional cost for the microwave energy requirement.

## 5.8 Neutralization of Pretreated WAS

In this study it was found that after microwave pretreatment pH of alkaline pretreated WAS was reduced from 12 to 10.2±0.2. Since the optimum pH conditions of anaerobic digestion is 6.4-7.5 (Vesilind, 1979), pH of pretreated WAS was reduced to 7.3±0.2 with HCl before anaerobic digestion. In a real WWTP again the neutralization becomes important; however studies have shown that up to feed pH of 9.5, anaerobic digestion is not negatively affected (MicroSludge System and Valo et. al. 2004). Moreover when pretreated WAS is combined with primary sludge before anaerobic digestion, dilution will also reduce the pH from 10 to lower values. As a result no neutralization would be required. However in any case cost of 25,000 YTL/year was assumed for neutralization of pretreated WAS with HCl. Cost of neutralization was decided according to the information given by Kimetsan Ltd. Marketing and Sailing Management, Ankara.

So, the total cost to the WWTP due to the addition of another unit which is combination of alkaline and microwave pretreatment will be,

912,500 YTL/year + 50,000 YTL/year + 25,000 YTL/year = 987,500 YTL/year
≈ 990,000 YTL/year

Since yearly savings of WWTP is 1,331,000 YTL/year,

Then net saving of WWTP will be 341,000 YTL/year.

Since alkaline pretreatment tank and microwave equipment cost for 1,800,000YTL; WWTP can break even and start profiting in 5.5 years after the construction of alkaline pretreatment tank and purchase of microwave equipment.

Other assumptions used in the cost calculation are,

- The cost analysis of MW+pH-12 pretreatment application in a WWTP was done as simple as possible. The main aim was to give an approximate year that a WWTP can move into profit. Therefore, for simplicity interest rate was not taken into consideration. It was assumed as the interest rate will affect the profits and losses with the same ratio.

- After microwave pretreatment of WAS the final temperature of the sludge will be higher than untreated WAS. When WAS is combined with primary sludge with 1:1 volume ratio, combined sludge temperature will again be higher than the no pretreatment case. As a result, the energy requirement for heating the sludge before mesophilic anaerobic digestion would be reduced as well. But this probability was not taken into consideration either.

- It was found that after anaerobic digestion COD and $NH_3$-N concentrations of pretreated digested sludge was higher than control. 76% increase in COD and 27.6% increase in supernatant $NH_3$-N were detected in this study. However when effluent is returned to the head of the WWTP, the effluent loading from anaerobic digestion will be very minor when compared to influent overall loading to WWTP. Thus cost factors are not considered (Müller et. al., 2004). Moreover, according to the information given by Ankara Central WWTP management, the plant can overcome that much of increases in the effluent from the anaerobic digestion when the effluent is returned to the head of the WWTP.

- According to literature, sterilization of WAS after MW irradiation (160°C) would lead to a destruction of pathogens. After anaerobic digestion of both primary and pretreated WAS, reduction in the pathogenic activity of digested sludge was expected. But since the pathogenic level of the digested sludge was not examined in this research, the probability of using digested sludge as a fertilizer was not considered too. If required standards are met, digested sludge can be used as a fertilizer which will neglect the transport and disposal cost of digested sludge in WWTP.

- The cost analysis was conducted for a fictitious WWTP that produced same amounts of primary and WAS. It should be reminded that since pretreatment is applied on WAS, savings of WWTP would be increased if WAS amount is higher than primary sludge. Since no pretreatment was applied on primary sludge, the amount of primary sludge reduction was unchanged in this example.

# CHAPTER 6

# SUMMARY AND CONCLUSIONS

The study tested the effectiveness of microwave pretreatment methods in combination with alkaline pretreatment for the first time in the literature. The experiments were conducted in three stages: preliminary work, anaerobic batch reactor studies and anaerobic semi-continuous reactor studies.

In the preliminary studies, the effect of alkaline doses, microwave irradiation at 160°C and the combination of alkaline and microwave pretreatments in terms of COD solubilization, turbidity and CST were studied. First the effect of solidified NaOH was investigated. Later on liquid form of NaOH was used for alkaline pretreatments in order to achieve the desired pH. For the selected pretreatment methods soluble carbohydrate and protein releases were also detected before anaerobic digestion. Observed results from conducted preliminary experiments are as follows:

- It was observed that doses higher than 0.35 g NaOH/ g VSS did not change the pH of pretreated WAS. It was found that among all alkaline doses and microwave pretreatment alone, the highest COD solubilization was achieved with the combination of MW with alkaline pretreatment.

- Experiments conducted with 2N NaOH in order to achieve the desired pH (10, 11, 12 and 12.5) have shown that as the pH of WAS was increased, activity of the microbial cells decreased since oxygen consumption rates were decreased. For MW-160°C pretreatment alone, no oxygen consumption in the system was detected which indicated that microwave pretreatment completely destroyed the activity of the cells. As a result, it was concluded that combination of alkaline and microwave pretreatment would also lead to zero microbial activity in the system.

