MUNICIPAL SLUDGE MINIMIZATION: EVALUATION OF ULTRASONIC AND ACIDIC PRETREATMENT METHODS AND THEIR SUBSEQUENT EFFECTS ON ANAEROBIC DIGESTION

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ABSTRACT

MUNICIPAL SLUDGE MINIMIZATION: EVALUATION OF ULTRASONIC AND ACIDIC PRETREATMENT METHODS AND THEIR SUBSEQUENT EFFECTS ON ANAEROBIC DIGESTION

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Sludge management is one of the most difficult and expensive problems in wastewater treatment plant operation. Consequently, ‘sludge minimization’ concept arose to solve the excess sludge production by sludge pretreatment.

Sludge pretreatment converts the waste sludge into a more bioavailable substrate for anaerobic digestion and leads to an enhanced degradation. The enhanced degradation results in more organic reduction and more biogas production. Therefore, sludge pretreatment is a means of improving sludge management in a treatment plant.

Among pretreatment methods, acidic pretreatment has been subject of limited successful studies reported in the literature. On the contrary; ultrasonic pretreatment was reported as an effective pretreatment method. Main objective of this study was to investigate the effects of these two pretreatment methods and their combination in order to achieve a synergistic effect and improve the success of both pretreatment methods.

Experimental investigation of pretreatment methods consists of preliminary studies for deciding the most appropriate pretreatment method. Anaerobic batch tests were conducted for optimization of the parameters of selected method. Finally, operation of semi-continuous anaerobic reactors was to investigate the effect of pretreatment on anaerobic digestion in details.

Preliminary studies indicated that, more effective pretreatment method in terms of solubilization of organics is ultrasonic pretreatment. Fifteen minutes of sonication enhanced 50 mg/L initial soluble COD concentration up to a value of 2500 mg/L. Biochemical methane potential tests indicated that the increased soluble substrate improved anaerobic biodegradability concurrently. Finally, semi-continuous anaerobic reactors were used to investigate the efficiency of pretreatment under different operating conditions.

Results indicate that at SRT 15 days and OLR 0.5 kg/m^3d ultrasonic pretreatment improved the daily biogas production of anaerobic digester by 49% and methane percentage by 16% and 24% more volatile solids were removed after pretreatment. Moreover, even after pushing reactors into worse operating conditions such as shorter solids retention time (7.5 days) and low strength influent, pretreatment worked efficiently and improved the anaerobic digestion.

Finally cost calculations were performed. Considering the gatherings from enhancement of biogas amount, higher methane percentage and smaller amounts of volatile solid disposal from a treatment plant; installation and operation costs of ultrasound were calculated. The payback period of the installation was found to be 4.7 years.

Key words: acidic pretreatment, sludge minimization, ultrasound, ultrasonic pretreatment

ÖZ

ARITMA ÇAMURU MİNİMİZASYONU: ULTRASONİK VE ASİDİK ÖNARITIM METOTLARININ DEĞERLENDİRİLMESİ VE ANAEROBİK ÖZÜMLEME ÜZERİNE ETKİLERİ

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Çamur, arıtma tesisi işletmesindeki en zor ve en pahalı problemlerden birisidir. Sonuç olarak da, oldukça fazla miktarda üretilen çamur sorununu çözmek için “çamur minimizasyonu” konseptini doğmuştur.

Çamur önarıtımı, atık çamuru biyolojik olarak daha kolay sentezlenebilecek bir substrata çevirerek havasız çürütmedeki bozunmayı hızlandırır. Hızlandırılmış bozunma daha fazla organik indirgenmesine ve daha fazla biyogaz üretimine sebep olur, bu yüzden de çamur önarıtımı arıtma tesislerindeki çamur yönetimini geliştiren bir modifikasyon olarak çalışır.

Önarıtım metotları arasında asidik önarıtım ile sınırlı sayıda başarılı çalışma rapor edilmiş, aksine ultrasonik önarıtım da verimli bir önarıtım metodu olarak rapor edilmiştir. Bu çalışmanın asıl amacı; bu iki önarıtım metodunun ve bunların birleşimlerinin, her iki metodu da iyileştirecek olası sinerjik etkilerinin incelemesidir.

Önarıtım metodlarının deneysel olarak incelenmesi; en uygun önarıtım metodunun seçilmesi için ön çalışmalar, seçilen en uygun metodun parametrelerinin optimizasyonu için havasız kesikli reaktör denemeleri ve son olarak da, yarı-sürekli havasız reaktörlerin işletilmesi ve önarıtımın havasız özümleme üzerine etkilerini inceleyerek yapılmıştır.

Ön çalışmalar göstermiştir ki, organiklerin çözünür hale geçirilmesi bakımından en etkili önarıtım metodu ultrasonik önarıtımdır. Onbeş dakika sonikasyon, 50 mg/L başlangıç çözünmüş KOİ değerini 2500 mg/L değerlerine kadar yükseltmiştir. Biyometan potansiyeli testleri de, artan çözünmüş substratın havasız biyodegradasyonunu iyileştirdiğini göstermiştir. Son olarak, yarı-sürekli havasız reaktörler farklı işletme koşullarında önarıtımın etkisini incelemek için kullanılmıştır.

Sonuçlar gösteriyor ki, 15 gün katı bekletme süresi ve 0,5 kg/m^3g organik yükleme hızı ile önarıtım sonrası havasız özümleyicinin günlük biyogaz üretimi % 49, metan yüzdesi % 16 artmış ve % 24 daha fazla uçucu katı giderilmiştir. Ayrıca, reaktörlerin işletim koşulları daha kısa katı bekletme süresi ve seyreltik giriş konsantrasyonu gibi etkilerle kötüleştirilse dahi önarıtım etkili biçimde çalışmış ve havasız özümlemeyi geliştirmiştir.

Son olarak, maliyet hesapları yapılmış ve biyogaz miktarındaki artış, daha fazla metan yüzdesi ve arıtma tesisinden daha az uçucu katı bertarafı konuları göz önünde bulundurularak, ultrasonik önarıtımın kurulum ve işletme maliyetlerinin geri ödeme süresi 4,7 yıl olarak hesaplanmıştır.

Anahtar Kelimeler: asidik önarıtım, çamur minimizasyonu, ultrason, ultrasonik önarıtım

To a peaceful World…

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LIST OF ABBREVIATIONS

BM: Basal Medium

BMP: Biochemical Methane Potential

COD: Chemical Oxygen Demand

CST: Capillary Suction Time

DS: Dry Solids

F/M: Food to Microorganism Ratio

HRT: Hydraulic Retention Time

LCC: Life Cycle Costing

MLSS: Mixed Liquor Suspended Solids

MLVSS: Mixed Liquor Volatile Suspended Solids

NH_3-N: Ammonia Nitrogen

OLR: Organic Loading Rate

sCOD: Soluble Chemical Oxygen Demand

SRT: Solids Retention Time

TCD: Thermal Conductivity Detector

tCOD: Total Chemical Oxygen Demand

TKN: Total Kjeldahl Nitrogen

TSS: Total Suspended Solids

US EPA: United States Environmental Protection Agency

VFA: Volatile Fatty Acids

VS: Volatile Solids

VSS: Volatile Suspended Solids

WAS: Waste Activated Sludge

YTL: New Turkish Liras

CHAPTER 1

INTRODUCTION

Solutions of environmental problems arising from urbanization conventionally include reactive and proactive approaches. Reactive solutions react to an existing problem; on the other hand, proactive approach tries to prevent the concern before it becomes a problem. Wastewater treatment plants can be counted as major tools of reactive solutions in environmental engineering.

Wastewater treatment plants consist of two major elements to be dealt with; wastewater and sludge. According to Tchobanoglous *et al.* (2003) the ultimate disposal of the concentrated contaminants removed by treatment is one of the most difficult and expensive problems in the field of environmental engineering.

By definition, biosolids are by-products of wastewater treatment process streams and require as much attention as the wastewater treatment stream does. Moreover as mandatory legislations become stricter and stricter throughout European countries, Turkey also started facing stringent environmental laws as a country, which is in the accession period of European Union. These restrictions are leading to more innovative wastewater treatment technologies that are producing more sludge.

The increasing awareness combined with increasing amounts of sludge drew attention on sludge and this combination obviously shows that, handling of excess sludge is one of the most problematic issues of wastewater treatment concept nowadays and this specific reason is also the initiative of this study. Not only the initiative but also the aim of the study is underlining the sludge-handling problem concurrently.

The increasing awareness led to alternative solutions to sludge production problems. Less sludge producing treatment techniques such as membrane reactors or extended aeration systems were put into work. But existing conventional systems still had the problem. Sludge minimization concept as a reactive approach arose to solve the excess sludge production by sludge pretreatment. Sludge pretreatment, which is a process applied once the sludge is formed, principally converts the waste sludge into a more bioavailable substrate for anaerobic digestion and leads to an enhanced degradation. The enhanced degradation leads to more organic reduction and more biogas production therefore, sludge pretreatment acts as a modification for improving sludge management in a treatment plant.

The broad aim of this study is to propose an alternative solution to excess municipal sludge production by means of sludge minimization in the light of laboratory tests. Two sludge pretreatment techniques were investigated, and subsequent anaerobic digestion was investigated as a part of this minimization technology.

The objective of the study was to perform a comprehensive work on the evaluation of acidic and ultrasonic pretreatment methods and their combinations. The most effective pretreatment method was to be selected both in terms of sludge disintegration and/or floc disruption.

The second objective was to study the selected sludge pretreatment option by anaerobic batch tests.

Afterwards, the pretreatment method was compared with a conventional anaerobic digester at different operational conditions in lab-scale anaerobic digesters by altering the solids retention time and influent sludge loading rate.

Last objective of the study was to perform a cost analysis including up to date costs and revenues of a treatment plant when upgraded with the selected pretreatment option that was investigated in lab-scale semi-continuous anaerobic digesters. The cost analyses contain the costs and revenues of both the baseline and the upgraded situation instead of a single pretreatment unit price.

Generally, the purpose of the study is to point the advantages and disadvantages of pretreatment on the path of sludge minimization. The reputation of anaerobic digestion as an environmentally friendly technology was increased with a pretreatment upgrade by enhancing the current advantages. This enhancement was also expected to be done in environmentally friendly and a “green” way by minimizing the costs and deficiencies of anaerobic sludge digestion.

The organization of the thesis is in an order of literature surveying, experimental methods and discussing the results of experimental analysis. Before concluding the study, a brief cost analysis was performed according to experimental investigations.

Experimental analyses consist of preliminary studies for deciding the most appropriate pretreatment method, anaerobic batch tests for optimization of the parameters of selected method and finally, operation of semi-continuous anaerobic reactors to investigate the effect of pretreatment on anaerobic digestion in details.

CHAPTER 2

LITERATURE SURVEY

2.1 Definition, Types and Quantities of Sludge

The solid residuals of a treatment process are called sludge. For a conventional wastewater treatment plant, primary sludge, secondary sludge or both are common solid products. Typical forms of solids that can be produced in a treatment plant can be listed as screenings, grit, scum/grease, primary sludge, chemical sludge, activated sludge, trickling-filter sludge, aerobic digested sludge, anaerobic digested sludge, composted sludge and septage (Tchobanoglous *et al.*, 2003).

Primary sludge is produced simply by separating heavy solid particles from wastewater line by gravitational force in a primary clarifier. On the other hand, secondary sludge is produced throughout the biological process and the mechanism is simply conversion of soluble organics to biomass i.e. particulate matter. Secondary sludge is separated from liquid phase in the secondary clarifier and the dense solids are called activated sludge as mentioned above.

General properties of sludge are: being semi-solid, odiferous, hard to manage and dangerous. Such a substance, containing high amounts of biologically active mass, organics, nutrients and water is naturally expected to be problematic (Vesilind, 1974).

Since sludge is produced as a compulsory by-product from a treatment facility, the quantities of sludge are also expected to be high. Sludge quantities can be calculated by using some generation factors. These factors contribute to the estimation of sludge production for a particular place if the population known. These factors are such that the sludge to be disposed of is of the order of 80 g DS person^{-1} day^{-1} in the European Union, whereas it is about 100 g DS person^{-1} day^{-1} in the USA (Kouloumbis *et al.*, 2000).

Members of European Union countries used to produce 6.6 million tons of dry solids in 1998 and estimated amount for 2005 was 11 million tons of dry solids annually (Khanal *et al.*, 2007). According to Brodersen *et al.* (2002) sludge production amounts increased in most European countries with the implementation of Urban Wastewater Directive. Statistical records show 7.6 million tons of total sewage sludge production in 2005 (Eurostat, 2008). According to US EPA, (1999) annual biosolid generation throughout USA from publicly owned facilities were 6.9 million tons of dry solids in 1998. Estimated amounts for annual generation of 2005 and 2010 were 7.6 and 8.2 million tons of dry solids, respectively.

In Turkey, 165 municipalities have treatment plants serving a population of 71 million according to 2004 data. According to statistical data, the estimated annual sludge production in 2020 is approximately 1 million tons of dry solids (Salihoğlu *et al.*, 2007).

Not only quantities but also properties of sludge make the handling of sludge critical. Therefore, sludge coming out of a treatment plant requires a unique and further treatment in other words, sludge stabilization. Furthermore necessity of sludge stabilization is dictated with stricter legislations. Turkey is also facing strict sludge stabilization regulations due to being a candidate country of European Union nowadays.

2.2 Sludge Stabilization in a Wastewater Treatment Plant

Both the primary and secondary sludge are quite objectionable and further stabilization processes become necessary. Sludge can cause ultimate environmental problems unless treated consciously and carefully. Although, there are numerous ways of handling waste activated sludge such as aerobic digestion, composting, lagoons, lime stabilization, heat stabilization, irradiation, sludge drying beds, etc., stabilization is conventionally done by anaerobic digestion in most of sludge treating plants.

Among all stabilization methods anaerobic digestion of activated sludge pulls attention since it reduces volatile solids, significantly deactivates pathogens, eliminates objectionable odors and produces biogas as an energy source concurrently.

Due to these unique properties of anaerobic digestion and since this work heavily concentrates on anaerobic digestion, more detailed description and literature information on stabilization by anaerobic digestion is given in the following chapters.

2.3 Mechanism of Anaerobic Digestion

As mentioned in section 2.2 previously, anaerobic digestion in a wastewater treatment plant is to stabilize excess sludge. This stabilization is conversion of organic matter into methane and carbon dioxide in an oxygen-free media biologically (Parkin and Owen, 1986).

Anaerobic digestion is a three-stage process, which involves many classes of bacteria and several intermediate steps. Three main steps followed are (Parkin and Owen, 1986) (Speece, 1996):

- Hydrolysis and liquefaction
- Acid formation
- Hydrogen and acetic acid formation
- Methane formation

Hydrolysis and liquefaction is conversion of complex and/or insoluble organics into simpler forms, therefore organics become bioavailable. Bioavailability stands for materials that can pass through cell wall due to their form and size. Hydrolysis step is significant since bacteria can utilize bioavailable organics. Hydrolysis and liquefaction can be done with extracellular, hydrolytic enzymes, which are generally very slow. After accomplishing hydrolysis step where organics are hydrolyzed, fermentation of organics into long-chain organic acids, sugars, amino acids and miscellaneous smaller organic acids takes part (Parkin and Owen, 1986). These steps are conversion of organics from one form to another and do not result in major stabilization.

After hydrolysis, acetic acid and hydrogen is produced by acetogens and hydrogen producing bacteria respectively (Parkin and Owen, 1986).

Methane formation is the step where stabilization occurs. Acetic acid and hydrogen as products of the previous step are major energy sources of methane formers (methanogens). Methane and carbon dioxide are ultimate products of anaerobic digestion. Since methane is insoluble it can be collected as gas efficiently. Carbondioxide is present in both gas fraction and liquid fraction and gas form is collected concurrently with methane (Parkin and Owen, 1986). Figure 2-1 shows the pathways of organic matter degradation during anaerobic digestion.

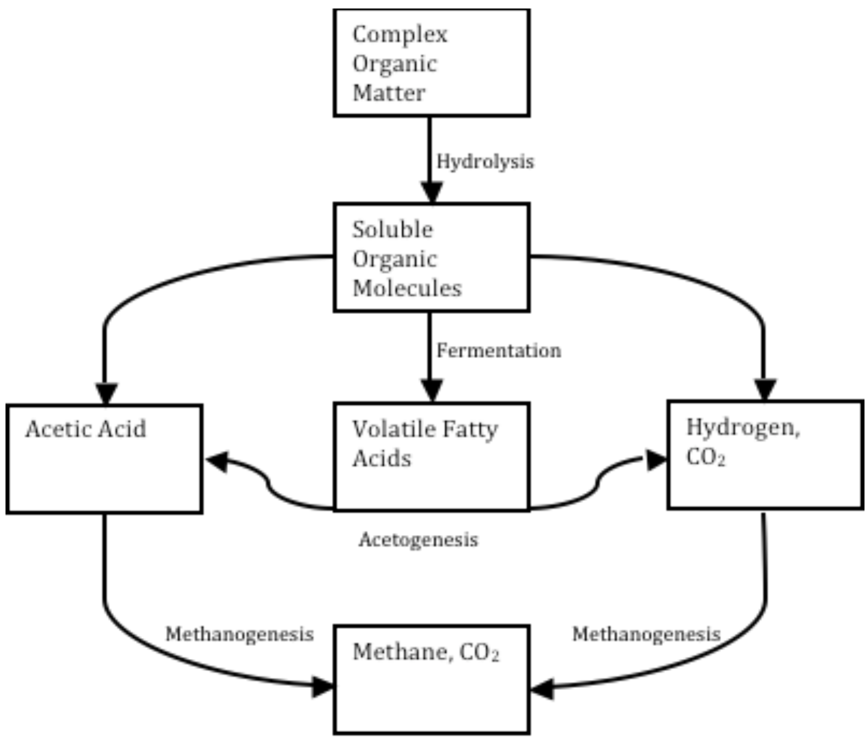

Figure 2-1. Mechanism of anaerobic digestion

The principle of pretreatment as is discussed in following sections in detail is to speed up the hydrolysis step.

2.4 Factors Influencing Anaerobic Digestion Process

Since methane formers (last group of microorganisms in mechanism) are quite sensitive to environmental conditions, anaerobic digestion process requires strict control of environmental conditions during operation.

For the success of the process of anaerobic digestion, environmental factors and operational parameters should be investigated in details. pH change, presence of heavy metals, micro and macro nutrients, alkalinity, temperature, toxicity, presence of detergents and other environmental factors affect the performance of digestion (Wang *et al.*, 1997).

Temperature: Anaerobic digestion has two common operating temperature ranges. Mesophilic digestion (30-38^{0}C) is the most frequently used municipal digester range whereas thermophilic operation (50-60^{0}C) is known to be quite effective; moreover there are numerous advantages reported over mesophilic digestion. These include improved organic destruction, improved organic removal rate, easy dewatering and removal of pathogens effectively. On the other hand, thermophilic range consumes more energy resulting in a higher operation cost (Parkin and Owen, 1986).

Newer research (Song *et al.*, 2004, Oles *et al.*, 1997) show that lab scale and pilot scale studies giving best results when two stage anaerobic digestion with thermophilic and mesophilic digestion is applied together under proper retention times.

pH & Alkalinity: Since a mixed culture is present during digestion, pH becomes an important environmental condition. According to McCarty (1964b), accepted range for anaerobic digestion is 6,5 - 7,6. pH drop is the major risk due to faster growth rate of acetogenic bacteria and increased concentration of volatile acids. Therefore alkalinity plays a vital role for buffering the system and preventing the cease of methanogens. The dominant alkalinity available for anaerobic digestion is bicarbonate alkalinity system (Parkin and Owen, 1986).

Toxicity: Even though toxic materials inhibit the digestion, any material somehow may inhibit the biological activity in an anaerobic digester free from its nature. Organic chemicals usually petrochemicals, heavy metals, ammonia nitrogen depending on pH, cations such as Na^+, K^+, Ca^{++} and Mg^{++}, sulfides and some other miscellaneous substances play inhibitory roles (Parkin and Owen, 1986).

Nutrients: Sufficient amount of nutrients such as nitrogen and phosphorus are required for an efficient anaerobic digestion due to production of microbial cell besides conversion to methane and carbon dioxide. Domestic sludge is known to contain sufficient amounts of nitrogen and phosphorus (McCarty, 1964a). Also trace metals including iron, nickel, cobalt, sulfur, calcium are required and domestic sludge is thought to contain required trace nutrients (Parkin and Owen, 1986).

Oxygen: Methane formers are sensitive to the presence of oxygen. Therefore oxygen is toxic and inhibits the methanogenic activity (Parkin and Owen, 1986). This also shows that methane-forming microorganisms within microbial consortia of anaerobic digestion are quite sensitive to environmental conditions.