- Experiments conducted for a larger range of alkaline pH, MW-160°C pretreatment, and combination of microwave and alkaline pretreatments showed that for alkaline pretreatment as pH increased COD solubilization and turbidity increased as well. With the increase in pH, deterioration in dewaterability was observed according to CST analyses. MW-160°C pretreatment COD solubilization showed the same behavior with pH-11 alkaline pretreatment, however because of the conditioning effect, better dewaterability of WAS was achieved after microwave pretreatment alone. As in previous studies combination of microwave with alkaline pretreatment led to further increases in COD solubilization as pH increased. Moreover it was found that deterioration of dewaterability due to alkaline pretreatments was improved when they were combined with microwave irradiation.

- For the pretreatments of pH-10, pH-12, MW (only), MW+pH-10 and MW+pH-12 soluble carbohydrate and protein releases were examined. It was found that as in the case of SCOD increases, MW+pH-12 led to maximum carbohydrate and protein releases compared to other pretreatment methods and the amount of protein release was higher than carbohydrate. This experiment also indicated that combined pretreatment, especially MW+pH-12, is more effective than individual pretreatments in terms of disintegrating the microbial cells.

After preliminary studies anaerobic small scale batch reactors were set for pH-10, pH-12, MW (only), MW+pH-10 and MW+pH-12 pretreated WAS in order to observe the biogas potentials of the pretreated sludges. After anaerobic digestion, qualities of digested sludges were also examined. Observed results from conducted experiments are as follows:

- Among the studied pretreatment methods, highest total gas and methane productions were achieved with the MW+pH-12 pretreated digested WAS with 16.3% and 18.9% improvements over control, respectively. In terms of SS and VSS reduction, the highest removal efficiency was achieved with MW (only) pretreatment however the removal efficiencies of MW (only) and MW+pH-12 pretreated digested sludges were very similar. In terms of dewaterability, it was observed that MW (only) and MW+pH-12 pretreated digested sludges had a better dewaterability property than untreated control sludges. Besides, as expected, after anaerobic digestion the highest SCOD and supernatant turbidity values were detected in the combined pretreated digested sludges.

According to the anaerobic batch digestions, the most effective pretreatment methods was found as MW+pH-12 in terms of more biogas and methane production, sludge minimization and dewaterability improvement. As a result MW+pH-12 pretreated sludge was digested in anaerobic semi-continuous reactors as a next step. Observed results from conducted experiments are as follows:

- MW+pH-12 pretreatment led to 43.5% and 53.2% more daily gas and methane productions compared to control systems. In terms of sludge minimization; TS, VS and TCOD reductions were improved by 24.9%, 35.4% and 30.6%, respectively. As it was found in the anaerobic batch reactors, MW+pH-12 pretreatment improved dewaterability of digested sludge where dewaterability was improved by 22%. Higher SCOD and $NH_3$-N concentrations were detected in effluent pretreated digested sludge; however, $PO_4$-P concentration did not vary so much. Increase in concentrations of effluent digested sludge is a drawback of MW+pH-12 pretreatment method. However since the effluent will be returned to the head of the WWTP, the increased loading in effluent will be minor when compared to the influent overall wastewater loading to the treatment plant. Experiments also indicated that pretreated and control digested sludges heavy metal concentrations were lower than the limits set by Soil Pollution Control Regulation.

- According to a simple cost analysis with on a fictitious WWTP, it was found that a WWTP can move into profit after 5.5 years. Since pretreatment is applied on WAS, if WAS production is dominated in treatment plants; the savings would be much higher.

With these findings it is concluded that MW pretreatment combined with alkaline pretreatment especially at pH-12 causes a very significant improvement of anaerobic digestibility of WAS and a major reduction in the quantity of sludge.

# CHAPTER 7

# RECOMMENDATIONS FOR FUTURE STUDY

The purpose of this study is to observe the sludge minimization potential and enhancement of biogas production by the combined alkaline and MW pretreatment techniques. Therefore, in the preliminary parts of this study, alkaline pretreatment was applied for constant durations without further attempts of optimizing the time of treatment. Moreover for microwave pretreatment a constant temperature profile and time was set. So therefore in further studies, the effect of time on the degree of sludge solubilization for the alkaline pretreatment can be investigated. For the microwave pretreatment, different durations and temperature profiles can be studied. Effect of increased sludge solids concentration can be tested. Since according to many earlier studies, high sludge concentrations can lead to more cost effective sludge disintegration.

In this study pathogenic microorganism level of digested sludge following pretreatment was not examined. In fact, after microwave irradiation of WAS at 160°C, complete sterilization was expected. In further studies, digested combined primary and pretreated WAS can be investigated in terms of pathogenic activity. Since if required standards are met, digested sludge can be used for land application which will eliminate transportation and disposal costs of digested sludge into landfill.