2.5 Important Operational Parameters of Anaerobic Digestion

Concurrently, operational conditions such as hydraulic retention time, solids retention time, organic loading rate, mixing and other controllable parameters play a vital role on the performance of anaerobic digestion.

Hydraulic Retention Time (HRT) & Solids Retention Time (SRT): HRT represents the time spent in a reactor for a water molecule. Operationally HRT is volume/flow as seen in equation 1. SRT represents the ratio of mass of solids in the reactor to mass of solids wasted daily. Not only modifying the reactor volume but also changing the recycle ratio SRT can be altered. For a single stage or high rate conventional anaerobic digester (with no recycle), HRT is equal to SRT. According to Vesilind (1974), typical SRT value for mesophilic anaerobic digestion lies between 10-20 days. According to McCarty (1964c) digestion at 35 ^{0}C requires minimum solids retention time of 4 days whereas typical value is 10 days. General approach should be determining the minimum SRT by using growth rate of microorganisms and choosing a larger SRT value to be on the safe side (Frostell, 1985). Longer retention times provide enough time for bacteria for synthesis and prevent washout however, Bolzonella *et al.* (2005) showed that longer retention time values decrease specific gas production.

$$SRT = \frac{V}{Q} \tag{1}$$

Briefly, as Rivero (2005) suspects, solid destruction increases with increasing SRT whereas, rate of destruction decreases.

Organic Loading Rate (OLR): Not only the reactor operation but also the influent characteristics affect the performance of digesters. OLR can be calculated according to equation 2 where C_{in} stands for influent volatile solids (VS) concentration, V_{in} stands for influent feeding volume per day and V stands for reactor volume.

$$OLR = \frac{C_{in} \times V_{in}}{V} \tag{2}$$

According to Tchobanoglous *et al.* (2003), typical range of volumetric organic loading rate is 1.0 – 5.0 kg COD / m^3 d. According to Reynolds and Richards (1995) this range lays between 0.64 – 1.60 kg VSS / m^3 d for low rate and 2.40 – 6.40 kg VSS / m^3 d for high rate digesters. An important advantage of anaerobic digestion is the ability of stabilizing stronger organic loads, therefore higher efficiencies are expected when organic loading rate is increased (Speece, 1996).

Mixing: Mixing provides effective contact between food and microorganisms. Dispersion of any unexpected toxic influent and shock loads improve the performance too. Temperature grading and stratification prevents effective digestion therefore mixing is necessary for solving these problems. Ineffective mixing reduces the active volume of a reactor, consequently sludge retention time decreases and washout becomes a potential problem. Adequate mixing is a critical issue for anaerobic digestion (Parkin and Owen, 1986).

2.6 Principle of Sludge Pretreatment

Since excess municipal sludge is relatively large in volume and is rich in organic content, anaerobic digestion as further stabilization is used commonly. Pretreatment has been developed to fulfill the need for subsequent sludge treatment and ultimate disposal (Müller, 2001). Sludge pretreatment enhances the performance of anaerobic digestion in many ways. Due to the physical state of waste sludge as a substrate, subsequent microbial degradation is not favored (Weemaes and Verstraete, 1998). As described in section 2.3 previously, the very first step of anaerobic digestion is hydrolysis and is also the rate-limiting step that makes the anaerobic digestion a very slow process (Tiehm *et al.*, 1997).

Briefly 70% of excess sludge is bacteria and hydrolysis of bacteria limits the whole anaerobic digestion process (Lehne *et al.*, 2001). This situation is resulting in high amounts of excess sludge to be dealt with.

Sludge pretreatment principally aims to overcome the slow rate of hydrolysis by converting the unfavored substrate into bioavailable substrate. For microorganisms, bioavailability can be achieved by solubilizing the substrate. Since substrate stands for excess sludge that is composed of formerly synthesized bacterial cells, solubilization means disintegration of cell walls and releasing intracellular materials into liquid phase.

As it is mentioned by Mason and Lorimer (2002) “The problem is that most simple one-cell organisms have an exceedingly tough cell wall which is only a few microns in diameter, and similar in density to the medium that surrounds it. On the other hand the protein and nucleic acid components contained within the cell are large macromolecules, easily denatured by extreme conditions of temperature or oxidation". Therefore, sludge pretreatment breaks up cell walls and produces bioavailable substrate for anaerobic digestion (Müller *et al.*, 2004, Weemaes and Verstraete, 1998).

2.7 Pretreatment Options

Pretreatment can be applied via various tools and methods. Generally pretreatment can be classified as mechanical, chemical, thermal or biological pretreatment or combination of these methods such as thermo-chemical pretreatment. In this part an introduction to the commonly used pretreatment method is made with specific emphasis on detailed literature analysis conducted on acid and ultrasonic treatments.

Mechanical Pretreatment

Mechanical pretreatment methods disintegrate the sludge by physical means such pressure, translational or rotational energy. The principle of mechanical pretreatment is to stress the sludge with different tools. Common mechanical methods are stirred ball mills, high pressure homogenizers, ultrasonic homogenizers, mechanical jet smash technique, high performance pulse technique and lysat-centrifugal- technique (Müller, 2001).

According to Strünkmann *et al.* (2006), depending on operational conditions and parameters 70% excess sludge reduction was achieved via mechanical pretreatment.

Ultrasonic pretreatment as a mechanical treatment method and also the focus of this study will be discussed in detail in Section 2.7.2.

Chemical Pretreatment

Chemical pretreatment involves the application of chemicals into sludge for cell wall dissolution. Common chemical methods include acid or alkali pretreatment, ozonation and hydrogen peroxide addition.

Since ozonation does not produce salt residues and no chemical is used, ozonation is of special interest among chemical processes (Müller, 2001).

HCl, H_2SO_4, NaOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$ are chemical agents used to alter the pH for acid or alkali pretreatment (De Franchi, 2005, Kim *et al.*, 2003). Alkali pretreatment has full-scale applications throughout the world. On the other hand, acidic pretreatment has relatively limited examples in the literature and requires more interest. The detailed literature review for acidic pretreatment can be found in Section 2.7.1.

Thermal Pretreatment

Thermal pretreatment releases intracellular bound water and generally involves heating in the range of 150 – 200 ^{0}C. The yield of soluble COD (sCOD) at 150 ^{0}C was about 15 – 20%, when the temperature was increased up to 200^{0}C the yield of sCOD became 30% (Weemaes and Verstraete, 1998).

Combined with chemical pretreatment, thermal pretreatment can also be applied. The process is called thermochemical pretreatment. Tanaka *et al.* (1997) showed dose of 0.6 g NaOH per g VSS increases the VSS solubilization around 15% for 1 hour of contact time. On the other hand, 5 minutes of heating at 130^{0}C with 0.3 g NaOH per g VSS achieved maximum solubilization.

Another thermohemical pretreatment study showed 30-50% hydrolysis yield was achieved by thermal acidic pretreatment performed with HCl and H_2SO_4 (Smith and Göransson, 1992).

Biological Pretreatment

Biological pretreatment disintegrates the sludge with or without enzymes (Müller, 2001). Generally biological pretreatment uses external enzymes, enzyme catalyzed reactions and autolytic processes for cracking the compounds of cell wall (Müller, 2001).

Yamaguchi *et al.* (2006) suggested a two-step pretreatment system including a biological reactor consisting of sludge degrading microorganisms. First step of pretreatment was alkali pretreatment that increased the pH above 9. Consequently sludge was introduced into biological degradation reactor where sludge was further degraded to simple molecules and pH became appropriate for further digestion.

2.7.1 Acidic Pretreatment

Acidic pretreatment is a rare chemical pretreatment method and is applied by the addition of acid to lower the pH of the sludge.

2.7.1.1 Mechanisms of Action of Acidic Pretreatment

Firstly, characteristics of waste activated sludge at low pH values can be investigated. The isoelectric point of sludge lies between pH 1 and pH 3 (Forster, 1971). Also according to Neyens *et al.* (2003) the net negative charges on the surface of sludge particles kept them apart. When the pH is decreased down to 2.6 – 3.6, the negative charge on the surface became neutral and at that point, the repulsive force between particles decreased down to minimum and physical stability such as easy dewatering and flocculation could be observed. Chen *et al.* (2001) showed that the viscosity of sludge at pH 2.5 is smaller than the untreated sludge. Also better settleability was observed at pH 2.5. These results indicate that acidic pretreatment favors dewaterability and a physically stable sludge.

2.7.1.2 Achievements by the Use of Acidic Pretreatment

Müller (2001) stated that sludge cells can be dissolved by acidic or alkali treatment at low or ambient temperatures.

Moreover, according to Neyens *et al.* (2003) acidic pretreatment disintegrated the cell wall. The same study shows that at pH 3 sludge volume could be decreased up to 75% by dewatering and soluble solids could be increased due to solubilization of intracellular solids. Ultimately pH 3 was decided to be the most appropriate pH for acidic pretreatment.

Another study showed that at room temperature 4 grams of sulphuric acid per gram TSS consumed a significant amount of suspended solids at 5 minutes of contact time. The reduction of TSS had been recorded to be 61% mostly independent from the initial solids concentration and temperature. The only parameter significantly effected the solubilization was found to be the acid dose in the same study (Woodard and Wukash, 1994).

Meuner *et al.* (1996, cited in De Giovanni, 2005) also showed that rapid hydrolysis of VSS through sulfuric acid treatment similarly, due to rapid mineralization of organic portion of sludge. Consequently, the amount of excess sludge was minimized. pH 1.5, 2, 2.5 and 3 were analyzed and maximum VSS reduction was observed in the lowest pH value, which consumed the highest amount of acid as expected.

Acidic pretreatment is thought to accelerate the hydrolysis step by breaking up the cell walls, mineralization of microbial cells, improve dewaterability and improve the overall performance of subsequent anaerobic digestion. On the other hand according to Weemaes and Verstraete (1998) only few successful results for chemical pretreatment at ambient temperature were reported. Elevated temperatures create aggressive reaction conditions and enhance the effects of pretreatment. Also another negative aspect of acidic pretreatment is the requirement of neutralization for subsequent biological application.

Due to this contradictory information in literature, acidic pretreatment was chosen to be one method of pretreatment studied in this work.

2.7.2 Ultrasonic Pretreatment

Ultrasonic pretreatment, converting ultrasound into a pretreatment tool consists of various parameters such as frequency, sonication power and sonication time. These parameters, and their effects on solubilization of organics, physical characteristics and anaerobic digestion are subject to further investigation in the following chapter.

2.7.2.1 Ultrasound

Ultrasound is a cyclic sound pressure with a frequency greater than the upper limit of human hearing. The limit of ultrasonic frequency is 20 kHz and goes up to 10 MHz. This range is classified as inaudible for human (Navaneethan, 2007). There are numerous application areas of ultrasonication among various branches of science such as biology, biochemistry, engineering, dentistry, geography, geology and medicine. For this study, as briefly described in the mechanical disintegration subsection under section 2.7, ultrasonication can also be used as a pretreatment tool for disintegration of excess sludge prior to anaerobic digestion (Mason and Lorimer, 2002).

The chemistry of sonication as a pretreatment tool is complex and is a combination of shearing, chemical reactions with radicals, pyrolysis and combustion (Lehne *et al.*, 2001).

Ultrasound is used to create acoustic cavitation for supplying energy to the liquid phase. Acoustic cavitation can be defined as formation, growth and subsequent collapse of microbubbles (cavitation bubbles) in very small time intervals. The formation of microbbbles is due to high-pressure applications to liquid. High-pressure applications cause to the critical molecular distance exceed and voids to appear. These violent collapses of microbubbles release high amounts of energy into a small area (Gogate, 2002). According to Tiehm *et al.* (2001) the internal temperature and pressure can increase up to 5000 ^{0}K and several hundred atmospheres, respectively.

Consequently, due to extreme local conditions some radicals (•OH, HO_2•. H•) hydrogen peroxide can be formed (Bougrier *et al.*, 2005). Following radical reactions can degrade pollutants, and sonochemical reactions can degrade volatile compounds by pyrolysis processes in micro bubbles (Pétrier and Francony, 1997).

A general expression in Perez-Elvira *et al.* (2006) is that ultrasonic homogenizers produced sCOD 6 times greater than untreated sludge and digesters produced 10 - 60% more biogas compared to conventional digesters. Also sonication had high impact on dewaterability.

2.7.2.2 Effects of Ultrasonic Pretreatment on Solubilization of Organics

During ultrasonication; operational frequency (frequency) as well as electrical power rating (ultrasonic intensity) and time of application are common adjustable parameters.

Sonication Frequency: According to Gogate (2002), common sonication frequency is between 20 – 200 kHz, whereas, cavitation occurs between 20 – 40 kHz (Roy *et al.*, 1985). Another study showed that mechanical forces became most efficient when ultrasound was operated below 100 kHz (Tiehm *et al.,* 2001). Ultrasonication was effective not only due to mechanical shear but also various sonochemical reactions, so sonic frequency became critical for following sonochemistry. These sonochemical reactions could be observed in a wide range such as 20 kHz and 1 MHz (Tiehm *et al.,* 2001).

The shear effect of ultrasonication becomes more efficient when the acoustic frequency is below 100 kHz. On the other hand sonochemical reactions dominate the liquid when the acoustic frequency is higher than 100 kHz (Tiehm *et al.,* 2001).

Tiehm *et al.* (2001) studied at different frequencies in the range of 41 kHz and 3217 kHz and showed that disintegration of WAS is most effective when the frequency is set to 41 kHz which is the lowest frequency studied, showing that micro-bubble radius is inversely proportional to frequency i.e. lower frequencies create larger cavitation bubbles and the explosion of larger bubbles release more shear stress into liquid.

Ultrasonic Power & Sonication Time: Ultrasonic power can be expressed in various ways: Ultrasonic density, which is power, applied per volume of sample; ultrasonic intensity, which is power applied per application area or ultrasonic dose, which is energy supplied per volume of sample (Hua and Hoffman, 1997).

Electrical power introduced into liquid is also affecting the degree of disintegration. Tiehm *et al.* (2001) showed a linear relationship between disintegration and ultrasonic intensity. Higher ultrasonic intensities are able to break the cell walls. Relatively lower levels of power disintegrate sludge flocs.

According to Tiehm *et al.* (2001) raising the sonication time, increased the sCOD, indicating cell lysis. 150 minutes of sonication achieved a 23.7% degree of disintegration whereas 60 minutes achieved 13.1% and 7.5 minutes achieved zero disintegration at 41 kHz sonic frequency. These results showed that not only sonication power but also application time of sonication proportionally changes the degree of disintegration.

Another study of the same team, supporting the positive effect of sonication time on disintegration with 6 kW energy and 31 kHz frequency showed that 96 seconds of sonication releases more than 6 g COD/L whereas 64 seconds of sonication released 4 g COD/L (Tiehm *et al.*, 1997).

On the other hand, according to Wang *et al.* (1999) sonication time more than 30 minutes, by 200 W and 9 kHz sonication did not lead to further organic destruction efficiently. Therefore, optimization of sonication time is critical.

According to Show *et al.* (2006), increase in sonication intensity decreased the mean particle size, which is indicating the break-up of flocs moreover, doubled the sCOD concentration by 0.52 W/mL sonication for 1 minute of application at 20 kHz frequency.

Chu *et al.* (2002) suggested that sCOD concentration increased slightly when weak ultrasonic pretreatment (20 minutes, 20 kHz and 0.3 W/mL) was applied, highlighting the importance of sonication intensity on cell lysis.

Bougrier *et al.* (2005) investigated the energy requirement for disintegration and showed a minimum energy requirement for cell break-up as 1000 kJ/kg TS. On the other hand Lehne *et al.* (2001) found 3000 kJ/kg TS to achieve a 10% disintegration.

According to Grönroos *et al.* (2005) sonication time has direct influence on sCOD concentration after pretreatment. Even though, low intensity and long time treatment is expected to have similar trends with high intensity, short time treatment; research show that high intensity, short treatment time is more effective in terms of releasing soluble organics.

Wang *et al.* (2005) investigated the shear and sonochemical effects of sonication separately. By suppressing the sonochemical effects, it was observed that the single shear effects were dominating the ultrasonic disintegration. Another outcome of the study showed that, increase in sonication intensity, improved the contribution of sonochemical effects.

Table 2.1 is the tabulated form of some example studies of ultrasonication of the literature. The common property of all studies is the sonication frequency that is approximately 20 kHz generally. The sonication power, excluding few extreme cases, vary in the range of 0 – 0.5 W/mL. As mentioned before, the sonication frequency and power is strongly dependent on the purpose of the research conducted.

The literature survey reveals that the disintegration of microbial mass for pretreatment purpose can be achieved by low frequency and high power applications.

Table 2.1. Some sonication density and frequencies from the literature

Study	Sonication Density W/mL	Sonication Frequency (kHz)
King and Forster (1990)	0 - 0.600	20
Wang *et al.* (1999)	0.200	9
Chu *et al.* (2001)	0.110-0.440	20
Chu *et al.* (2001)	0.330	20
Tiehm *et al.* (2001)	1.800 W/cm^2	41 – 3217
Lafitte-Trouque and Forster (2002)	0.470	23
Onyeche *et al.* (2002)	0.500	20
Blume and Neis (2004)	0.010 - 0.400	20
Jyoti and Pandit (2004)	2.400	22
Bougrier *et al.* (2005)	0.450	20
Grönroos *et al.* (2005)	0.100 – 0.200	22 - 40
Wang *et al.* (2005)	0.096 - 0.720	20
Wang *et al.* (2006a)	0.528 - 1.440	20
Show *et al.* (2006)	0 - 0.520	20
Show *et al.* (2007)	0.180 – 0.520	20

2.7.2.3 Effect of Ultrasonic Pretreatment on Dewaterability

Water present in excess sludge is a problematic component that is hard to separate. Various methods such as using filter press, belt filter press, centrifuge or vacuum filtration, for dewatering are used and even ultimate mechanical dewatering can obtain only 25-40% solid content at most. Therefore, sludge disposal due to high volumes of water becomes a burden and requires a solution (Khanal *et al.*, 2007).

According to Chu *et al.* (2001), ultrasonic applications do not have any effect on surface charges of suspended solids. As described in acidic pretreatment section (Section 2.7.1), surface charge plays a significant role on dewaterability but ultrasonication does not contribute dewatering by surface charge neutralization. Same study examined the CST values prior and after sonication and reported a slight detoriation at 0.11 W/mL but significant detoriation at 0.33 W/mL sonication power. These results clearly point an obvious decrease in the dewaterability of sonicated sludge with CST values increased from 197.4 seconds to 488.9 seconds under 60 minutes of ultrasound application.

King and Forster (1990) showed that increase in the concentration of fine particles increases CST value of sludge. Ultrasonication decreases the mean particle size, in other words, sonication increases the concentration of smaller particles causing worse dewatering substantially. Show *et al.* (2006) and Vesilind (1988) showed a linear relationship between solids concentration and CST for both inert and mixed digested sludge in previous studies.

King and Forster (1990) reported similar results even at very low levels of sonication. From 3 seconds up to 30 seconds of sonication with 65-W power input resulted with very high CST values. However, a decrease in CST was found after 300 seconds of sonication.

According to Vesilind (1994), water can be classified as free water, interstitial water, vicinal water and water of hydration and another study proposes that interstitial water that is held inside the sludge cell can be released and becomes free water after cell disruption (Erdinçler and Vesilind, 2003).

Erdinçler and Vesilind (2003) applied 30 seconds of burst sonication in four sets and observed a slight decrease from 19.7 to 17.1 seconds and these results were explained by hydrolyzation of extracellular and intracellular materials disintegrating the colloidal properties of these compounds. On the contrary, Wang *et al.* (2006b) concluded that sonication deteriorated sludge dewaterability with increasing sonication time and density.

Briefly there are contradicting results reported in the literature that found both increasing and decreasing CST values after sonication.

However, all these investigations were done immediately after sonication but not after subsequent anaerobic digestion. For this reason, as a pretreatment tool, ultrasonication should be treated as a whole with subsequent digestion.

Ultrasound pretreatment of sludge could enhance the dewaterability of sludge following digestion. Ultrasonic treatment improved the mean cake solids content by 1.64 ± 0.32% in comparison to an unsonicated control in the study of Hogan *et al.*, (2004) as cited in Khanal *et al.* (2007).

2.7.2.4 Effect of Ultrasonic Pretreatment on Anaerobic Digestion

Since ultrasonic pretreatment achieve cell disintegration and solubilization, hydrolysis step is expected to accelerate. Consequently, anaerobic digestion is also expected to go through some changes.

Improvement of anaerobic digestion is generally indicated by some parameters such as, more volatile solids (VS) reduction or improved biogas production. Ultimate results of a successful ultrasonic pretreatment promote anaerobic digestion.

Tiehm *et al.* (2001) investigated the VS reduction during anaerobic digestion in a digester with 8 days of SRT, for sludge treated at 41 kHz sonication frequency. The results obtained from the study showed the improvement of VS reduction from 21.5 % to 22.7 % by 7.5 minutes of ultrasonic pretreatment. Highest VS reduction (33.7 %) was achieved after longest sonication (150 minutes). The relationship between sonication frequency and subsequent anaerobic digestion was quite similar to the relationship for solubilization. In other words, lowest frequency, leads to highest VS reduction.

Another similar study showed that a conventional digester operated at 22 days SRT has 45.8 % reduction of VS, whereas, 47.3 % reduction of VS was achieved at 12 days SRT by ultrasonic pretreatment. Study underlines that; ultrasonic pretreatment is a promising method to reduce the digester volume (Tiehm *et al.*, 1997).

Grönroos *et al.* (2005) investigated ultrasonication with 19 days batch anaerobic assays. 27 kHz, 200 W/L of sonication enhanced the methane yield from 3.22 m^3/kg sCOD to 8.09 m^3/kg sCOD both for 2.5 minutes and 10 minutes of pretreatment. Anaerobic biodegradability of substrate plays a limiting role and requires detailed optimization. Similarly, Wang *et al.* (1999) reported the importance of optimization of sonication time in their research, due to significant improvement of methane production up to 30 minutes of sonication time and no further improvement in terms of biogas production.

Bougrier *et al.* (2005) also investigated batch anaerobic digesters. Minimum 25% biogas production enhancement was obtained after sonication. 1000 kJ/kg TS was found to be the limit value of energy requirement. 1000 kJ/kg TS energy was accepted to be the threshold value of cell disruption.

The solids concentration also plays a vital role on sonication and subsequent anaerobic digestion. Onyeche *et al.* (2002) pointed that concentrated sludge samples, treated with ultrasound showed higher gas production compared to their reference samples. However, the consumption of energy also increased and no net benefit was gained by sonication of dense samples.

Contrary to other findings of the literature, some studies showed no benefit of sonication. Anaerobic digesters operated at mesophilic and thermophilic ranges were evaluated for both sonicated and untreated sludge in semi-continuous digesters. Ultrasonic pretreatment (23 kHz, 47 W and 90 seconds) did not enhance the biogas production significantly (Lafitte-Trouque and Forster, 2002).

Ultrasonic pretreatment has also full-scale implications. Demonstration from Singapur investigated two egg shaped anaerobic digesters fed with mixed primary and thickened secondary sludge. Volume of each digester was reported as 5000 m^3 and sonicated reactor produced 45 % more biogas compared to control reactor daily (Xie *et al*., 2007).

Full-scale demonstration trials using ultrasonic technology have been completed within the UK and the USA with major water companies such as Thames Water, Severn

Trent Water, Wessex Water, Anglian Water, Yorkshire Water, North West Water and the Orange County Sanitation District in the USA (WWI, 2003).

Germany is also another leading country in full-scale ultrasonic applications for enhancement of anaerobic digestion. The list of enhanced sludge treatment plants is as follows: Bad Bramstedt, Ahrensburg, Bamberg, Freising, Meldorf, Beverungen, Illertissen/Ulm, Kleinsteinbach, Hennef, Bad Liebenzell and Bünde (Ultrawaves, 2007).

Netherlands, Switzerland, Poland, Denmark, Hungary, China and Japan are some other countries that implemented the ultrasonication technology to conventional anaerobic digesters (Ultrawaves, 2007).

CHAPTER 3

MATERIALS AND METHODS

3.1 Inoculum & Waste Activated Sludge

Inoculum and waste activated sludge samples were supplied from Ankara Metropolitan Municipality Central Wastewater Treatment Plant, which has an approximate 950,000 m^3/d design flowrate (ASKI, 2008).

Inoculum was used for seeding both batch reactors and semi continuous reactors and was taken from the anaerobic digesters of wastewater treatment plant. Anaerobic digesters of the plant operate at 35 ^{0}C with a 14 days SRT (ASKI, 2008). Inoculum samples were filtered through a sieve with 1.4 mm pore size for eliminating larger fraction and provide homogeneity of the digested sludge. Inoculum was stored at 4 ^{0}C for preventing microbial activity.

Since waste activated sludge is mixed with primary sludge prior to anaerobic digestion during plant operation, waste activated sludge was taken from return activated sludge stream of the treatment plant. Activated sludge samples were either aerated with air pumps or stored at 4 ^{0}C depending on subsequent analysis. Typical maximum storage time of samples were set to be 3 days for aeration and 10 days for refrigeration.

3.2 Experimental Set-up

Experimental studies involved the preliminary studies conducted to select a pretreatment method and its optimal operation conditions. In the following parts batch and semi-continuous anaerobic digesters were operated to observe the effect of pretreatment on the digestion efficiency.

3.2.1 Pretreatment Studies

The following sections describe the experimental details of pretreatment methods used during the study. Pretreatment methods will be described under acidic pretreatment set-up, ultrasonic pretreatment set-up and combination of mild ultrasound with acidic pretreatment set-up sections.

Acidic Pretreatment Set-Up

Acidic pretreatment was done by using either 1 N or 2 N HCl. The application of acid was via introducing droplets of acid into 350 mL of waste activated sludge that is continuously agitated with magnetic stirrer and the pH was adjusted to 1.5, 2.5 and 4.5 and 20 minutes of contact time at constant pH was provided before performing any analysis.

Ultrasonic Pretreatment Set-Up

Ultrasonication was done via *Sartorius Labsonic-P* brand lab scale sonicator. The sonication frequency of the device was 24 kHz and maximum energy input was 400 W. The energy input also depends on the sonication probe. In this study, two different probes were available; 14 mm probe and 22 mm probe. Sonication with 14 mm probe was nominated as mild sonication; on the other hand sonication with 22 mm probe was strong sonication. The maximum powers that can be supplied via 14 mm and 22 mm probes were 100 W and 255 W, respectively.

The specifications and test conditions of mild and strong sonication are tabulated in Table 3.1 and Table 3.2.

Table 3.1. Specifications and test conditions of mild sonication

Sonication Frequency (kHz)	24
Sonication Density (W/mL)	0.2
Sonication Intensity (W/cm^2)	2.9
Temperature Control	No
Time of Sonication (min.)	1, 3 or 5

Table 3.2. Specifications and test conditions of strong sonication

Sonication Frequency (kHz)	24
Sonication Density (W/mL)	0.51
Sonication Intensity (W/cm^2)	4.8
Temperature Control	No
Time of Sonication (min.)	5, 10, 15, 20, 25 or 30

Combination of Mild Ultrasound with Acidic Pretreatment Set-Up

The two methods were combined with their standard application procedures that were described previously in a sequence of mild sonication following chemical addition to achieve solubilization and disturb the sludge flocs with minute amounts of energy subsequently.

3.2.2 Analyses Conducted to Indicate the Effectiveness of Pretreatment

After the pretreatments were done, their effectiveness was assessed by measuring a series of parameters. These included sCOD, oxygen consumption rate, capillary suction time (CST), turbidity, MLSS and MLVSS concentration. An increase in sCOD would indicate cell solubilization and floc disruption; similarly an increase in CST and turbidity would also imply similar issue. The decrease in oxygen consumption rate would indicate if there is an inactivation for aerobic microorganisms (WAS) originating from the pretreatment method applied. Therefore, after each pretreatment application all of these parameters were measured in pretreated and control sludge.

3.2.3 Biochemical Methane Potential (BMP) Test

For setting and operating biochemical methane potential (BMP) tests the study of Owen *et al.* (1979) was taken as a guide.

Experiments were conducted using 240 mL glass serum bottles with 120-mL effective volume. Proper amounts of waste activated sludge; anaerobic digested sludge seed and basal medium (BM) were mixed.

Tests were conducted to investigate the effect of acidic pretreatment and strong sonication on anaerobic digestion so waste activated sludge was pretreated with acid at pH values 1.5, 2.5 and 4.5 for acidic pretreatment and sonicated for 0, 10, 15 and 20 minutes for ultrasonic pretreatment. Pretreatment was done according to Section 3.2.1 Additionally, before setting up acidic pretreatment reactors neutralization was done with the addition of NaOH. Three replicate reactors were set for all conditions.

To fulfill the initial F/M ratio of 0.5 for anaerobic digesters volumes of waste activated sludge, anaerobic digested seed and basal medium were adjusted (g VS Waste Activated Sludge/g VS Anaerobic Digested Seed). The composition of BM is given in Table 3.3.

After preparing the serum bottles, they were purged with pure nitrogen gas to eliminate oxygen from the system. Reactors then were sealed with proper septum and incubated at 35±1 ^{0}C for about 1.5 months. Since sealing the reactors was done as soon as possible the gas composition of the headspace was considered to be 100% N_2 at t=0.

Table 3.3. Constituents of basal solution

Constituent	Concentration (g/L)	Constituent	Concentration (g/L)
KH_2PO_4	2.580	$MnCl_2.4H_2O$	0.3×10^{-3}
$Na_2HPO_4.7H_2O$	4.788	$CuSO_4.5H_2O$	0.557
$NaHCO_3$	0.600	$NaEDTA.2H_2O$	2.847
NH_4Cl	1.800	$ZnCl_2$	0.300
$MgSO_4.7\ H_2O$	0.780	$Na_2(Mo)O_4.H_2O$	0.480
$CaCl_2.2\ H_2O$	0.720	$CoCl_2.6H_2O$	0.300
$FeSO_4.7\ H_2O$	16.8	$NiCl_2.6H_2O$	0.550
H_3BO_3	0.300	**Constituent**	**Concentration (mL/L)**
$Al_2(SO_4)_3.\ 18\ H_2O$	0.720	HCl (concentrated)	6

Since BMP is a batch test, no feeding or wasting was done. Gas production and gas composition were investigated during the operation of reactors for 2-3 times per week. Manual shaking for proper contact of seed and substrate was done daily.

Total COD was determined at the end of reactor operation for ultrasonic pretreatment in order to observe the improvements in COD reduction after reactor operation.

3.2.4 Semi-Continuous Anaerobic Reactors

Experiments were conducted using 3-L glass reactor with 2-L of effective volume. Headspace was externally connected to a 4-L glass column and used for the collection of produced biogas. The gas column was put on a water filled container in which the water was saturated with brine solution that was prepared with 10 % NaCl w/v and 2 % H_2SO_4 v/v in order to minimize the dissolution of produced gas from the reactor. The illustrative photograph of the reactor and the gas collection column can be seen in Figure 3-1.

A magnetic stirrer provided continuous agitation for digesters. Daily wasting and feeding was done through a glass valve with the mouth opening large enough to fill and draw sludge using plastic syringes. Since the system was totally isolated from atmosphere, the liquid level of the gas collection column could be adjusted by sucking the headspace gas from the top of the column. *Millipore vacuum pump* was used for this purpose. The reactor and gas collector set-up were checked for leak proof condition by extensive tests prior to the reactor set-up.

2 control reactors (C) and 2 pretreatment reactors (P) had been set in a constant temperature room providing 35±1 ^{0}C which is appropriate for mesophilic anaerobic digestion. Control reactors and pretreatment reactors with their replicates were named as Control A, Control B and Pretreatment A, Pretreatment B, respectively (or shortly as C_A, C_B and Pr_A, Pr_B, respectively).

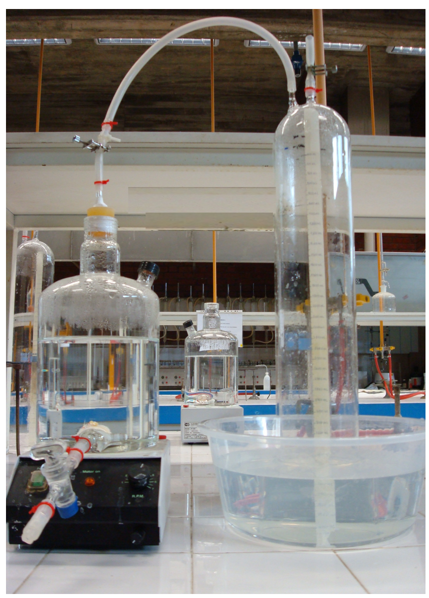

Figure 3-1. An illustrative photo of glass reactor and gas collection unit

Control reactors were fed with no pre-processed waste activated sludge, whereas pretreatment reactors were fed with ultrasonically pretreated waste activated sludge. Pretreatment was done according to procedures explained in Section 3.2.1.

Adjusted operational parameters for anaerobic digesters were SRT, HRT and OLR. The differences in operation were separately evaluated and entitled as *Set I*, *Set II* and *Set III*.

Due to the characteristics of the feed sludge provided from treatment plant, OLR was first calculated and then expressed as 'corresponding OLR'. Table 3.4 summarizes the operational parameters of reactors during each set of operation.

Table 3.4. Summary of operational parameters

Set	**SRT/HRT (days)**	**C_{in} (g VS/L)**	**V_{in} / V_r (mL / L)**	**Corresponding OLR (kg VS/m^3*d)**
I	15	7.50	133 / 2	0.5
II	7.5	7.50	133 / 1	1
III	7.5	3.75	133 / 1	0.5

C_{in}: Concentration of sludge fed to reactor.
V_{in}: Volume of the sludge fed to reactor.
V_r: Volume of the reactor.

Although three separate operational conditions were studied, the reactors were not set separately. Initially anaerobic seed and activated sludge were mixed and acclimated for 8 days until no gas production is observed. Consequently the operational parameters were altered properly. 8 days of lag period was not reported in terms of biogas production or other parameters since start-up period is not representative for the whole process.

At the end of the first period or *Set I*, half of the mixed liquor was removed from the feed/waste valve. Since the liquid volume is halved and the daily feeding stayed constant, new operational SRT became 7.5 days and corresponding OLR become 1 kg

VS/m^3d. The influent characteristics were kept the same and the only parameter changed was the volume of the reactor.

Before setting *Set III* at the end of *Set II* whole system was left in suspended conditions and no feeding was done for 7 days. As a result, system depleted high concentrations of VS and became adopted for *Set III*. The only difference between *Set II* and *Set III* were the VS concentrations in the feed.

During operation of the reactors, total gas production, total COD, soluble COD, MLSS and MLVSS, pH, gas composition, total and volatile solids were investigated. After reaching steady state and collecting enough steady state data, reactors were discontinued. Table 3.5 and Table 3.6 show the frequency of analyses conducted.

Reactors' concentrations of volatile solids were monitored in terms of daily variations and steady state was accepted when coefficient of variation of the data is smaller than 10%. Between days 53 and 64, *Set I*; between days 74 and 86, *Set II* and between days 93 and 100, *Set III* was considered as steady state.

3.3 Analytical Methods

Analyses conducted during laboratory study, using mixed liquor were; oxygen uptake rate, pH, MLSS and MLVSS, capillary suction time, total COD, total and volatile solids concentration. All these analyses were conducted on waste activated sludge or anaerobic digested sludge samples. Below are the standard procedures followed during all experimental studies.

- **Oxygen Consumption Rate:** *YSI 51B Oxygen Meter* was used to measure oxygen concentration. Analyses were done according to Standard Method 2710B (APHA, 2005)
- **pH:** *CyberScan PC 510-pH meter* was used for pH measurement.
- **MLSS & MLVSS:** The analyses were conducted by following the Standard Method 2540D and 2540E procedures for MLSS and MLVSS determination, respectively (APHA, 2005).

- **Capillary Suction Time:** Capillary suction time analyses were conducted according to Standard Method 2710G (APHA, 2005). *Triton Electronics Ltd. Type 304M Capillary Suction Timer* was used during the experiments. Duplicate and triplicate samples were used for CST analysis.
- **Total COD:** *HACH DR2000 spectrophotometer* and *HACH low range (0-150 mg COD/L), high range (0-1500 mg COD/L) digestion kits* were used for total and soluble COD determination. HACH reactor digestion method or Hach's United States Environmental Protection Agency (USEPA) approved dichromate COD method was followed (Jirka and Carter, 1975). Duplicate samples were used for analysis.
- **Total & Volatile Solids:** Standard Methods 2540B and 2540E were used for total solids and volatile solids analyses, respectively (APHA, 2005). Duplicate samples were used for analysis.

Among all the analyses described for mixed liquor sampling, turbidity analyses were conducted by using the supernatant of the samples gathered via 2 hours of gravity sedimentation and conducted after collection of at least 5 mL of sample.

- **Turbidity:** This parameter was investigated using *HACH Turbidimeter 2100N* following Standard Methods 2130B (APHA, 2005). Duplicate measurements were done for turbidity analysis.

sCOD, ammonia-nitrogen, ortho-phosphate, volatile fatty acids, carbohydrate and protein determination methods will be reported. All these analyses listed were conducted for liquid samples. For obtaining liquid samples, sludge samples were filtered through *Millipore* 0.45 μm-*pore opening size filter papers* by *Millipore Vacuum Pump* and *filtration kit*. Subsequently the analyses were conducted.

However, depending on the solid concentration and filterability of sludge sample, *Hettich Rotofix 32A centrifuge* was used at 3500 rpm for 10 minutes prior to filtration of supernatant to shorten the filtration time.

- **Soluble COD:** The determination method for the parameter is exactly same with the method of total COD determination. Duplicate samples were used for analysis.
- **Ammonia Nitrogen (NH_3-N):** Standard methods; 4500-NH_3-C titrimetric method was used for NH_3-N determination. Duplicate samples were used for analysis. (APHA, 2005).
- **Ortho Phosphate:** Standard methods 4500-P E; ascorbic acid method was used for PO_4-P determination (APHA, 2005). Spectrophotometric measurements were done at 880 nm wavelength by *Cole Parmer 1200* spectrophotometer. Duplicate samples were used for analysis. Related calibration curve is presented in Appendix.
- **Carbohydrate:** Phenol-sulphuric acid method of Dubois *et al.* **(**1956**)** was followed for carbohydrate determination. Glucose standard solution was used for preparation of calibration curves. Spectrophotometric measurements were done at 490 nm wavelength by *Pharmacia LKB Novaspec II* spectrophotometer. Triplicate samples were used for analysis. Related calibration curve is presented in Appendix.
- **Protein:** Folin-phenol method according to Lowry *et al.* (1951) was used for protein determination. Bovine serum albumine (BSA) standard solution was used for preparation of calibration curves. Spectrophotometric measurements were done at 750 nm wavelength by *Pharmacia LKB Novaspec II* spectrophotometer. Triplicate samples were used for analysis. Related calibration curve is presented in Appendix.

Analytical methods described above were conducted using either mixed liquor or filtrate of the mixed liquor. Analyses conducted for gaseous samples are described in the following part.

- **Gas Volume:** Volume of the produced gas for semi-continuous anaerobic reactors were detected by water displacement method. A graduated gas collection vessel was used. A graduated pipette connected to a water reservoir was used to measure the collected gas volume in BMP tests with water displecement principle.

- **Gas Composition:** Gas composition was measured with *Agilent Technologies 6890N Gas Chromatograph* with Thermal Conductivity Detector (TCD). A 30.0 m x 530 µm x 40.0 µm nominal *HP-Plot Q capillary column* was used with the column temperature initiated at 45 °C for 1 minute, then reached to 65 °C at a ramp rate of 10°C/min. Helium as the carrier gas had a flow rate of 3 mL/min. 100 µL *Hamilton gas tight syringe* was used for gaseous sampling and injections. Duplicate measurements were done.

Lastly, solids obtained from mixed liquors, dried at *Heareus Drying Oven* at 103 ^{0}C were used for the following analyses.

- **Heavy Metals:** Before heavy metal analyses necessary pretreatments were done according to microwave digestion method of Özsoy (2006). *Perkin Elmer AAnalyst 400 Flame Atomic Absorption Spectrometry* with electrode discharge lamp were used for detecting the concentration of Ni, Cd, Zn, Pb, Cr, Cu, Ca and Mg.

Hg analysis was done by *Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometry* with cold vapor hydride system. Duplicate samples were used for all metal analysis.

Table 3.5. Frequencies of experimental analyses

Parameter	**Frequency**
Total Gas Production	Daily
Gas Composition	Twice a week
Total & Volatile Solids	Twice a week
Total COD	Once a week
Soluble COD	Once a week
MLSS & MLVSS	Once a week
pH	Once a week

Table 3.6. Experimental analyses at the end of *Set I*

Parameter	**Frequency**
Ammonia-N	At the end of set
Ortho-P	At the end of set
Soluble Glucose	At the end of set
Soluble Protein	At the end of set
Capillary Suction Time	At the end of set
Heavy Metals	At the end of set

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 Preliminary Studies

This part of the study involves pretreatment of waste activated sludge by acidic and ultrasonic treatment methods and related preliminary experiments.