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# APPENDIX A

# TEMPERATURE PROFILE OF MICROWAVE IRRADIATION

Table A. 1 Program stages of microwave pretreatment

| Program Stages | Time (min) | Temperature (°C) | Power (W) |
|---|---|---|---|
| Stage 1 | 10 | 140 | 600 |
| Stage 2 | 5 | 170 | 600 |
| Stage 3 | 1 | 100 | 500 |

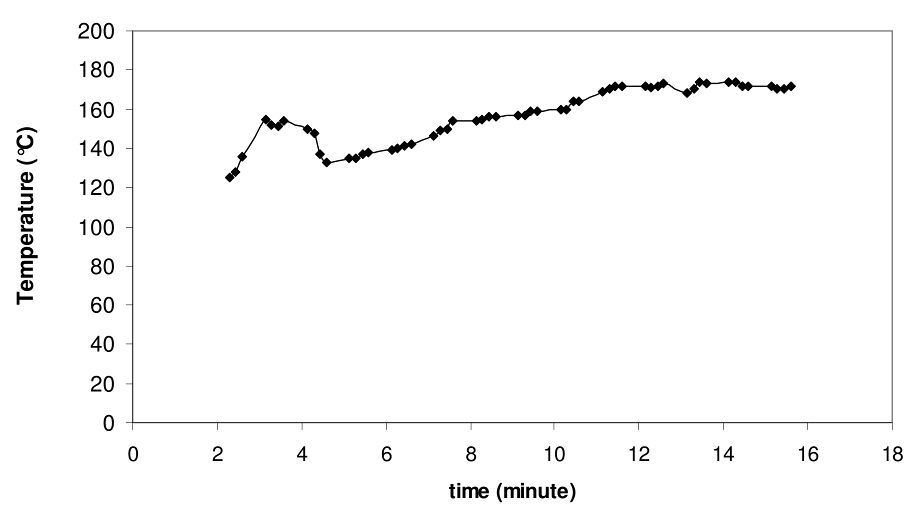

Figure A. 1 Temperature profile of microwave pretreatment

# APPENDIX B

# CALIBRATION CURVES

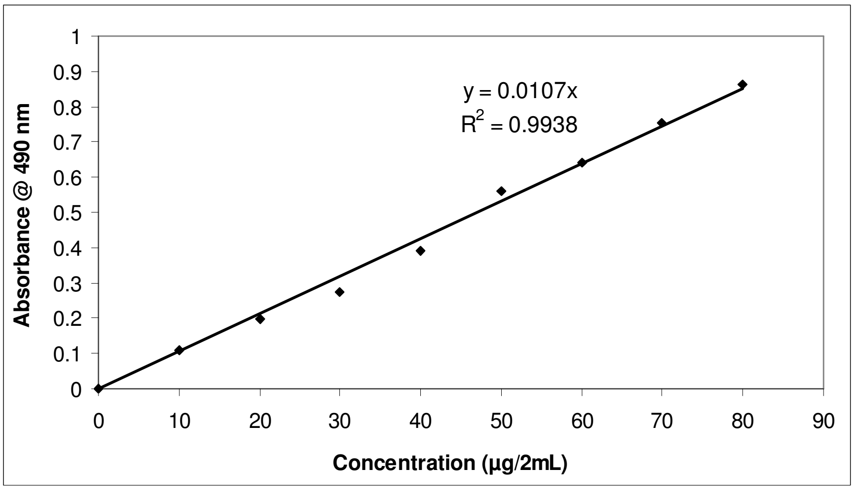

Figure B. 1 Carbohydrate calibration curve measured by Dubois method for preliminary studies

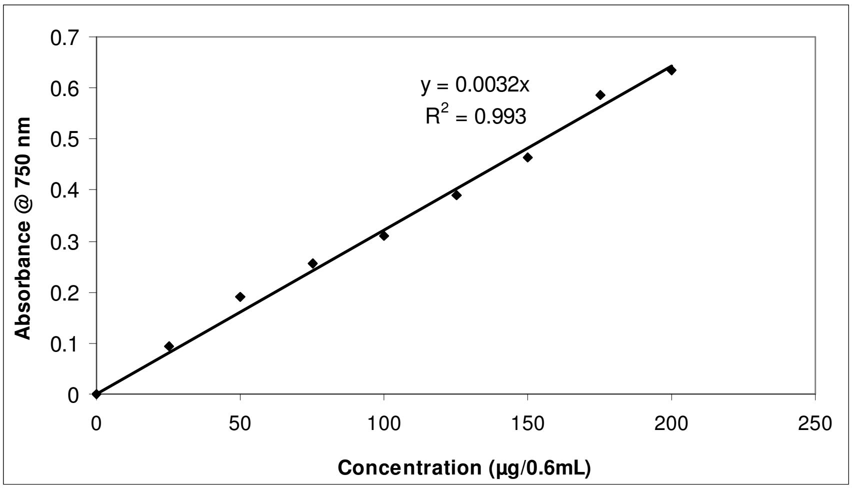

Figure B. 2 Protein calibration curve measured by Lowry method for preliminary studies

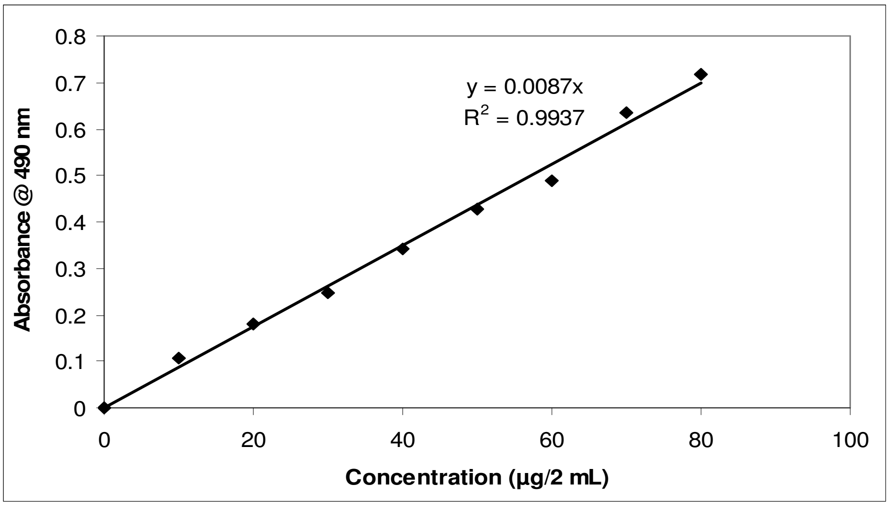

Figure B. 3 Carbohydrate calibration curve measured by Dubois method for anaerobic semi-continuous reactors

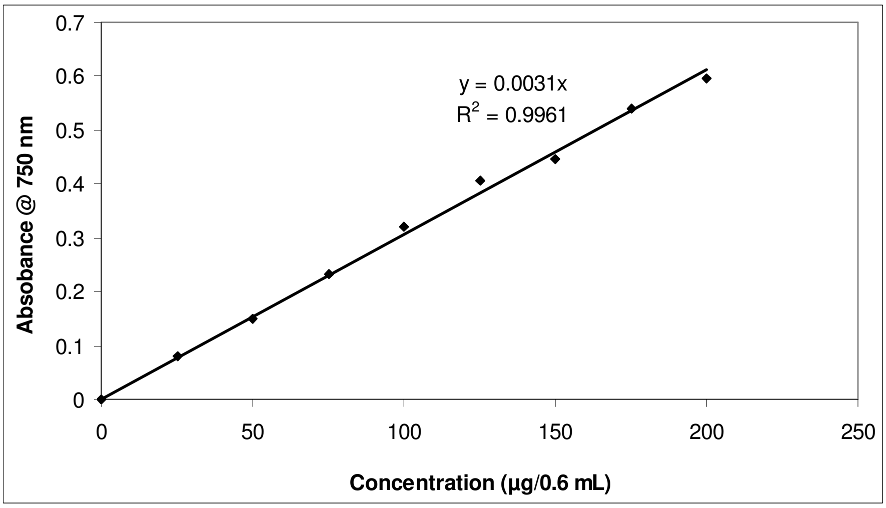

Figure B. 4 Protein calibration curve measured by Lowry method for anaerobic semi-continuous reactors

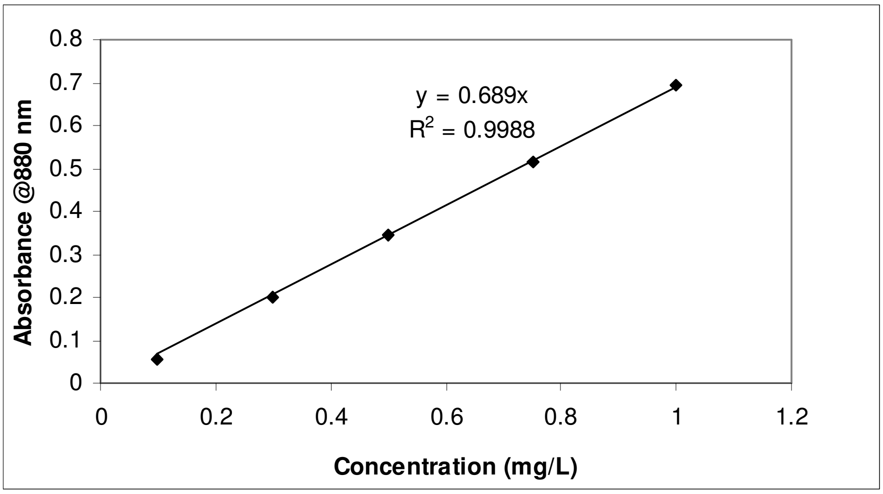

Figure B. 5 Calibration curve for soluble PO4-P analysis by persulfate method for anaerobic semi-continuous reactors

# APPENDIX C

# TOTAL GAS and METHANE PRODUCTIONS OF ANAEROBIC BATCH REACTORS and ANAEROBIC SEMI-CONTINUOUS REACTORS

Table C. 1 Total gas production of anaerobic batch reactors

| Day | Control Total Gas Production (mL) | Control Cumulative Total Gas Production (mL) | pH-10 Total Gas Production (mL) | pH-10 Cumulative Total Gas Production (mL) | pH-12 Total Gas Production (mL) | pH-12 Cumulative Total Gas Production (mL) | MW (only) Total Gas Production (mL) | MW (only) Cumulative Total Gas Production (mL) | MW+pH-10 Total Gas Production (mL) | MW+pH-10 Cumulative Total Gas Production (mL) | MW+pH-12 Total Gas Production (mL) | MW+pH-12 Cumulative Total Gas Production (mL) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **2** | 32.45<br>(1.202)* | 32.45 | 28.70<br>(5.545) | 28.70 | 32.50<br>(0.707) | 32.50 | 31.93<br>(1.514) | 31.93 | 32.55<br>(4.132) | 32.55 | 40.93<br>(1.709) | 40.93 |
| **5** | 24.40<br>(1.141) | 56.85 | 24.43<br>(1.721) | 53.13 | 28.80<br>(2.121) | 61.30 | 36.17<br>(1.209) | 68.10 | 36.60<br>(1.273) | 69.15 | 34.40<br>(1.273) | 75.33 |
| **7** | 12.15<br>(0.071) | 69.00 | 12.23<br>(0.833) | 65.37 | 12.33<br>(0.874) | 73.63 | 15.37<br>(0.493) | 83.47 | 12.97<br>(0.569) | 82.12 | 13.35<br>(0.354) | 88.68 |
| **10** | 7.55<br>(0.636) | 76.55 | 7.93<br>(0.379) | 73.30 | 7.20<br>(0.361) | 80.83 | 9.00<br>(0.173) | 92.47 | 7.90<br>(0.173) | 90.02 | 7.85<br>(0.071) | 96.53 |