4.1.1 Acidic Pretreatment

In this part, acid was added to waste activated sludge to observe its effect over a wide pH range. As a strong acid, ‘HCl’ was used and the change of pH was tracked as given in Figure 4-1. By this study, a baseline was prepared indicating the trends of chemical consumption.

The addition of acid in Figure 4-1 initially drops the pH rapidly down to pH 2.5 and further addition of acid does not let the pH change too quickly after that point. For this reason pH 2.5 seems to be a critical value, whereas higher and lower pH values should also be investigated. For detailed investigations, pH 1.5, pH 2.5 and pH 4.5 were selected and thought to be appropriate for understanding the behavior of sludge in acidic conditions.

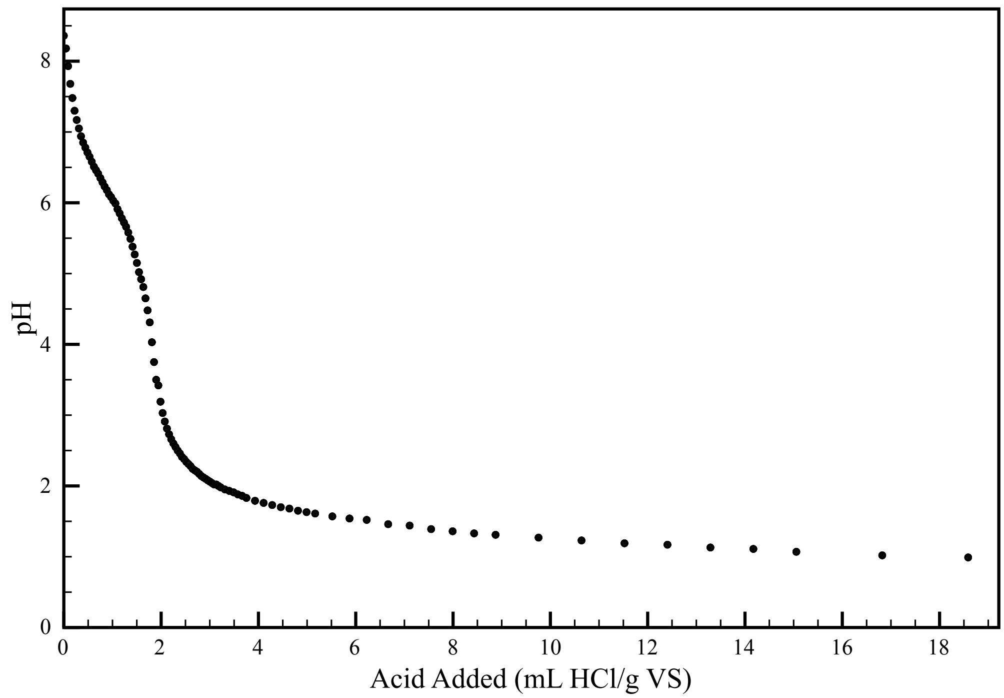

Figure 4-1. pH change with addition of 1 N HCl

Effect on Solubilization of Organics

Many studies indicate that following pretreatment; sludge samples can be evaluated by the changes of sCOD concentrations (Chen *et al.*, 2007, Andreasen *et al.,* 1997, Hatziconstantinou *et al.*, 1996). In this part of the study, soluble COD concentrations were analyzed and compared with untreated control sludge samples.

The sCOD values were normalized with respect to volatile solids concentrations and plotted. Volatile solids are representing the microbial cells in activated sludge and meaning of normalization is the amount of solubilization of COD from these microbial cells in waste activated sludge to the liquid phase.

As seen in Figure 4-2 there is a slight improvement of sCOD up to 450 mg COD/L after acidic pretreatment, where untreated sludge has a concentration of 50 mg COD/L initially. In Figure 4-2 at pH 1.5, sCOD concentrations of sludge are increased by 900%. For acidic pretreatment method, increase in the amount of chemicals consumed, improved the concentration of sCOD. Highest sCOD was obtained by decreasing the pH down to pH 1.5. The sCOD amounts decreased at pH 2.5 and further decreased at pH 4.5.

According to Chen *et al.* (2007), sCOD under alkali conditions were significantly higher than the other pH values. Some previous studies use the alkali disintegration for dissolving the solids completely and express the soluble organic portion after alkali pretreatment (Tiehm *et al.*, 2001, Lehne *et al.*, 2001).

Comparing with the other pretreatment methods in the literature, solubilization, as an indicator of successful pretreatment, seems to be enhanced slightly by acidic treatment in this study. Doğan *et al.* (2008) reported this enhancement as sCOD from 61.5 mg/L (control) to 1998.0 mg/L by microwave pretreatment. This reported enhancement is more than 3000% increase of sCOD with pretreatment.

According to Weemaes and Verstraete (1998) only few studies reported successful results for acidic treatment at ambient temperature so elevated temperatures might also be useful for acidic pretreatment.

Addition of chemicals increases the ionic strength of the sludge and upsets the pH, so requires subsequent neutralization for further biological processes. An example shows that 54% of total running cost is taken up by chemical costs in a full-scale ultrasound application project (Weemaes and Verstraete, 1998).

From here pretreatment by acid at pH 1.5 seemed to be the best condition in terms of cell disintegration and solubilization even though the soluble COD values were not at the very desirable levels.

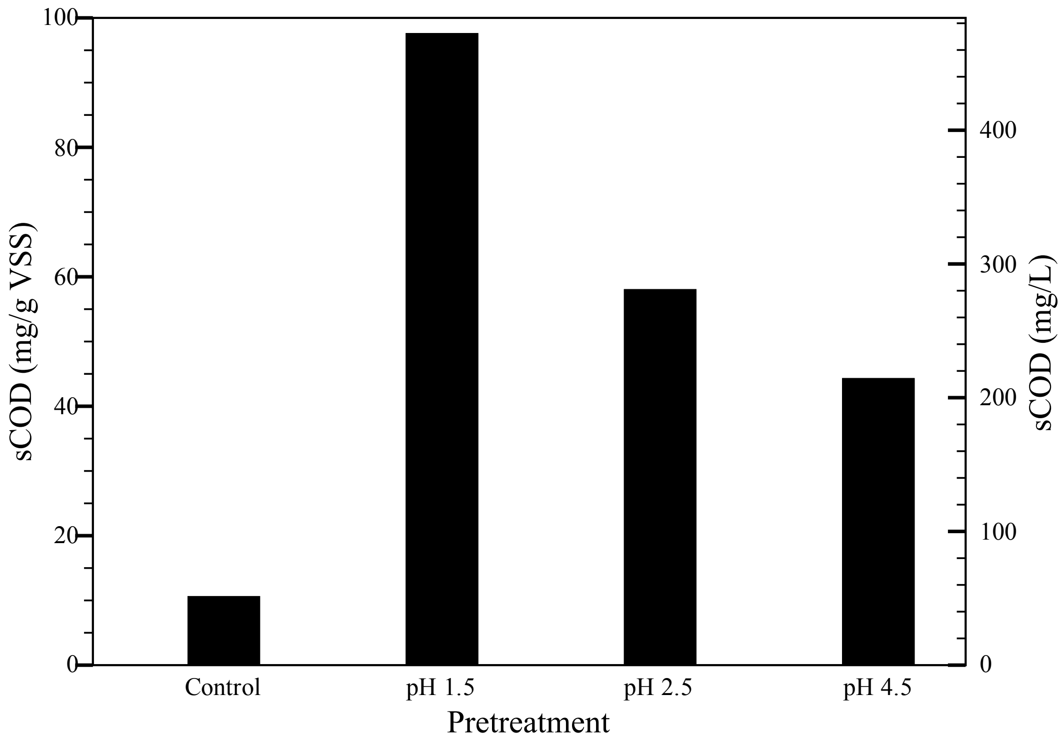

Figure 4-2. sCOD concentration after acidic pretreatment

Effect on Cell Viability

Viability of aerobic microbial cells can be observed by the rate of decrease of soluble oxygen concentration in activated sludge (Lehne *et al.*, 2001). If the rate of change of soluble oxygen concentration is zero, it proves that there is no consumption of present oxygen in the sample, where consumption of oxygen is the indicator of living cells in the activated sludge. This parameter was used as an indirect indication of sludge disintegration.

Since the samples of sludge subjected to pretreatment are activated sludge and aerobic microorganisms, analyzing dissolved oxygen consumption of a sample after application of chemicals is a good way to examine the effect of pretreatment on viable cells. By checking the effect of pretreatment method with oxygen consumption ability of microorganisms shows the success of disintegration for waste activated sludge. In Figure 4-3 the dissolved oxygen concentrations were plotted against time to observe the oxygen uptake rate. pH 1.5 and pH 2.5 showed a constant concentration of around 7.5 - 8 mg/L, whereas for pH 4.5, a slow decrease was observed indicating that only a portion of viability was lost after pH 4.5 treatment compared to untreated sample.

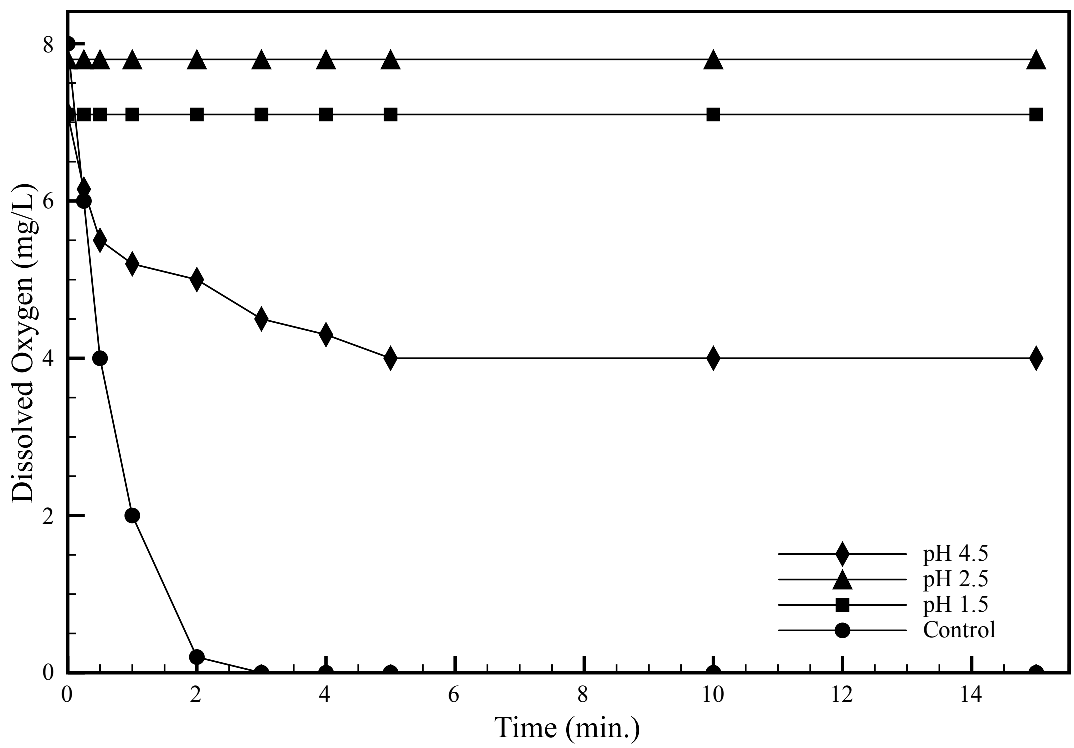

Figure 4-3. Oxygen consumption concentrations after acidic pretreatment

Effect on Cell Disruption Measured by CST

Pretreatment methods are generally known to worsen the dewaterability due to floc disintegration and cell disruption (Müller *et al.*, 2004). In this study, capillary suction time was used as a tool for understanding the disturbing effect of pretreatment. Since pretreatment is aimed to disintegrate cell structure or at least disturb the sludge floc structure, CST is a purposive tool to understand whether sludge structure is disrupted or not. Harder dewaterability of sludge indicates a better disrupted sludge. Therefore, in this study CST analyses in preliminary studies were used for indicating the cell break-up indirectly. Therefore the purpose is not to assess the actual dewaterability but to get an indirect idea about the floc break-up and cell disintegration. In Figure 4-4, pH 1.5 and pH 4.5 are making a contribution to the increase of CST as expected but application of pH 2.5 is decreasing the CST to a value even better than that of control sludge. According to Smith and Göransson (1992) and Weemaes and Verstraete (1998), acidic thermal sludge treatment also provided excellent dewatering characteristics. The results support that pH 2.5 act like a chemical conditioning method more than a pretreatment method.

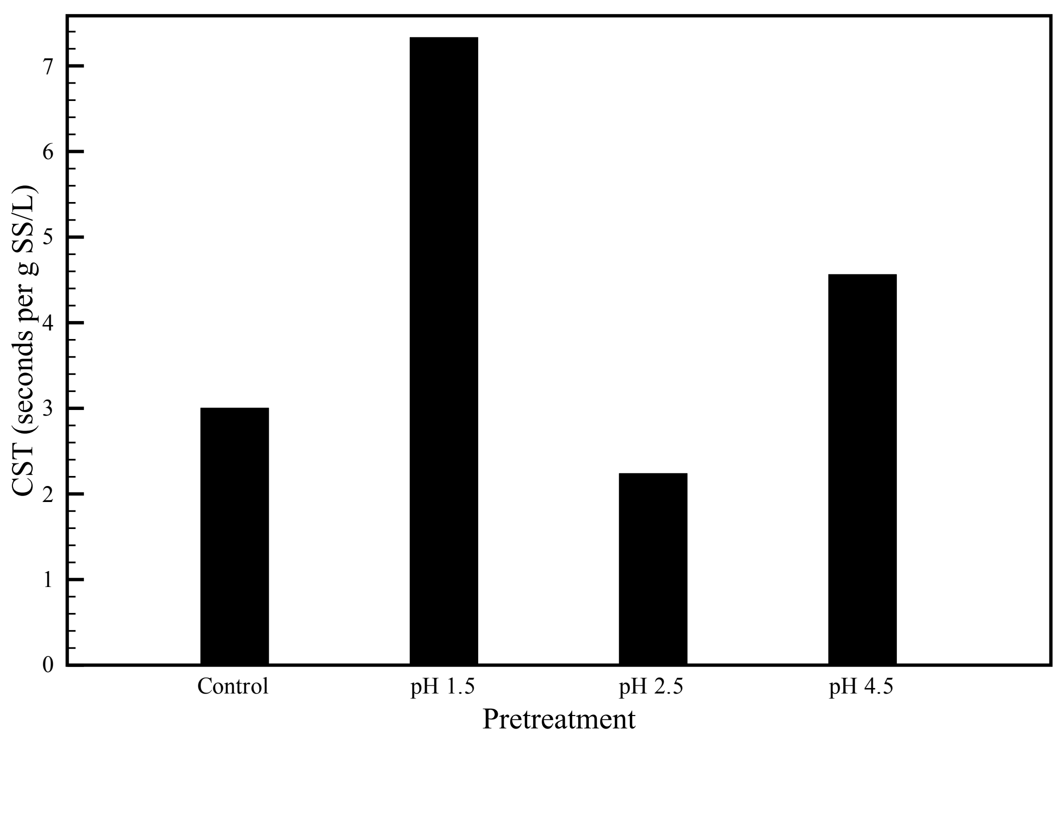

Figure 4-4. Normalized CST values after acidic pretreatment

Effect on Turbidity

Turbidity as a parameter was used as an other indirect indicator just like CST. High turbidity of supernatant indicates the disruption of flocs. Turbidity values for pretreated sludge indirectly point the level of disintegration accordingly. The dewaterability of sludge and turbidity of the supernatant show very similar trends.

Just like the CST values for pH 2.5, turbidity values become lower compared to control values as seen in Figure 4-5. These results are showing a clearer supernatant as expected from a well settling sludge. Other pH values decreased the quality of supernatant 7 times for pH 1.5 and 2 times for pH 4.5. These results indicate that there is a good disintegration, especially at pH 1.5.

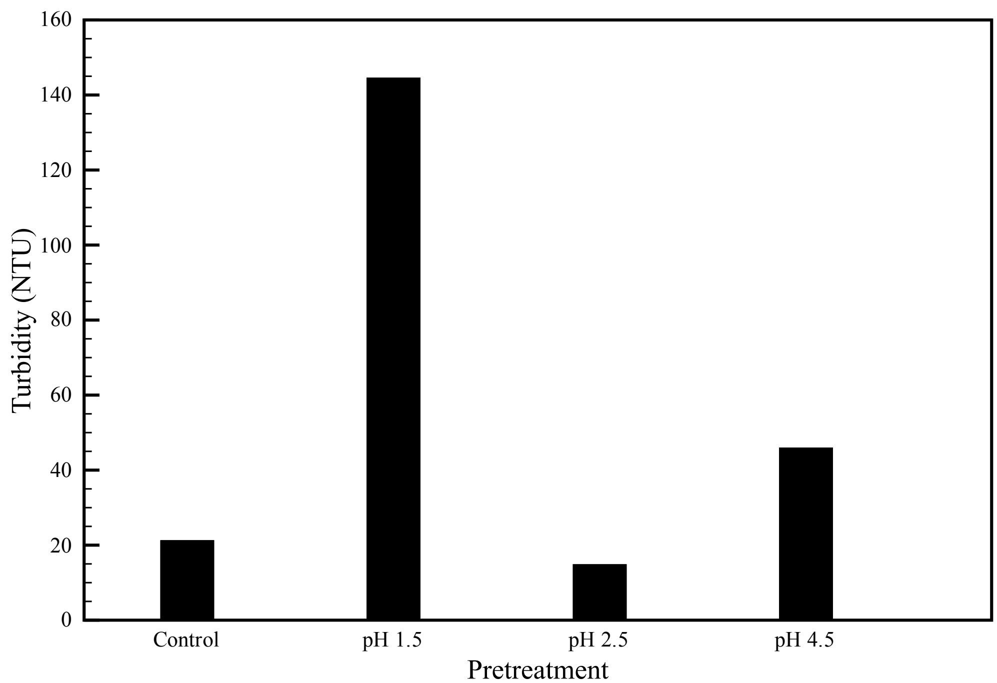

Figure 4-5. Turbidity values after acidic pretreatment

4.1.2 Ultrasonic Pretreatment

Ultrasonication was investigated under two subsections as described in Materials and Methods Chapter. Parameters for disintegration were both evaluated for mild and strong sonication.

4.1.2.1 Mild Ultrasonic Pretreatment

The purpose of applying mild sonication was to uncover the abilities of such a method towards sludge disintegration. The motivation to use a mild ultrasonication (US) was not to develop a method that would be used solely for sludge disintegration. It was already known that such a method would not achieve a great deal of cell disruption to contribute to sludge minimization. Rather, the purpose was to use it with the acidic pretreatment, the performance of which was not very high with the hope that ultrasonication would enhance the effectiveness of acid treatment.

Along with the mechanical effects, an important factor brought in, is the thermal effect during sonication. Ultrasonication is known to increase the temperature of the media dramatically especially at the local level. In order to assess the temperature effects, the temperature profile was checked and presented in Figure 4-6. To avoid a temperature higher than 30 ^{0}C, which would affect the system, maximum treatment time was set to be 5 minutes in this part.

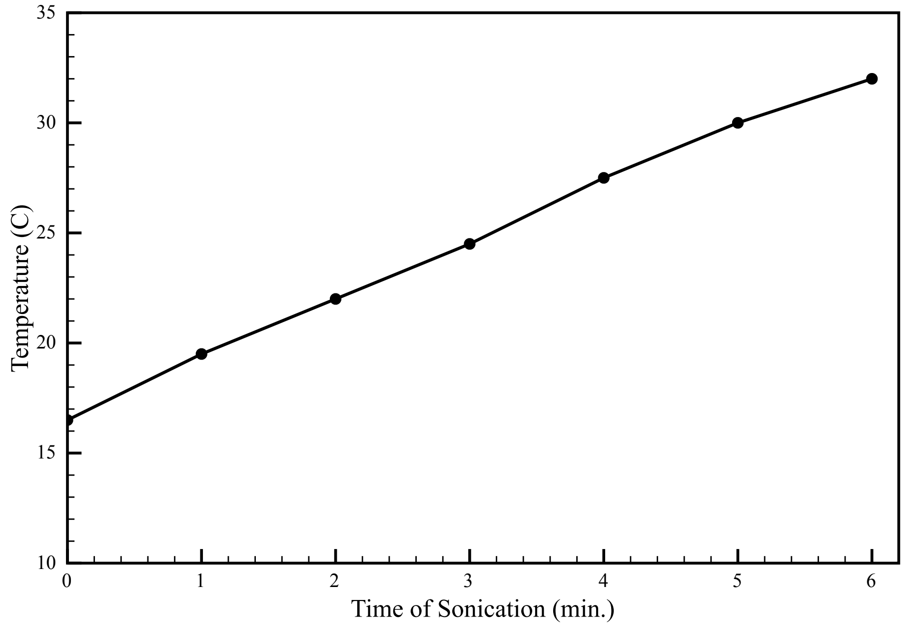

Figure 4-6. Temperature profile for waste activated sludge after mild sonication

Effect on Solubilization of Organics

Mild sonication applications indicated similar solubilization trends with acidic pretreatment in terms of concentrations of sCOD. For acidic pretreatment, increase in the amount of acid added, had enhanced the solubilization; similarly mild sonication changed the sCOD concentration with increasing time of application. However mild sonication as well as acidic pretreatment indicated no significant impact on soluble organic concentration to fulfill one of the ultimate goals of this preliminary study, which was obtaining solubilization of organics effectively.

Chu *et al.* (2002) underlines the importance of strength of sonication and found only a slight increase in solubilization of organics with weak ultrasonication.

Figure 4-7 shows a very slight increase in sCOD as mentioned above due mostly to floc disruption. The intensity of sonication was probably not enough to release intracellular organic material but enough to disrupt floc structure, therefore disintegration occurred up to a certain degree.

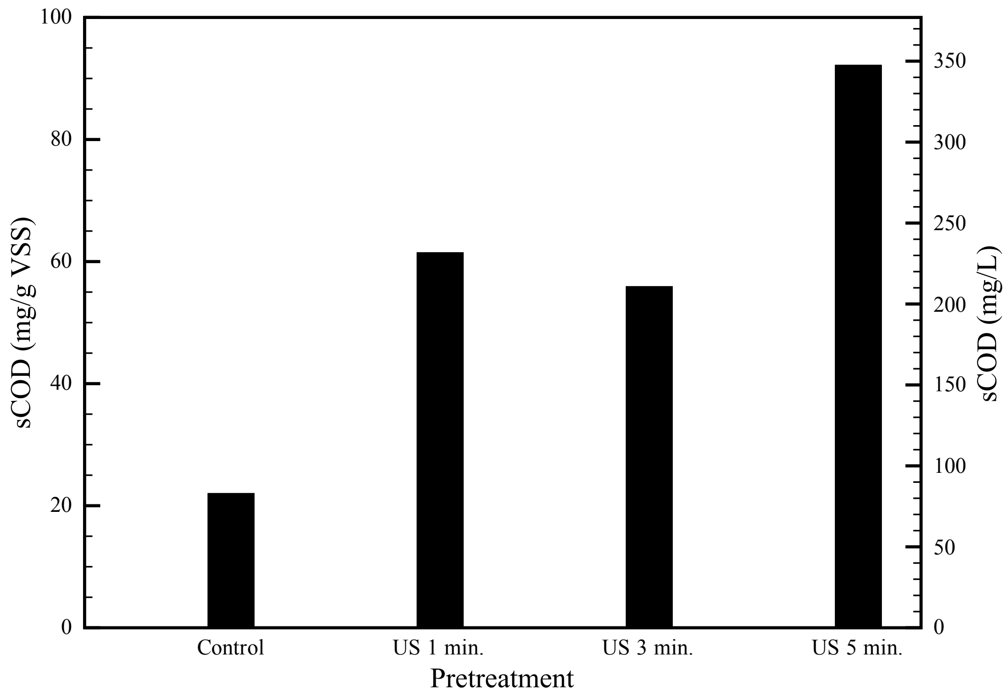

Figure 4-7. sCOD concentration after mild sonication

Effect on Cell Disruption Measured by CST

For further investigations, trends of dewaterability after application of weak ultrasonic pretreatment and subsequent CST values were investigated in Figure 4-8. These results indicate that even an extremely weak pretreatment application provides disintegration in floc structure and an increase in CST values.

A sonication that lasts up to five minute for 60 W of energy input can be counted as a very mild sonication compared to studies conducted previously. Also according to Wang *et al.* (2005) temperature increase is one of four possible pathways of ultrasonic disintegration methods and by controlling and keeping the temperature at reasonable levels thermal effects of ultrasonication on disintegration was aimed to be neglected.

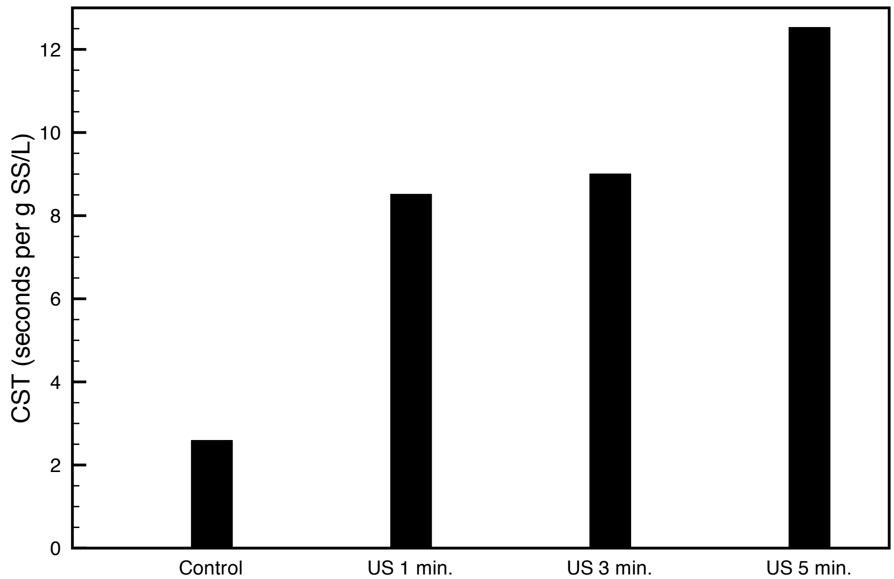

Figure 4-8. Normalized CST values after mild sonication

As seen in Figure 4.8, it is obvious that even a very mild pretreatment method has a positive effect on disintegrating the sludge flocs; consequently this is decreasing the dewaterability.

Effect on Turbidity

Figure 4-9 shows a dramatic increase of turbidity after 1 minute of sonication. This distinct increase keeps on with time up to 5 minutes and turbidity values climb to 2000 NTU. The disruption of floc structure and/or disintegration of cell wall lead to a turbid supernatant of settled sludge. Even subsequent turbidity results of mild ultrasonication support this statement.

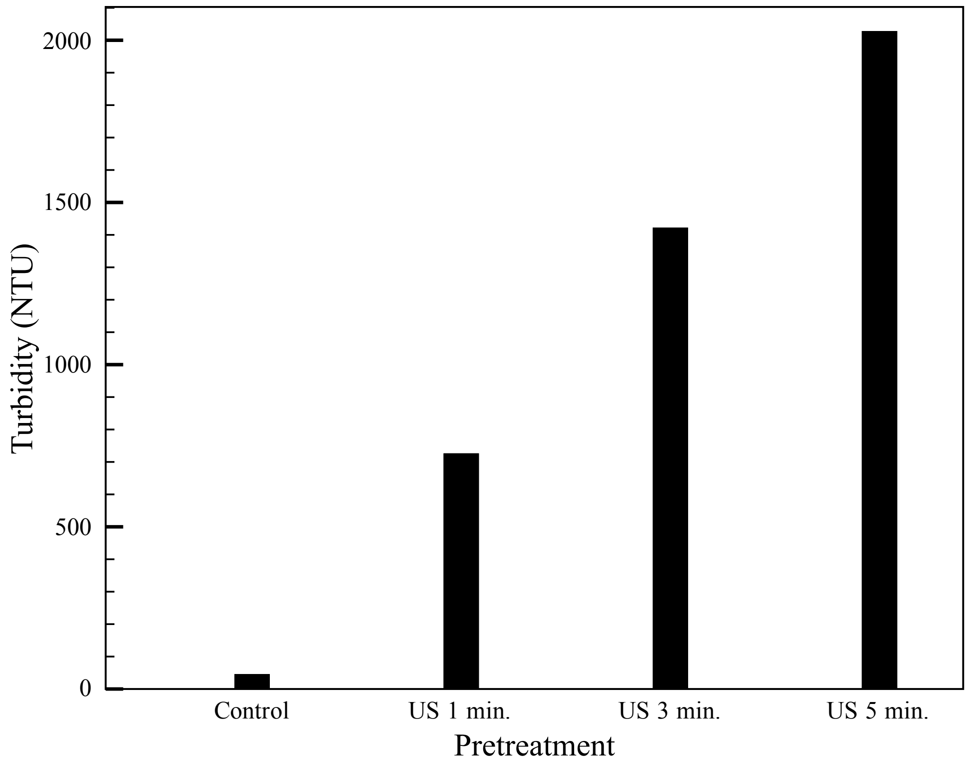

Figure 4-9. Turbidity values after mild sonication

4.1.2.2 Strong Ultrasonic Pretreatment

Since mild sonication resulted with no significant benefits on disintegration, the intensity of sonication was decided to be increased. In this part effects of temperature were disregarded because, control of temperature in a real life sonication application is not realistic. Thus, temperature went up to 80 ^{0}C during sonication process as seen on Figure 4-10.

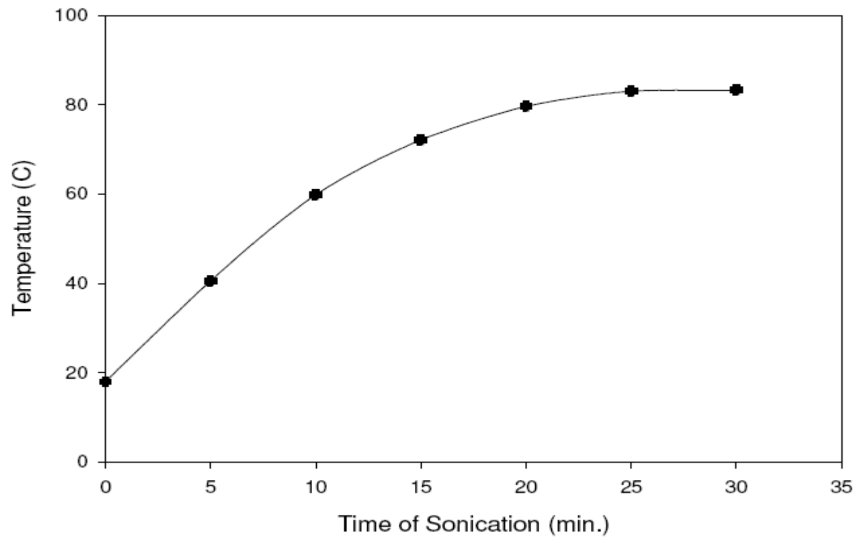

Figure 4-10. Temperature profile for waste activated sludge after strong sonication

Effect on Solubilization of Organics

As seen in Figure 4-11, degree of disintegration increases until 15 minutes of sonication and indicates a fluctuating trend with increasing time of sonication. It can be observed that climax of soluble COD can be achieved by 15 minutes of strong sonication.

Show *et al.* (2006) applied very similar sonication density for 1 minute and doubled the amount of soluble organics. In this study 15 minutes of sonication enhanced 50 mg/L sCOD up to a value of 2500 mg/L. Longer sonication times lead to more complex chemistry and result with fluctuations in terms of sCOD. The decrease after 15 minutes of sonication are most probably due to the thermal effects of sonication and entrapment of organics into floc structure.

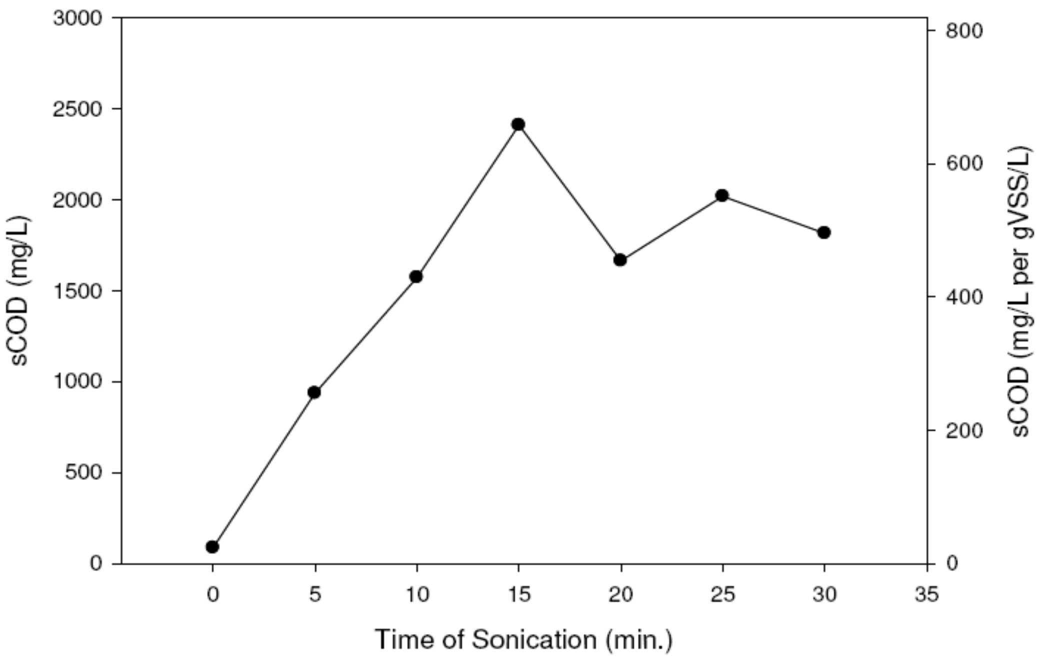

Figure 4-11. sCOD concentrations after strong sonication

Effect on Cell Disruption Measured by CST

The dramatic increase of CST can be observed up to 10 minutes of sonication also decrease after 15 minutes of sonication can be due probably to reflocculation and thermal conditioning. Worsening of dewaterability by a factor of 8 to 9 compared to untreated sludge can be seen in Figure 4-12.

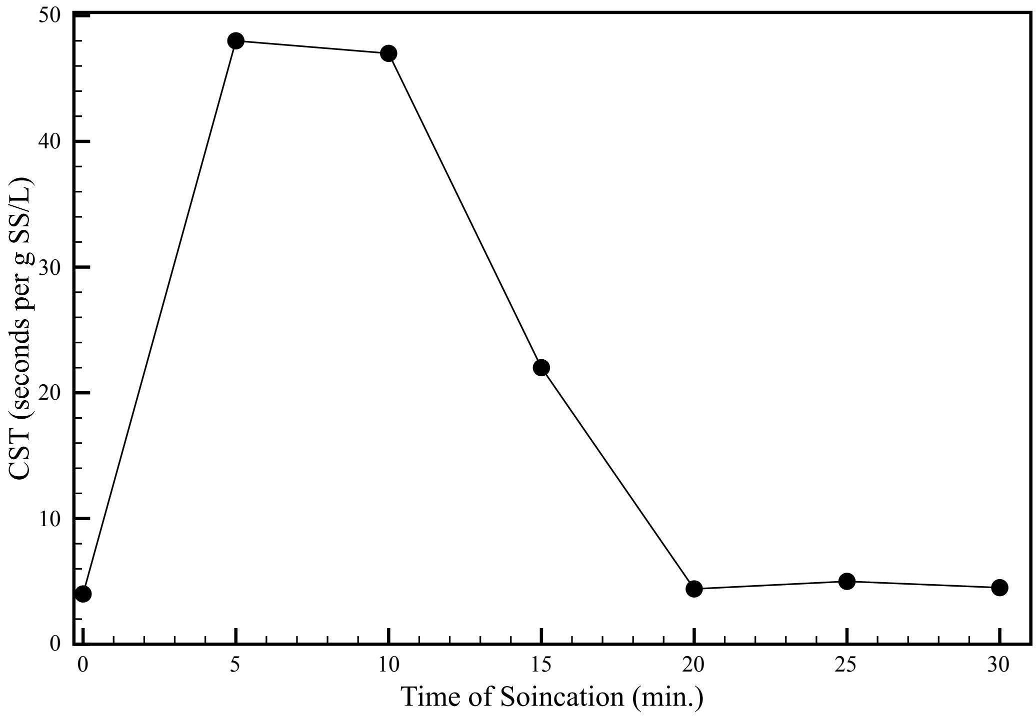

Figure 4-12. Normalized CST values after strong sonication

Chu *et al.* (2001) found 0.33 W/mL of sonication cause approximately two times longer capillary suction time after 40 minutes of ultrasonic pretreatment. Reason of relatively small increase of CST after 20 minutes sonication in Figure 4-12 might be the same with the study of Chu *et al.* (2001) which is thermal conditioning of the sample due to high temperatures.

Effect on Turbidity

The turbidity values climbed up to 2500 NTU as seen in Figure 4-13. The dramatic increase was observed in first 5 minutes, when compared with mild sonication, one should expect to see a similar trend with dewaterability in stronger sonication too, however, stronger sonication has major temperature effect due to uncontrolled temperature rise this time and dewaterability is fluctuating; on the contrary turbidity is continuously increasing.

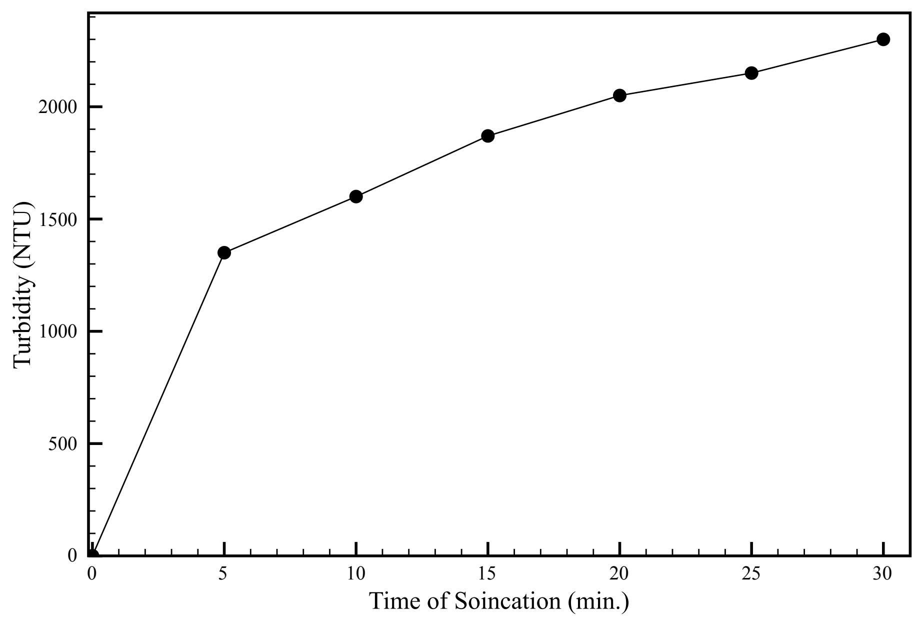

Figure 4-13. Turbidity values after strong sonication

4.1.3 Combination of Acidic and Ultrasonic Pretreatment

In Sections 4.1.1 and 4.1.2, pretreatment methods were separately evaluated and results showed that acidic pretreatment had a very low performance compared to ultrasonic pretreatment methods for enhancing the solubility of sludge. Primary requirement of a pretreatment method is the effectiveness of solubilization prior to digestion, however acidic pretreatment was not capable of dissolving organic matter effectively.

By combining sonication and acidic pretreatment methods, the synergistic improvement of sludge disintegration is aimed by disturbing the floc structures and releasing organic matter into liquid phase and consequently, decrease the overall consumption of energy and chemical.

This combination was expected to improve the performance of acidic pretreatment by application of ultrasonic waves mildly and disintegrating the flocs to release the entrapped organics. Additionally, the physical characteristics of the pretreated sludge was expected to be much better, compared to single ultrasonic pretreatment.

Briefly, the aim of integration of these two separate methods was to cancel the negative physical effects of ultrasonication and improving the solubilization rate of acidic pretreatment and obtaining an overall decrease in the application time or energy of ultrasound.

Effect on Solubilization of Organics

When the solubilization of organics from waste activated sludge was examined by the combined method, results were not synergistic in terms of solubilization of organics. Evaluating Figure 4-14, one can see that single mild ultrasonication is the peak value even with the combined methods applied. The lower the pH value, the worse the solubilization was indicating the antagonistic effect of acid on ultrasonic treatment causing decrease in sCOD with the addition of acid.