*( ) Standard deviation

Table is continued on the next page.

Table C. 1 Total gas production of anaerobic batch reactors (Cont'd)

| Day | Control Total Gas Production (mL) | Control Cumulative Total Gas Production (mL) | pH-10 Total Gas Production (mL) | pH-10 Cumulative Total Gas Production (mL) | pH-12 Total Gas Production (mL) | pH-12 Cumulative Total Gas Production (mL) | MW (only) Total Gas Production (mL) | MW (only) Cumulative Total Gas Production (mL) | MW+pH-10 Total Gas Production (mL) | MW+pH-10 Cumulative Total Gas Production (mL) | MW+pH-12 Total Gas Production (mL) | MW+pH-12 Cumulative Total Gas Production (mL) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **14** | 9.55<br>(0.353)* | 86.10 | 9.73<br>(0.586) | 83.03 | 8.80<br>(0.305) | 89.63 | 8.20<br>(0.436) | 100.67 | 8.13<br>(0.153) | 98.15 | 7.63<br>(0.153) | 104.17 |
| **20** | 7.95<br>(0.212) | 94.05 | 9.33<br>(0.750) | 92.37 | 8.80<br>(0.608) | 98.43 | 8.40<br>(0.794) | 109.07 | 9.37<br>(0.321) | 107.52 | 10.13<br>(0.306) | 114.30 |
| **27** | 10.00<br>(1.131) | 104.05 | 10.73<br>(0.208) | 103.10 | 9.87<br>(0.814) | 108.30 | 10.10<br>(0.458) | 119.17 | 8.23<br>(0.404) | 115.75 | 10.60<br>(0.361) | 124.90 |
| **36** | 7.65<br>(0.212) | 111.70 | 7.60<br>(0.854) | 110.70 | 7.43<br>(0.513) | 115.73 | 6.57<br>(0.306) | 125.73 | 6.93<br>(0.451) | 122.68 | 7.63<br>(0.351) | 132.53 |
| **49** | 7.65<br>(0.495) | 119.35 | 7.97<br>(0.351) | 118.67 | 7.70<br>(0.173) | 123.43 | 6.37<br>(0.404) | 132.10 | 6.63<br>(0.351) | 129.32 | 6.27<br>(0.153) | 138.80 |

*( ) Standard deviation

Table C. 2 Methane content of anaerobic batch reactors

| **Day** | **Average Methane Content of Control Reactors** (%) | **Control Methane Production (mL)** | **Control Cumulative Methane Production (mL)** | **Average Methane Content of pH-10 Reactors** (%) | **pH-10 Methane Production (mL)** | **pH-10 Cumulative Methane Production (mL)** | **Average Methane Content of pH-12 Reactors** (%) | **pH-12 Methane Production (mL)** | **pH-12 Cumulative Methane Production (mL)** |
|---|---|---|---|---|---|---|---|---|---|
| **2** | 13.872 (0.439)* | 22.53 | 22.53 | 14.571 (1.026) | 23.12 | 23.12 | 14.868 (0.807) | 24.16 | 24.16 |
| **5** | 20.207 (0.126) | 13.17 | 35.70 | 21.775 (0.417) | 14.69 | 37.81 | 21.824 (0.754) | 15.33 | 39.49 |
| **7** | 22.267 (0.171) | 5.38 | 41.08 | 23.899 (0.444) | 5.68 | 43.49 | 23.791 (0.686) | 5.49 | 44.98 |
| **10** | 24.497 (0.236) | 4.75 | 45.83 | 26.126 (0.437) | 4.97 | 48.46 | 25.786 (0.751) | 4.45 | 49.43 |
| **14** | 26.524 (0.493) | 5.17 | 51.00 | 28.194 (0.502) | 5.43 | 53.90 | 27.674 (0.807) | 4.88 | 54.31 |
| **20** | 28.612 (0.403) | 4.99 | 55.99 | 30.380 (0.501) | 5.68 | 59.57 | 29.766 (0.824) | 5.34 | 59.65 |
| **27** | 30.371 (0.628) | 5.32 | 61.31 | 32.064 (0.458) | 5.63 | 65.20 | 31.408 (0.609) | 5.23 | 64.88 |
| **36** | 31.750 (0.615) | 4.21 | 65.52 | 33.328 (0.644) | 4.18 | 69.38 | 32.882 (0.606) | 4.36 | 69.24 |
| **49** | 33.503 (0.611) | 4.85 | 70.38 | 35.068 (0.510) | 5.06 | 74.43 | 34.610 (0.568) | 4.91 | 74.15 |

*( ) Standard deviation [Analysis was conducted 4 times for control, 6 times for the others]

Table is continued on the next page.

Table C. 2 Methane content of anaerobic batch reactors (Cont'd)

| **Day** | **Average Methane Content of MW(only) Reactors** (%) | **MW (only) Methane Production (mL)** | **MW (only) Cumulative Methane Production (mL)** | **Average Methane Content of MW+pH-10 Reactors** (%) | **MW+pH-10 Methane Production (mL)** | **MW+pH-10 Cumulative Methane Production (mL)** | **Average Methane Content of MW+pH-12 Reactors** (%) | **MW+pH-12 Methane Production (mL)** | **MW+pH-12 Cumulative Methane Production (mL)** |
|---|---|---|---|---|---|---|---|---|---|
| **2** | 13.601 (0.819) | 22.03 | 22.03 | 15.493 (0.908) | 25.18 | 25.18 | 15.335 (0.354) | 26.21 | 26.21 |
| **5** | 24.023 (0.528) | 22.24 | 44.26 | 25.724 (0.327) | 22.72 | 47.90 | 25.310 (0.238) | 21.67 | 47.89 |
| **7** | 26.041 (0.690) | 6.14 | 50.40 | 27.487 (0.320) | 5.86 | 53.75 | 27.069 (0.301) | 5.90 | 53.79 |
| **10** | 27.461 (0.685) | 4.75 | 55.15 | 29.454 (0.410) | 4.88 | 58.64 | 29.113 (0.475) | 4.94 | 58.73 |
| **14** | 29.316 (0.525) | 4.82 | 59.97 | 31.385 (0.278) | 5.06 | 63.70 | 30.920 (0.321) | 4.71 | 63.44 |
| **20** | 31.194 (0.615) | 5.06 | 65.03 | 32.384 (1.111) | 6.84 | 70.54 | 32.792 (0.340) | 5.76 | 69.20 |
| **27** | 32.911 (0.361) | 5.56 | 70.59 | 33.784 (0.348) | 4.60 | 75.14 | 34.500 (0.572) | 5.88 | 75.07 |
| **36** | 33.682 (0.469) | 3.21 | 73.80 | 34.709 (1.138) | 2.74 | 77.89 | 34.534 (0.709) | 3.76 | 78.84 |
| **49** | 35.426 (0.314) | 4.52 | 78.32 | 36.523 (0.646) | 4.77 | 82.65 | 36.537 (0.280) | 4.89 | 83.73 |

Table C. 3 Methane content of anaerobic semi-continuous reactors after steady state

| **Day** | **Control Reactor 1 Methane Content (%)*** | **Control Reactor 1 Total Gas Production (mL/d)** | **Control Reactor 1 Methane Production (mL/d)** | **Control Reactor 2 Methane Content (%)*** | **Control Reactor 2 Total Gas Production (mL/d)** | **Control Reactor 2 Methane Production (mL/d)** | **MW+pH-12 Reactor 1 Methane Content (%)*** | **MW+pH-12 Reactor 1 Total Gas Production (mL/d)** | **MW+pH-12 Reactor 1 Methane Production (mL/d)** | **MW+pH-12 Reactor 2 Methane Content (%)*** | **MW+pH-12 Reactor 2 Total Gas Production (mL/d)** | **MW+pH-12 Reactor 2 Methane Production (mL/d)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **56** | 58.50 | 225 | 131.62 | 57.98 | 225 | 130.45 | 61.40 | 350 | 214.89 | 56.51 | 350 | 197.78 |
| **59** | 58.58 | 250 | 146.44 | 57.03 | 250 | 142.59 | 61.78 | 350 | 216.23 | 55.71 | 350 | 194.99 |
| **63** | 60.56 | 250 | 151.40 | 59.25 | 250 | 148.12 | 62.74 | 350 | 219.59 | 58.68 | 375 | 220.03 |
| **66** | 58.65 | 225 | 131.97 | 58.73 | 225 | 132.14 | 63.30 | 325 | 205.71 | 57.91 | 350 | 202.68 |
| **70** | 56.60 | 250 | 141.51 | 55.26 | 250 | 138.15 | 62.50 | 350 | 218.74 | 59.28 | 350 | 207.50 |
| **74** | 56.37 | 250 | 140.92 | 55.21 | 250 | 138.02 | 65.05 | 350 | 227.67 | 59.48 | 350 | 208.19 |
| **76** | 58.55 | 275 | 161.02 | 58.97 | 275 | 162.18 | 61.16 | 375 | 229.33 | 57.66 | 375 | 216.23 |
| **79** | 59.33 | 250 | 148.32 | 59.73 | 250 | 149.31 | 62.07 | 350 | 217.26 | 57.79 | 350 | 202.27 |
| **82** | 60.14 | 250 | 150.35 | 59.81 | 250 | 149.52 | 62.65 | 375 | 234.92 | 57.44 | 350 | 201.03 |
| **84** | 60.95 | 250 | 152.37 | 58.30 | 250 | 145.75 | 62.01 | 375 | 232.54 | 56.49 | 375 | 211.84 |
| **91** | 59.53 | 225 | 133.95 | 58.11 | 225 | 130.74 | 61.95 | 350 | 216.83 | 56.34 | 350 | 197.18 |
| **Average** | 58.89 | 245.45 | 144.53 | 58.03 | 245.45 | 142.45 | 62.42 | 354.55 | 221.25 | 57.57 | 356.82 | 205.43 |
| **Std. deviation** | 1.46 | 15.08 | 9.44 | 1.60 | 15.08 | 9.77 | 1.07 | 15.08 | 8.79 | 1.24 | 11.68 | 8.10 |