The evaluation of acidic pretreatment, mild and strong ultrasonic pretreatment and combination of mild ultrasonic and acidic pretreatment methods shows that acidic pretreatment is not an effective way of sludge disintegration but a nice way of sludge conditioning.

Ultrasonic pretreatment is quite effective than acidic pretreatment unless acidic pretreatment is combined with.

Due to antagonistic combination of acidic and mild ultrasonic pretreatment, single sonication with strong enough power was decided to be further evaluated.

Therefore, the study will focus on the selection of optimum pretreatment time of strong sonication in the following chapters.

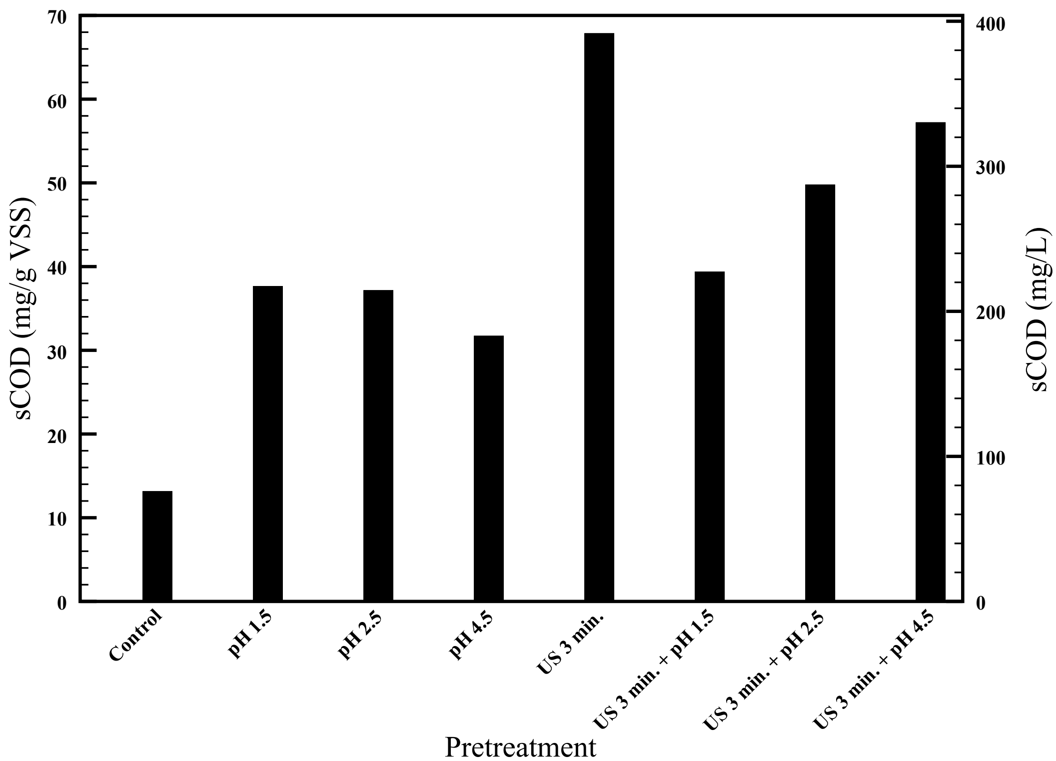

Figure 4-14. sCOD concentrations after combination of mild ultrasonic and acidic pretreatment

Effect on Cell Disruption Measured by CST

Flocculant property of low pH was argued on acidic pretreatment part in detail. When combined with mild ultrasonic pretreatment this advantageous property seems like effective as anticipated.

Lowest CST values were achieved when pH 2.5 is present within the treatment method (Figure 4-15). Free from sonication time, pH 2.5 enhanced the dewaterability when combined with ultrasound as compared to ultrasound only. Compared to single sonication values, all acid additions improved the dewaterability. Best pH value was detected to be pH 2.5 whereas worst pH was detected as pH 4.5 in terms of dewaterability. These results show quite similar trends with single acidic pretreatment.

Subsequent dewaterability of mildly sonicated sludge can be improved by pH 2.5 application. This can be interpreted in two ways. Either a utopic ultrasonic pretreatment resulting with good dewaterability and low energy consumption or a reflocculation and antagonistic effect of combination of two methods. The solubilization values will play a decision-making role on optimizing the best available pretreatment method.

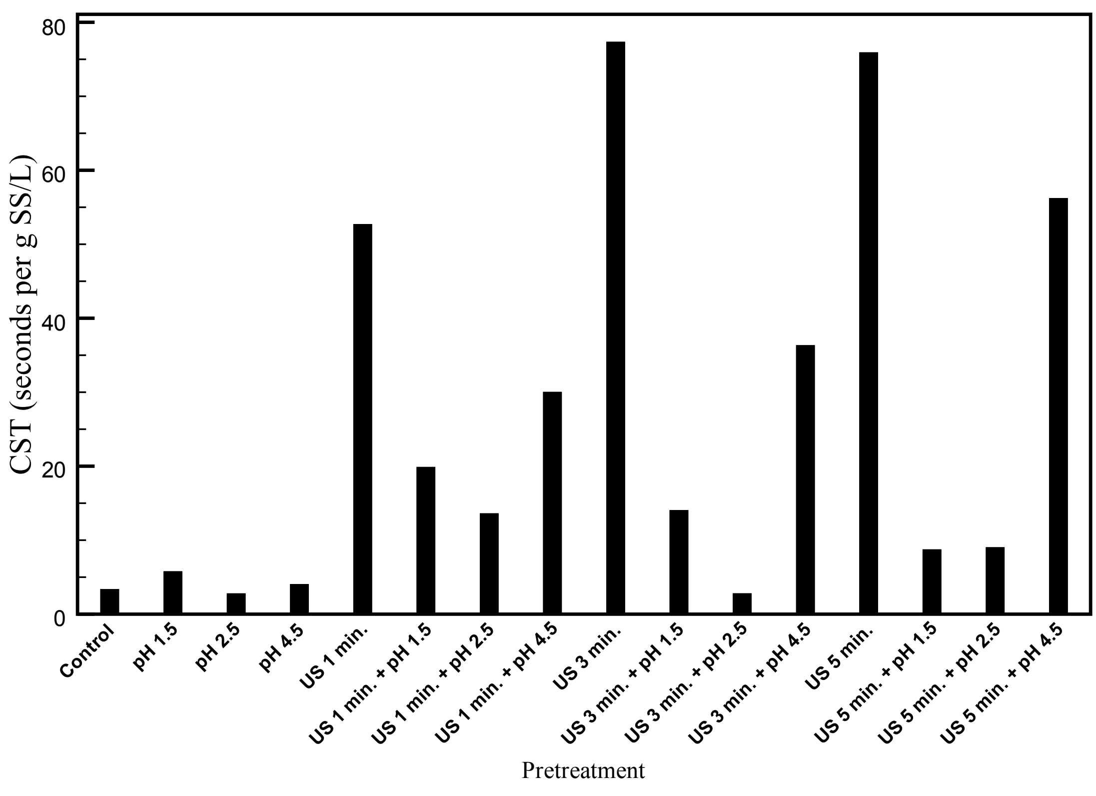

Figure 4-15. Normalized CST values after combination of mild ultrasonic and acidic pretreatment

Effect on Turbidity

Reactions of activated sludge to combination of pretreatment methods on dewaterability show very similar results to turbidity values as seen in Figure 4-16. Not only single acidic pretreatment but also combination of mild sonication with acidic pretreatment improves the quality of supernatant. Moreover, pH 1.5 and pH 4.5 as well as pH 2.5 decrease the supernatant turbidity. Also, increasing time of sonication generally increase the turbidity at all pH values.

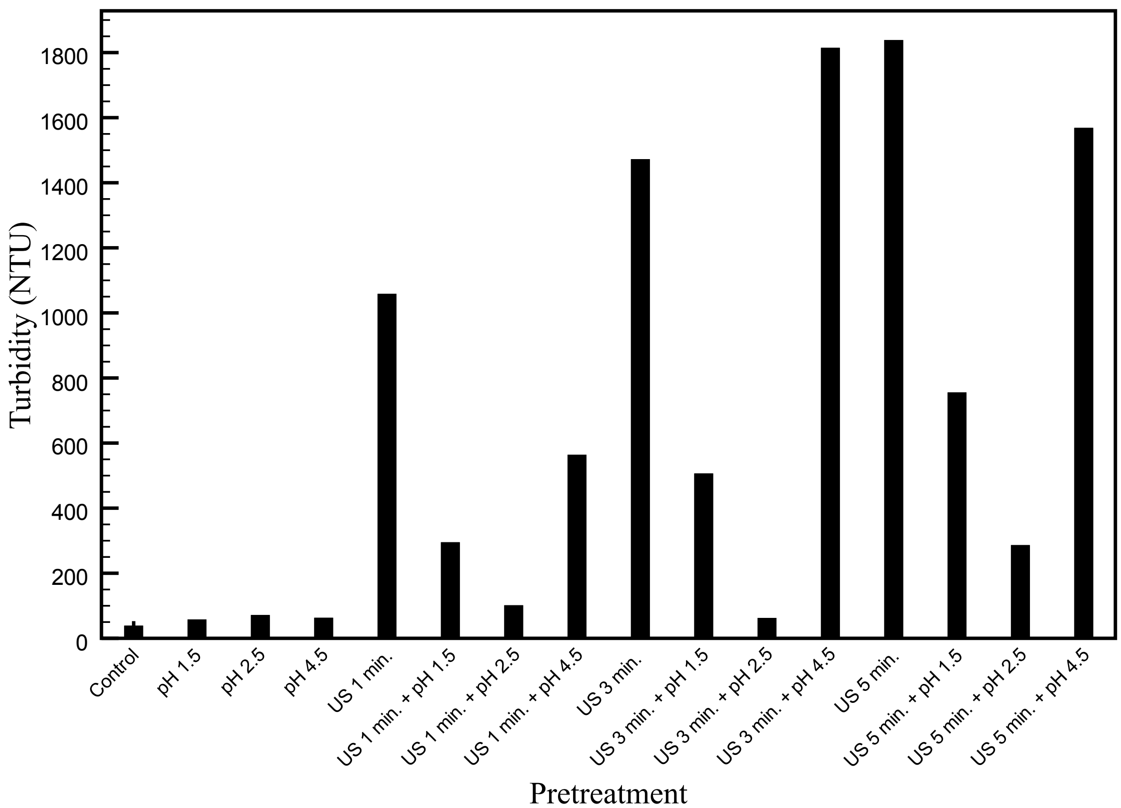

Figure 4-16. Turbidity values after combination of mild ultrasonic and acidic pretreatment

These results support that combination of mild sonication and acidic pretreatment contribute positively to the physical characteristics of sludge such as dewaterability and turbidity. On the other hand, these parameters are indirect indicators of pretreatment; a better settling sludge or a clearer supernatant are not the primary objectives of preliminary studies; even though they are desirable qualities after solubilization of sludge.

4.2 Biochemical Methane Potential (BMP) Test

BMP test was performed in order to investigate the subsequent digestibility of pretreated sludge and during these investigations, separate acidic and ultrasonic methods were investigated. Since the combined method acted mostly antagonistically, the BMP tests were not conducted with the combined method.

4.2.1 Biochemical Methane Potential (BMP) Test for Acidic Pretreatment

Acidic pretreatment was less effective than ultrasonic pretreatment in terms of solubilization of organics as discussed in the preliminary stages of the study and even the combination of acidic and ultrasonic pretreatment methods were not able to enhance acidic pretreatment. Therefore, unless there is an unexpected effect of acidic pretreatment method, anaerobic digestibility was expected to be relatively lower.

Biogas Production and Content

Figure 4-17 and Figure 4-18 show the total biogas production and methane production of BMP reactors, respectively. No significant improvement was achieved; on the contrary control reactors produced higher amounts of gases in 47 days of reactor operation period. Apart from improvement, 6 -15 % decreases in methane production were observed in acidic pretreatment reactors.

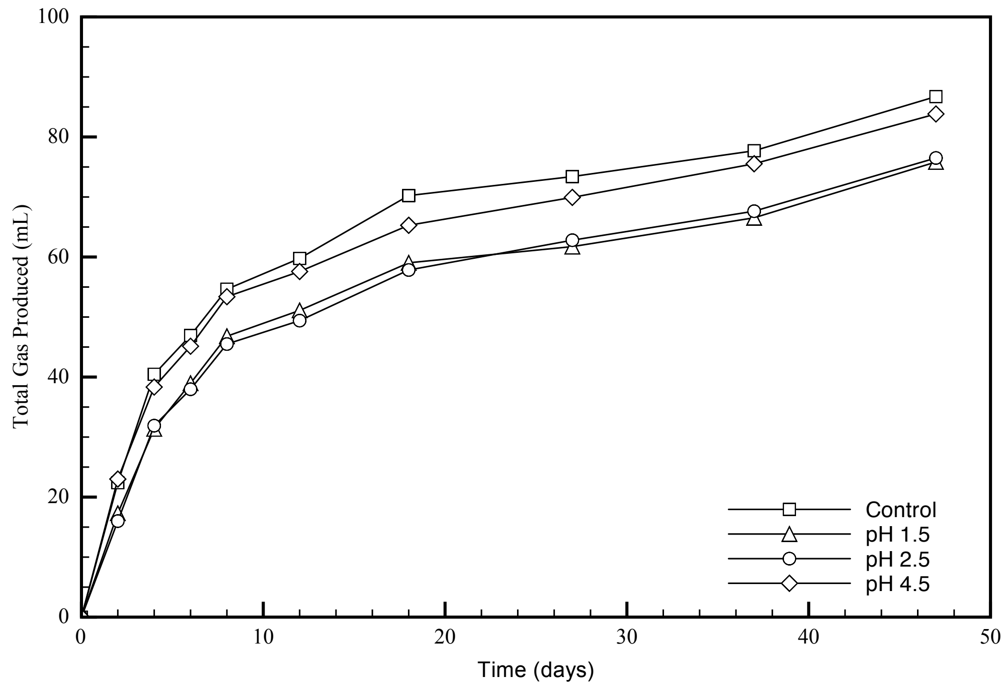

Figure 4-17. Total biogas production during BMP test for acidic pretreatment

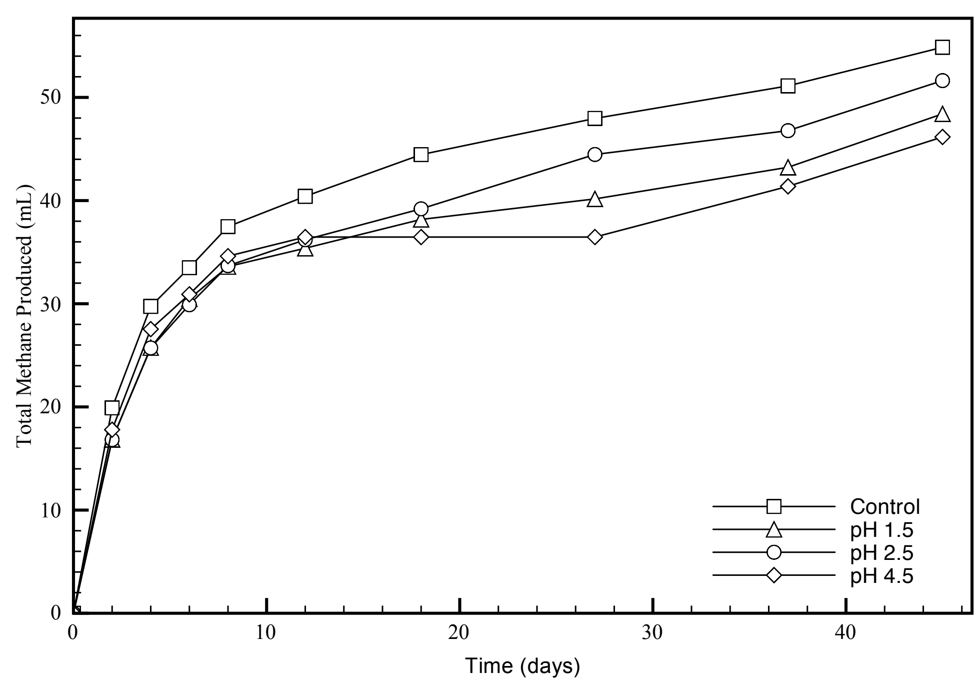

Figure 4-18. Total methane production during BMP test for acidic pretreatment

4.2.2 Biochemical Methane Potential (BMP) Test for Ultrasonic Pretreatment

Biogas Production and Content

Figure 4-19 shows the biogas production of untreated and sonicated (with strong sonication) sludge samples in batch reactors during 49 days of digestion. The final production results show the highest biogas production was achieved after 15 minutes of sonication however when Figure 4-20 is inspected, the difference of methane production makes it hard to use gas production as a parameter for decision making.

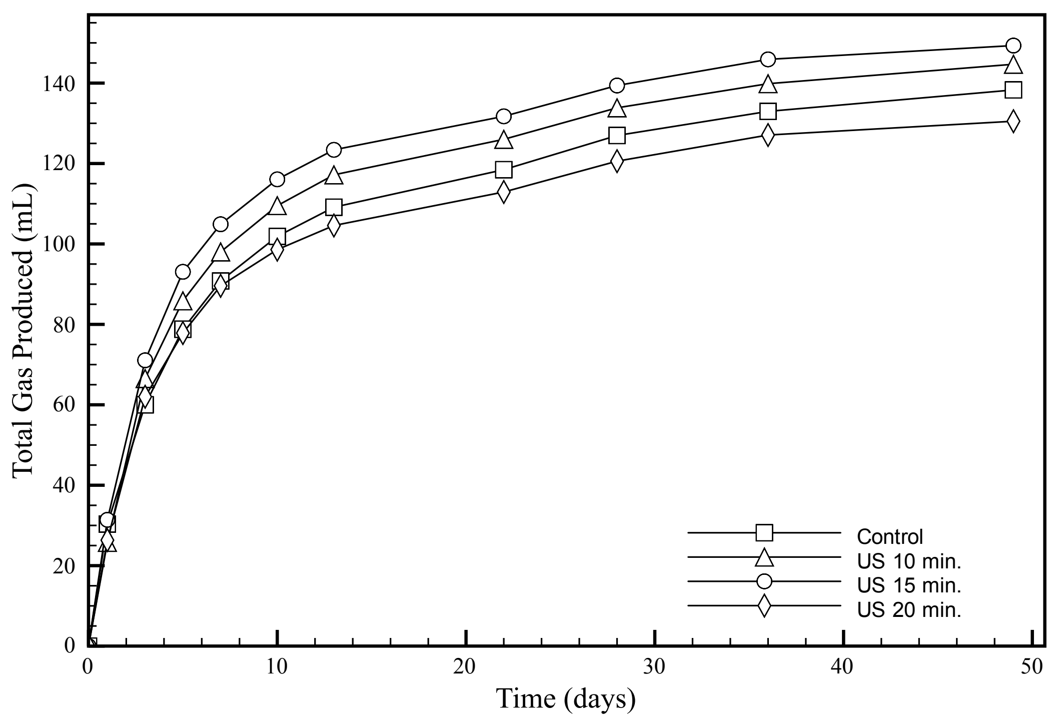

Figure 4-19. Total biogas production during BMP test for ultrasonic pretreatment

Figure 4-20 is the daily methane production during 49 days of digestion period. Although there is an improvement after 10 minutes and 15 minutes of sonication compared to control reactors, it is difficult to come up with distinct conclusions about the relationship of time of sonication and anaerobic digestion with single batch test results. Also there is a slight decrease in 20 minutes of sonication similarly in soluble COD concentrations there used to be a decrease in 20 minutes as seen in Figure 4-11 previously.