* Average of two analysis

# APPENDIX D

# EFFLUENT QUALITY OF SEMI-CONTINUOUS ANAEROBIC REACTORS

Table D. 1 Effluent TS concentrations of control reactors

| Day | Effluent TS concentration of Control 1 (mg/L) | TS Reduction of Control 1* (%) | Effluent TS concentration of Control 2 (mg/L) | TS Reduction of Control 2* (%) |
|---|---|---|---|---|
| **53** | 7244 | 33.87 | 7340 | 32.99 |
| **56** | 7480 | 31.71 | 7548 | 31.09 |
| **60** | 6752 | 38.36 | 7120 | 35.00 |
| **63** | 7352 | 32.88 | 7116 | 35.04 |
| **67** | 7288 | 33.47 | 7208 | 34.20 |
| **72** | 7160 | 34.64 | 7052 | 35.62 |
| **75** | 7000 | 36.10 | 6768 | 38.21 |
| **78** | 6856 | 37.41 | 6724 | 38.62 |
| **82** | 6712 | 38.73 | 6810 | 37.83 |
| **89** | 6912 | 36.90 | 6835 | 37.60 |
| **92** | 6876 | 37.23 | 6792 | 38.00 |
| **Average** | 7057.45 | 35.57 | 7028.45 | 35.84 |
| **Std. deviation** | 259.69 | 2.37 | 267.85 | 2.45 |

**% reduction was calculated with respect to influent TS concentration of each control reactor which was 10954 mg/L on the average where standard deviation was 454.83. 53$^{nd}$ day is believed to be the start of steady state period.*

Table D. 2 Effluent TS concentrations of pretreatment reactors

| Day | Effluent TS concentration of Pretreatment 1 (mg/L) | TS Reduction of Pretreatment 1* (%) | Effluent TS concentration of Pretreatment 2 (mg/L) | TS Reduction of Pretreatment 2* (%) |
|---|---|---|---|---|
| **53** | 7452 | 40.85 | 7496 | 40.50 |
| **56** | 7548 | 40.09 | 7436 | 40.98 |
| **60** | 7425 | 41.07 | 7420 | 41.11 |
| **63** | 7336 | 41.77 | 7200 | 42.85 |
| **67** | 7044 | 44.09 | 7068 | 43.90 |
| **72** | 6868 | 45.49 | 6760 | 46.34 |
| **75** | 6808 | 45.96 | 6848 | 45.65 |
| **78** | 6744 | 46.47 | 6676 | 47.01 |
| **82** | 6540 | 48.09 | 6552 | 48.00 |
| **89** | 6688 | 46.92 | 6568 | 47.87 |
| **92** | 6594 | 47.66 | 6514 | 48.30 |
| **Average** | 7004.27 | 44.41 | 6958.00 | 44.77 |
| **Std. deviation** | 373.29 | 2.96 | 380.39 | 3.02 |

**% reduction was calculated with respect to influent TS concentrations of each pretreatment reactor which was 12598.90 mg/L on the average where standard deviation was 396.53. 53nd day is believed to be the start of steady state period.*

Table D. 3 Effluent VS concentrations of control reactors

| **Day** | **Effluent VS concentration of Control 1 (mg/L)** | **VS Reduction of Control 1* (%)** | **Effluent VS concentration of Control 2 (mg/L)** | **VS Reduction of Control 2* (%)** |
|---|---|---|---|---|
| **53** | 4272 | 43.61 | 4300 | 43.24 |
| **56** | 4472 | 40.97 | 4532 | 40.18 |
| **60** | 4280 | 43.50 | 4300 | 43.24 |
| **63** | 4356 | 42.50 | 4248 | 43.93 |
| **67** | 4368 | 42.34 | 4312 | 43.08 |
| **72** | 4392 | 42.03 | 4360 | 42.45 |
| **75** | 4344 | 42.66 | 4248 | 43.93 |
| **78** | 4288 | 43.40 | 4224 | 44.24 |
| **82** | 4185 | 44.76 | 4239 | 44.04 |
| **89** | 4239 | 44.04 | 4221 | 44.28 |
| **92** | 4281 | 43.49 | 4175 | 44.89 |
| **Average** | 4316.09 | 43.03 | 4287.18 | 43.41 |
| **Std. deviation** | 79.71 | 1.05 | 96.19 | 1.27 |

**% reduction was calculated with respect to influent VS concentrations of each control reactor which was 7575.68 mg/L on the average where standard deviation was 136.95. 53<sup></sup>*

Table D. 4 Effluent VS concentrations of pretreatment reactors

| **Day** | **Effluent VS concentration of Pretreatment 1 (mg/L)** | **VS Reduction of Pretreatment 1* (%)** | **Effluent VS concentration of Pretreatment 2 (mg/L)** | **VS Reduction of Pretreatment 2* (%)** |
|---|---|---|---|---|
| **53** | 3196 | 58.09 | 3276 | 57.04 |
| **56** | 3256 | 57.31 | 3276 | 57.04 |
| **60** | 3210 | 57.91 | 3224 | 57.73 |
| **63** | 3180 | 58.30 | 3148 | 58.72 |
| **67** | 3084 | 59.56 | 3156 | 58.62 |
| **72** | 3160 | 58.57 | 3164 | 58.51 |
| **75** | 3132 | 58.93 | 3092 | 59.46 |
| **78** | 3216 | 57.83 | 3148 | 58.72 |
| **82** | 3076 | 59.67 | 3040 | 60.14 |
| **89** | 3228 | 57.67 | 3172 | 58.41 |
| **92** | 3166 | 58.49 | 3158 | 58.59 |
| **Average** | 3173.09 | 58.39 | 3168.55 | 58.45 |
| **Std. deviation** | 57.39 | 0.75 | 70.50 | 0.92 |

**% reduction was calculated with respect to influent VS concentrations of each pretreatment reactor which was 7626.51 mg/L on the average where standard deviation was 123.22. 53<sup>nd</sup> day is believed to be the start of steady state period.*

Table D. 5 Effluent TCOD concentrations of control reactors

| **Day** | **Effluent TCOD concentration of Control 1 (mg/L)** | **TCOD Reduction of Control 1* (%)** | **Effluent TCOD concentration of Control 2 (mg/L)** | **TCOD Reduction of Control 2* (%)** |
|---|---|---|---|---|
| **53** | 6200 | 47.16 | 6360 | 45.80 |
| **56** | 6420 | 45.29 | 6250 | 46.73 |
| **60** | 6355 | 45.84 | 6500 | 44.60 |
| **63** | 6425 | 45.24 | 7150 | 39.06 |
| **67** | 6260 | 46.65 | 6790 | 42.13 |
| **72** | 6570 | 44.01 | 6960 | 40.68 |
| **75** | 6445 | 45.07 | 6885 | 41.32 |
| **78** | 6305 | 46.27 | 6695 | 42.94 |
| **82** | 6315 | 46.18 | 6375 | 45.67 |
| **89** | 6695 | 42.94 | 6980 | 40.51 |
| **92** | 6510 | 44.52 | 6813 | 41.94 |
| **Average** | 6409.09 | 45.38 | 6705.27 | 42.85 |
| **Std. deviation** | 144.24 | 1.23 | 294.46 | 2.51 |

**% reduction was calculated with respect to influent TCOD concentrations of each control reactor which was 11733.64 mg/L on the average where standard deviation was 655.93. 53<sup>nd</sup> day is believed to be the start of steady state period.*

Table D. 6 Effluent TCOD concentrations of pretreatment reactors

| Day | Effluent TCOD concentration of Pretreatment 1 (mg/L) | TCOD Reduction of Pretreatment 1* (%) | Effluent TCOD concentration of Pretreatment 2 (mg/L) | TCOD Reduction of Pretreatment 2* (%) |
|---|---|---|---|---|
| **53** | 4930 | 59.78 | 5135 | 58.10 |
| **56** | 5432 | 55.68 | 5325 | 56.55 |
| **60** | 5095 | 58.43 | 5325 | 56.55 |
| **63** | 4920 | 59.86 | 5235 | 57.29 |
| **67** | 4975 | 59.41 | 5030 | 58.96 |
| **72** | 5265 | 57.04 | 5120 | 58.23 |
| **75** | 5235 | 57.29 | 5175 | 57.78 |
| **78** | 5280 | 56.92 | 5190 | 57.65 |
| **82** | 5070 | 58.63 | 5085 | 58.51 |
| **89** | 5105 | 58.35 | 5645 | 53.94 |
| **92** | 5280 | 56.92 | 5388 | 56.04 |
| **Average** | 5144.27 | 58.03 | 5241.18 | 57.24 |
| **Std. deviation** | 166.37 | 1.36 | 173.40 | 1.41 |

**% reduction was calculated with respect to influent TCOD concentrations of each pretreatment reactor which was 12256.36 mg/L on the average where standard deviation was 595.72. 53$^{nd}$ day is believed to be the start of steady state period.*

# APPENDIX E

# HEAVY METAL CONCENTRATION LIMITS

Table E. 1 Heavy metal concentrations of control and pretreatment reactors and the limitations given by Soil Pollution Control Regulation

| | **Ni (mg/kg)** | **Cd (mg/kg)** | **Zn (mg/kg)** | **Pb (mg/kg)** | **Cr (mg/kg)** | **Cu (mg/kg)** | **Hg (mg/kg)** |
|---|---|---|---|---|---|---|---|
| C1 | 20.367 | 0 | 647.117 | 19.167 | 76.883 | 121.567 | 0.749 |
| C2 | 20.867 | 0 | 927.117 | 16.933 | 54.616 | 114.600 | 0.608 |
| P1 | 14.633 | 0 | 1047.117 | 7.767 | 45.516 | 95.800 | 3.623 |
| P2 | 14.467 | 0 | 893.783 | 6.967 | 33.450 | 92.030 | 1.728 |
| Limit | 400 | 40 | 4000 | 1200 | 1200 | 1750 | 25 |