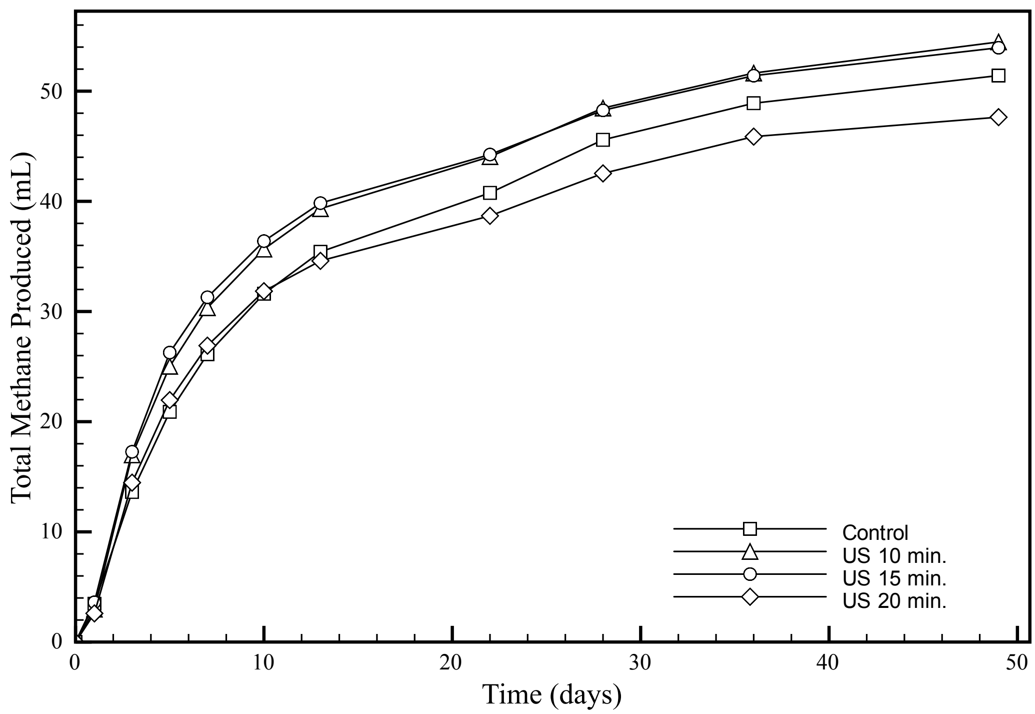

Figure 4-20. Total methane production during BMP test for ultrasonic pretreatment

Total COD (tCOD) Content

Table 4.1 shows the tCOD removal percentages of untreated and sonicated batch reactors during 49 days of digestion period. All pretreated reactors show consistently higher removal of COD in the reactors. The inconsistency between the methane production and the COD reduction can be explained by experimental errors since the difference between the gas production of pretreatment reactors are low and hard to comment on.

In summary, the COD removal of batch tests does not solely point a specific treatment time neither do the biogas production. Results from the preliminary studies must also be involved in selecting the treatment time.

Table 4.1. Influent and effluent COD concentrations and relative COD reductions of batch reactors

	Control	**US 10 min.**	**US 15 min.**	**US 20 min.**
Initial COD (mg/L)	8970	8270	8240	8245
Final COD (mg/L)	6503	5695	5732	5467
COD reduction (%)	27.50	31.14	30.44	33.70

4.3 Semi-Continuous Anaerobic Reactors

Although results of BMP test point both the 10-minutes and 15-minutes of sonication with a very small difference on biogas production, the preliminary tests indicate that there is a significant difference in COD solubilization ability of sonication at 15-minutes compared to 10-minutes. Thus, *US 15 min.* was decided to be further investigated in semi-continuous reactors from all the pretreatment methods studied.

Three sets of experiments with different operational parameters were conducted in this part. All sets are investigated according to VS reduction, COD reduction, biogas production, soluble COD concentrations, MLVSS values and pH changes. The VS and COD reduction data, biogas and methane production data as well as other tabulated data such as MLVSS reduction belong to defined steady state conditions.

Even though reactors with SRT of 7.5 days and OLR of 0.5 kg VS/m^{3}d were working under critically limiting conditions, our study showed that by pretreatment, the performance of these reactors can be significantly increased approaching and surpassing the performance of untreated control reactors operated with more favorable conditions.

All average values that were tabulated and summarized were calculated from the data gathered during steady state conditions.

4.3.1 Set I

Reactors were operated by daily constant feeding and wasting to satisfy the operational conditions of *Set I* and the findings are reported below.

VS Content

To satisfy the required OLR (0.5 g/m^3.d), a theoretical influent VS concentration was calculated as 7518.79 mg/L and plotted as a straight line on Figure 4-21. The effluent VS concentration shows sharp decrease for pretreatment, Pr_A and Pr_B reactors as compared to influent, on the contrary VS concentrations of control, C_A and C_B, increase for about 25 days. The operation took approximately 1.5 months (3 SRT) to reach to a steady state. Since the reactors were fed with the same concentration of VS, the difference after reaching steady state is due only to pretreatment.

The summary of *Set I* in terms of VS reduction are tabulated in Table 4.2. The VS reduction percentages were calculated by processing the steady state data of influent and effluent VS concentrations. Briefly control reactors used to have 44.76 % VS reduction whereas pretreatment reactors have 55.76 % VS reduction. These average values show an enhancement of 24.58 % in VS reduction by pretreatment. The improvement of VS reduction from 21.5 % to 22.7 % of another study of Tiehm *et al.* (2001) had achieved quite similar results to this study.

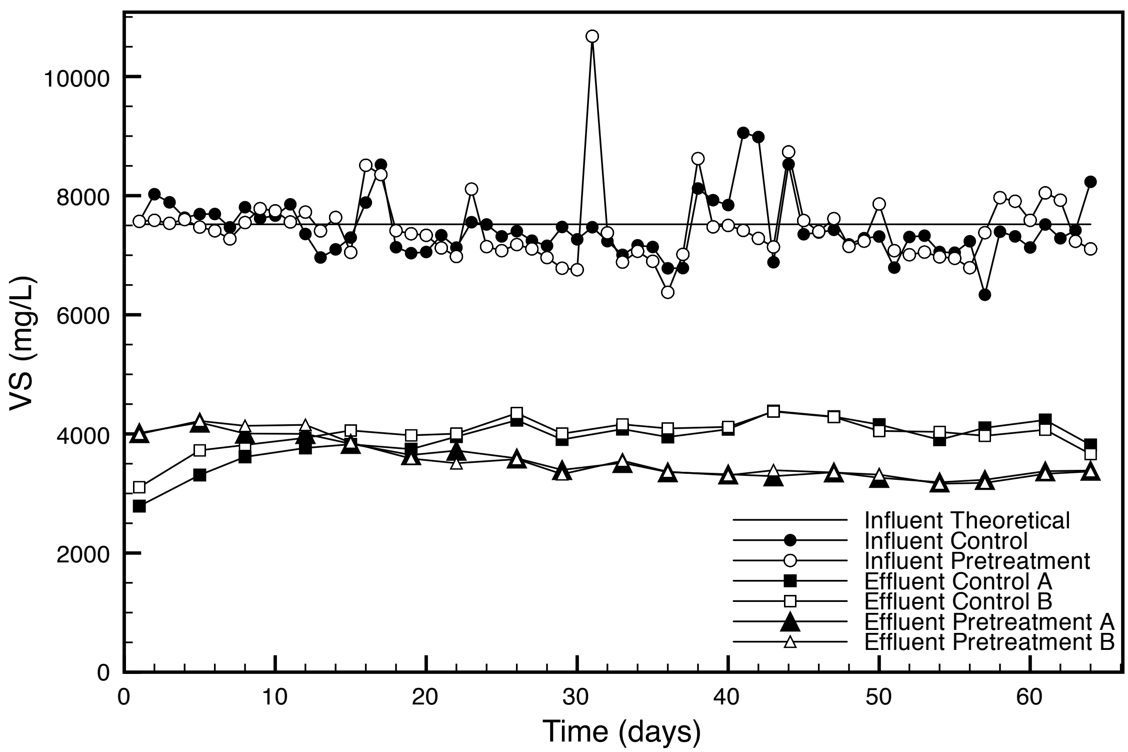

Figure 4-21. Influent and effluent VS concentrations for *Set I*

Table 4.2. Influent and effluent VS concentrations and relative VS reductions of *Set I*

	C_A	C_B	Pr_A	Pr_B
Influent VS (mg/L)	7273.67 ± 428.60	7273.67 ± 428.60	7409.00 ± 456.97	7409.00 ± 456.97
Effluent VS (mg/L)	4013.25 ± 189.99	3933.00 ± 186.84	3294.25 ± 100.02	3260.50 ± 104.78
VS reduction (%)	44.21	45.30	55.51	56.00

Biogas Production and Content

The daily biogas production values reach the steady state at a longer time period than expected (Figure 4-22). Even though large amounts of initial fluctuations were observed, after about 3 times SRT, gas production data from the pretreatment reactors exceeded the gas production data from control reactors and the gap became clearer.

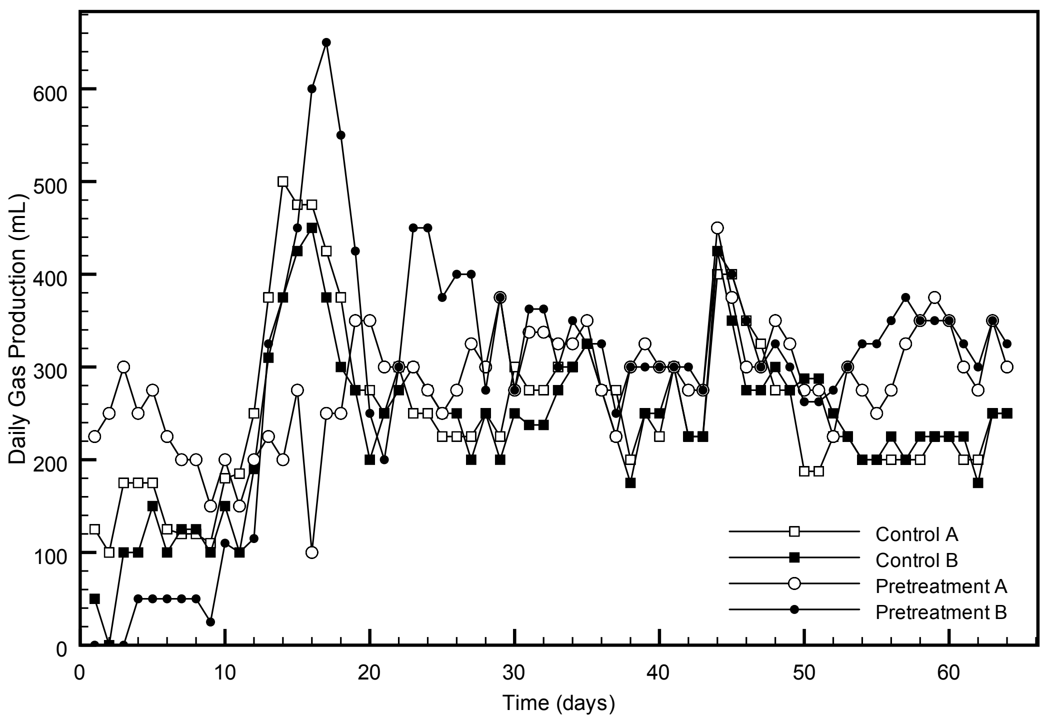

Figure 4-22. Daily biogas production of *Set I*

Figure 4-23 indicates the importance of daily gas production differences in a cumulative manner. If the trend line is projected even to the future, overall difference between control and pretreatment reactors becomes more significant obviously. Only 64 days of operation created 3 - 4 L of volumetric biogas production difference in a 2 L size reactor.

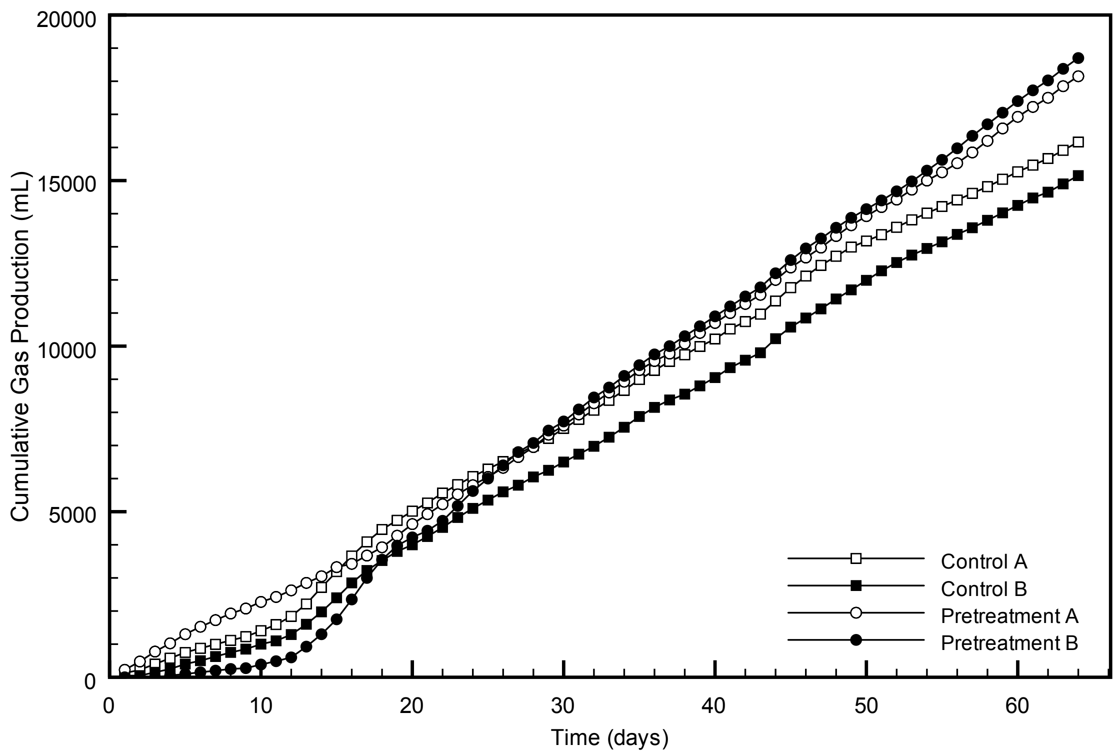

Figure 4-23. Cumulative biogas production for *Set I*

The steady state daily biogas production graph was replotted in a larger scale in Figure 4-24. Depending on the feed characteristics, daily variations in an acceptable range were observed during steady state but an obvious improvement on biogas production was recorded for pretreatment reactors compared to control reactors. The reason for the apparent difference between replicates of Control reactors (C_A and C_B) is the leakage of approximately total 600 mL of gas into 'Control B' reactor during operation.

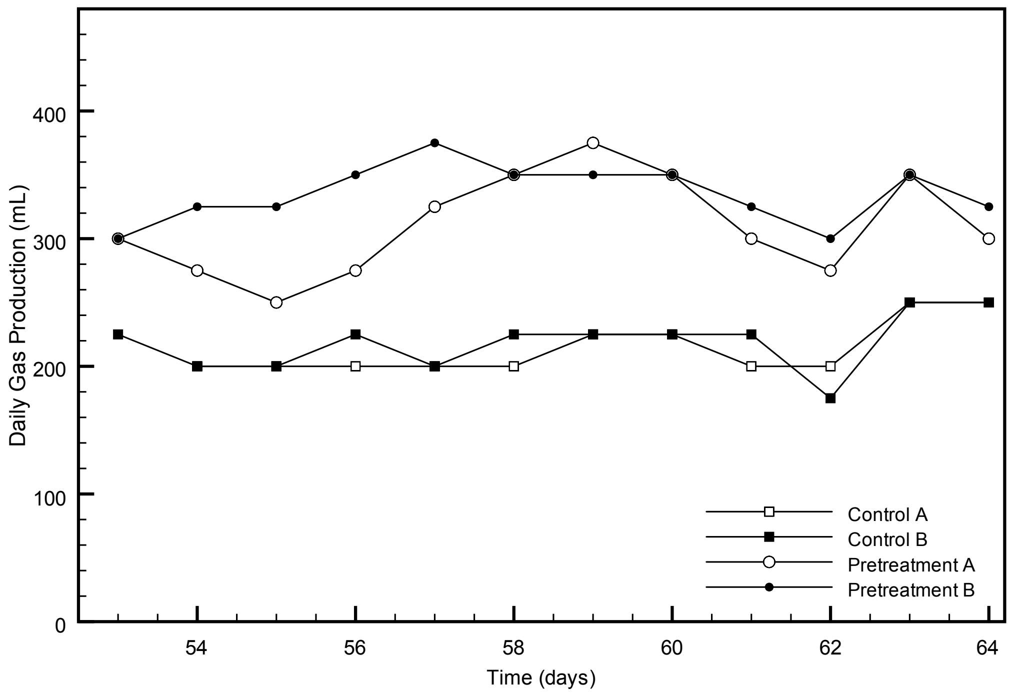

Figure 4-24. Daily biogas productions of *Set I* at steady state

Figure 4-25 is presenting the daily methane production volumes at steady state. The plots of total biogas and methane are quite similar as expected. However the difference between control and pretreatment reactors is greater since the methane content in pretreatment reactors is also higher than in control reactors.

Table 4.3 is a tabulated summary of average total gas production, methane percentage of biogas, calculated methane production and biogas production per removal of grams of VS. The pretreatment is not only enhancing the total gas production but also enriching the methane content of the produced biogas.

The methane production had been enhanced approximately 76% compared to control reactors and the overall improvement of biogas production is 50% where Xie *et al.* (2007) achieved 45% improvement in biogas production in a real treatment plant by ultrasonic pretreatment. Higher enhancements should be expected in real case studies than in laboratory studies. Moreover, since the biogas is rich in methane, the improvement of methane production increases up to 75% in sonicated reactors.

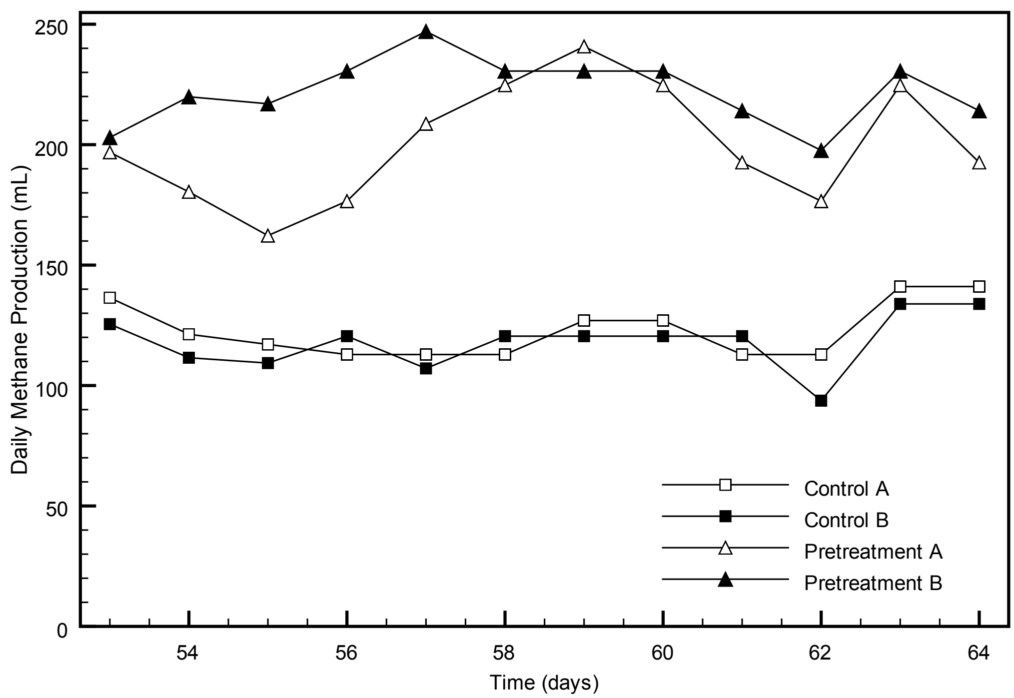

Figure 4-25. Daily methane productions of *Set I* at steady state

Table 4.3. Daily average biogas production and methane content of *Set I* - steady state data

	C_A	C_B	Pr_A	Pr_B
Daily Gas Production (mL)	215 ± 19.8	219 ± 21.7	313 ± 39.1	335 ± 22.5
Methane Percentage (%)	58.5 ± 2.97	54.7 ± 1.57	64.9 ± 0.99	66.8 ± 1.26
Daily Methane Production (mL)	123 ± 11.4	118 ± 11.4	200 ± 24.5	222 ± 13.8
mL CH_4/g VS removed	284	266	366	403

To comment on the methane production volumes per grams of volatile solid removed; there is an increase of 40 % in sonicated reactors relative to control reactors.

According to another study conducted in our laboratory, control and thermal pretreatment reactors used to produce 332 and 374 mL CH_4/g VS removed respectively (Doğan, 2008), whereas; the theoretical amount is around 700 mL CH_4/g VS. According to Parkin and Owen (1986) this type of variations are most probably due to practical and analytical handicaps of particular steps of the study.

tCOD Content

Total COD reduction efficiency increase after sonication in anaerobic reactors. The average COD reduction is increased from 47.67 % to 52.78 %, which is a relative 10.72 % improvement of COD removal in an anaerobic digester as seen in Table 4.4.

Methane production per gram of COD removed shows 57.78 % enhancement with sonication. The volatile solids removal efficiencies show similar improvements indicating the consistency of these results. Theoretically, at 35°C, 395 mL of methane is produced per 1 g of COD removed (Speece, 1996). However, the numbers in Table 4.4 are consistently lower than this theoretical value and this could be explained by the consumption of organics resulting in growth of new bacterial cells (Parkin and Owen, 1986).

Table 4.4. Influent and effluent COD concentrations and relative COD reduction of *Set I*

	C_A	C_B	Pr_A	Pr_B
Influent COD (mg/L)	13588 ± 892	13588 ± 892	13568 ± 1115	13568 ± 1115
Effluent COD (mg/L)	7448 ± 944	6775 ± 77.8	6423 ± 484	6390 ± 836
COD reduction (%)	45.2	50.1	52.7	52.9
mL CH_4/g COD removed	151	130	211	233

sCOD Content

Initially the soluble organics accumulate in the reactors to the end of lag period. This accumulation improves the soluble COD values up to 2500 mg/L for about 12 days as seen in Figure 4-26. After methanogens start consuming the accumulated bioavailable food there is a sharp decrease of sCOD until 25 days. This sharp decrease concurrently produces high volumes of biogas as seen in Figure 4-22. The outlier data observed in 40th day of operation for *Pretreatment B* is due probably to an experimental error since there is no other indication of that unexpected peak in the data flow of gas production or reactor operation. When the reactors reach steady state there were no significant difference in sCOD concentrations, indicating a proper operation of reactors with consumption of sCOD effectively for both reactors.

sCOD corresponds to the organics in the digester supernatant, which is typically returned to the head of the treatment plant for an actual plant operation. From the findings of this part, it is obvious that the pretreatment reactor produces no extra load compared to the control reactor.

Protein Content of sCOD

According to Pavlostathis and Giraldo-Gomez (1991) dry matter of activated sludge consists of 32% to 53.7% crude protein, which means that protein is a major ingredient of organics in activated sludge. Therefore one can think that when COD solubilization is high, the protein content and carbohydrate content of the supernatant increases too. Due to this, a dramatic increase in the effluent concentration will lead to an additional load on the whole treatment process.

According to Wang *et al.* (1999) significant release of protein after digestion in the aqueous phase was observed as expected since however as seen in Figure 4-27, 16.8 % average increase was observed in protein concentrations in pretreated digesters when compared to control reactors.

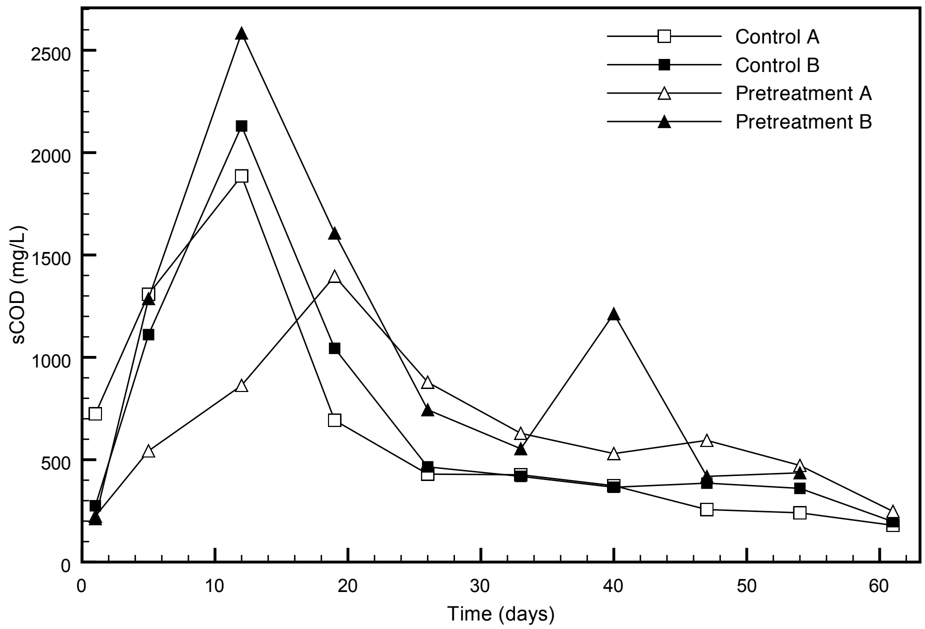

Figure 4-26. Daily sCOD concentrations for *Set I*

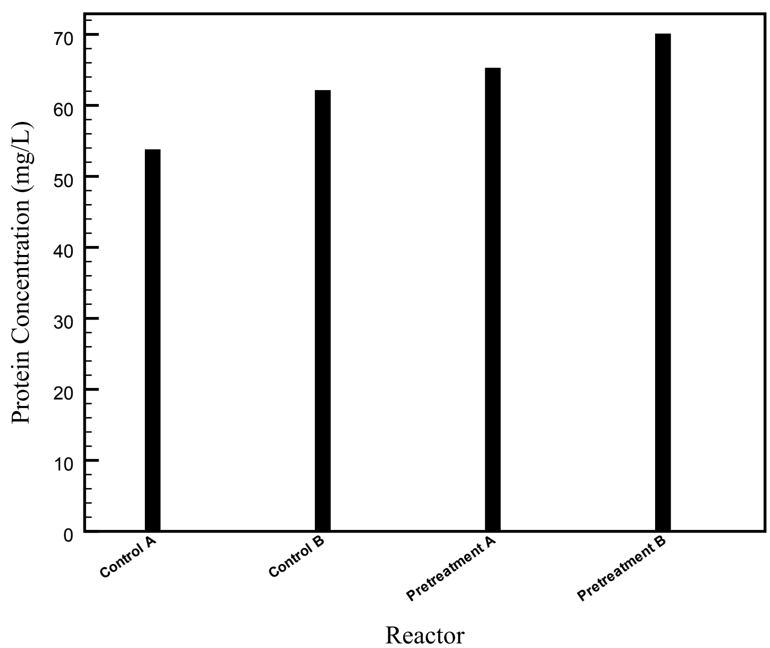

Figure 4-27. Protein concentrations at the end of *Set I*

Carbohydrate Content of sCOD

According to Pavlostathis and Giraldo-Gomez (1991), 7 % of dry matter in activated sludge can be accounted for total carbohydrates. The correlation between protein and carbohydrates show that 4.5 to 7.5 times more protein can be expected than carbohydrate in an activated sludge sample.

As seen in Figure 4-28, the carbohydrate concentrations are approximately 4 times smaller than protein concentrations and the pretreatment reactors show an increase due to release of cellular organics.

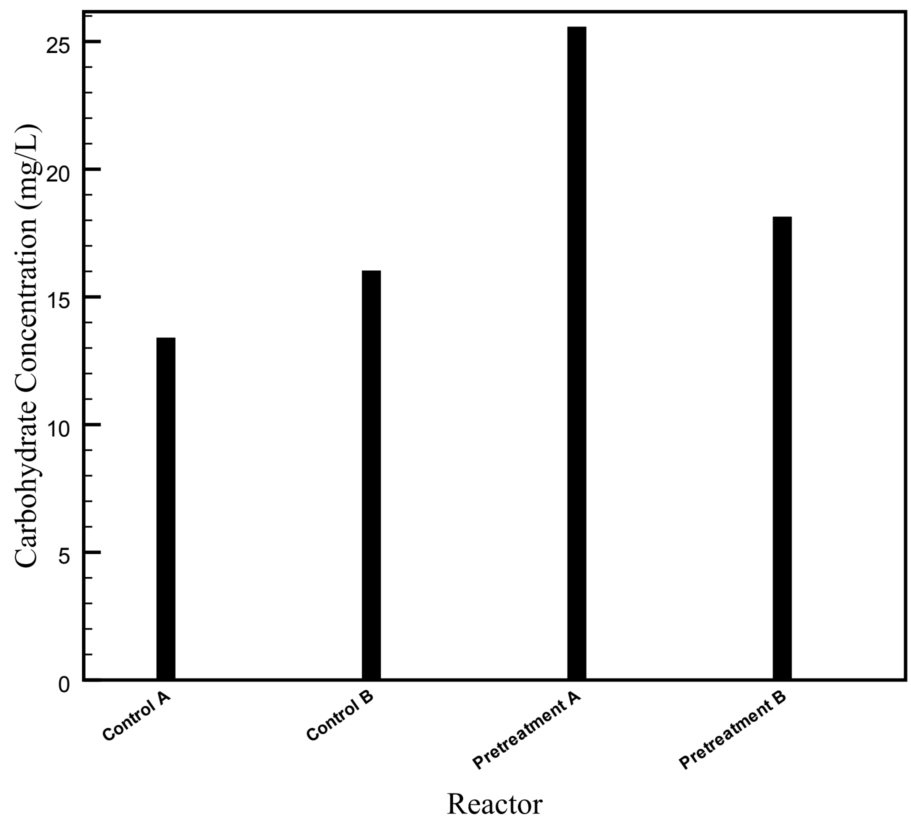

Figure 4-28. Carbohydrate concentrations at the end of *Set I*

MLVSS Concentration

Since MLVSS is a major constituent of volatile solids and an indicator of organisms, a similar reduction is expected after pretreatment. Table 4.5 is the steady state average MLVSS concentrations of all reactors.

Table 4.5. Average MLVSS concentrations for *Set I*

	C_A	C_B	Pr_A	Pr_B
MLVSS (mg/L)	3675	3660	2845	2950

Figure 4-29 shows the daily variations of MLVSS and pretreated sludge show lower MLVSS concentrations. Briefly 21% relative reduction was achieved in MLVSS concentrations in pretreated reactors.

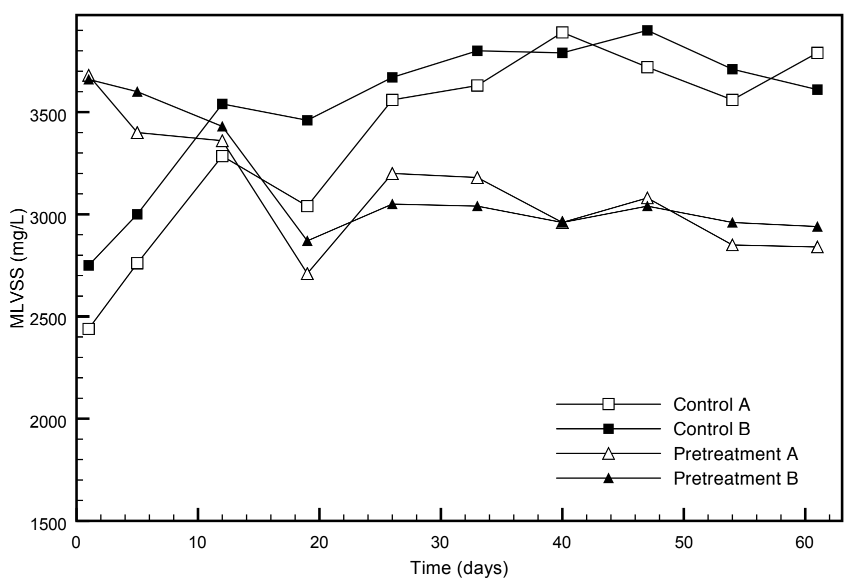

Figure 4-29. Daily MLVSS concentrations for *Set I*

pH

pH was also tracked as an indicator of proper operation and used as a tool to understand the ongoing process. pH was in the range of 7.4 – 7.9 all throughout the reactor operation period which is very close to proper range of anaerobic digestion and only a very insignificant drop of pH was observed in the initial operation period. Other indicators such as high sCOD and low biogas production in that dedicated time prove a possible VFA accumulation for a short period of time. The buffering capacity let the system keep on and the pH increased and continued in a stable manner after all as seen in Figure 4-30.

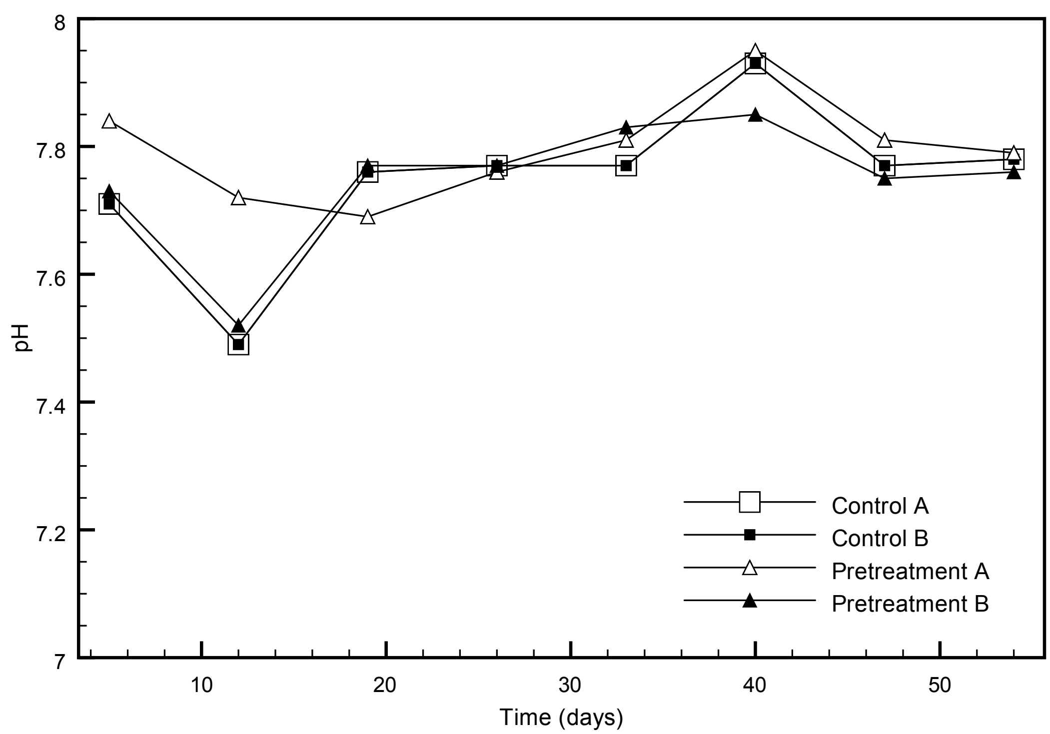

Figure 4-30. Daily pH values for *Set I*

At the end of *Set I,* additional experiments on sludge samples were conducted in order to inspect and discuss the possible advantages and disadvantages of pretreatment. These experiments included NH_3 – N, ortho PO_4^{-3}-P analysis in sludge supernatant and CST and selected metal concentration measurements in sludge samples. If the supernatant is returned back to the head of a treatment plant, the performance of the plant may deteriorate due to the fact that pretreatment puts an additional load on the whole plant. In that case, pretreatment should be reconsidered carefully.

To be able to make such a judgment, in addition to sCOD measurements, NH_3 – N and PO_4^{-3}-P measurements were conducted.

Ammonia-Nitrogen Content

Pretreatment due to its nature causes enrichment of supernatant in an anaerobic digester in terms of any possible pollutant, which was entrapped in cell structure. Soluble ammonia is also expected to show an increase in digesters. As seen in Figure 4-31, ammonia-N increased approximately 27% and rose up to 550 mg/L. Doğan (2008) found a very similar result which was 27.6% increase of ammonia-N after pretreatment by a thermochemical method. According to Khanal *et al.* (2007) the release of trapped nitrogen in the solid phase is often increased with increasing intensity of sonication. This situation concurrently carries a potential overload to the influent stream of treatment plant since supernatant of digesters are generally circulated back to inflow stream.

Another study investigating the TKN concentrations after ultrasonication and results shows that sonication does not help to deplete the nitrogen but convert it from organic N to soluble nitrogen (Bougrier *et al.*, 2005).

Phosphorus Content

Ortho-phosphate was measured due to the similar reasons to ammonia-N. The observed increase was 15% as seen in Figure 4-32 when pretreatment was applied before conventional anaerobic digestion. This is in fact, not a big concern since the increase in concentration is limited.

Therefore, the results of NH_3-N and PO_4-P may necessitate the consideration of additional load due to supernatant recirculation even though the increases are not very significant. The extra load of sCOD brought by the disintegration using ultrasonication can be considered negligible when compared to control reactor.

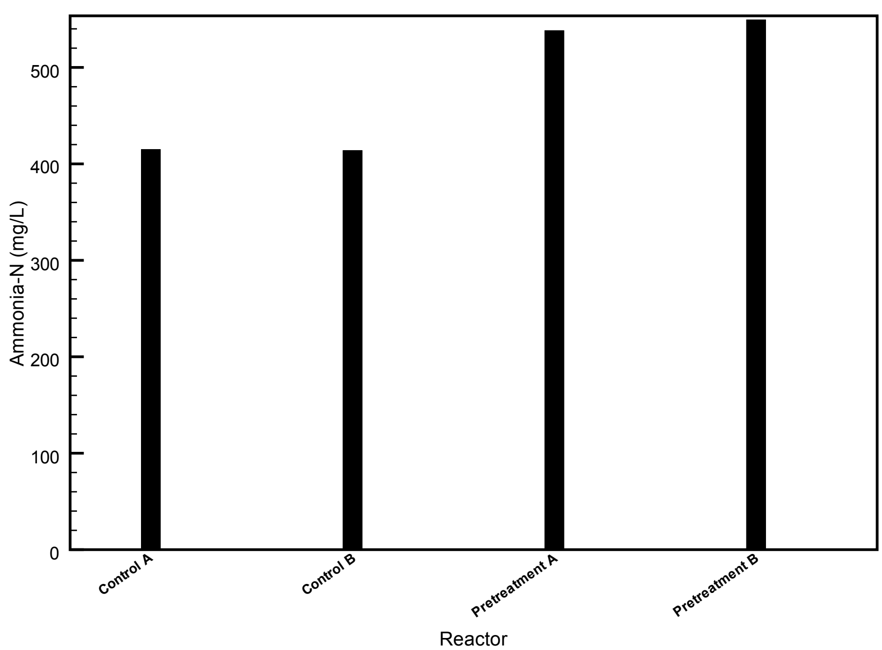

Figure 4-31. Ammonia concentrations of final analysis

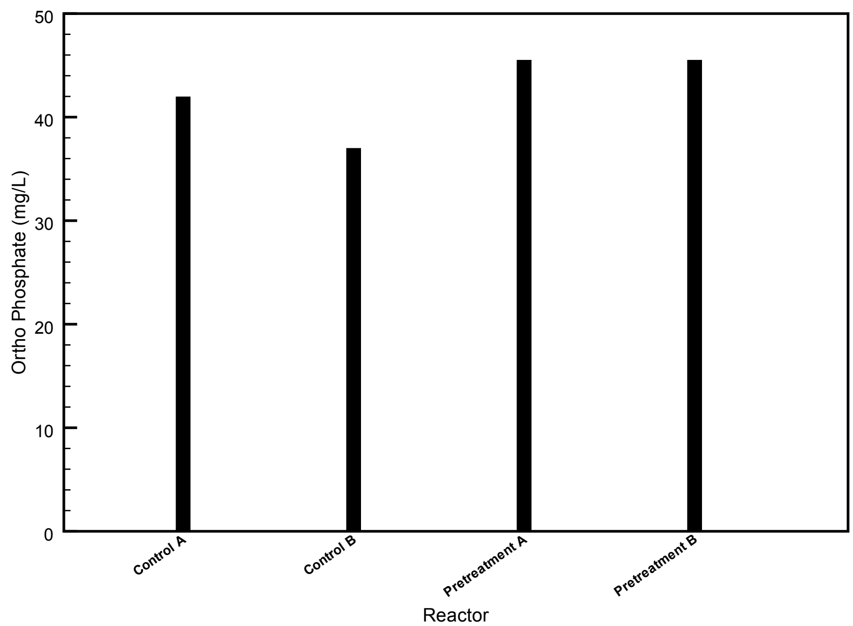

Figure 4-32. Ortho-phosphate concentrations of final analysis

CST

During preliminary studies dewaterability of the sludge was found to be significantly decreasing after pretreatment. The practical details for sequence of operation becomes critical at this point i.e. the dewaterability of sludge influent to the digester does not mean too much if sludge enters the digester as it leaves the sonication unit. Actually, sludge dewatering becomes an issue after it leaves the digester.

Figure 4-33 shows that sludge at the influent line of the digester has well dewatering properties in case of untreated (control) sludge. However, pretreated sludge enters the digester with a much worse dewaterability. Digestion has an interesting effect on CST; after digestion the CST of control sludge becomes slightly higher than the CST of pretreated sludge. Altogether digestion worsens sludge dewaterability, however, its effect seems to be much less in the case of ultrasonically pretreated sludge.

Similarly Chu *et al.* (2001) found an increase from 197.4 seconds to 304.6 seconds for 20 minutes sonication with a sonication density of 0.22 W/mL. On the other hand, Khanal *et al.* (2007) mentions the improvement of dewaterability after digestion, as an advantage of ultrasonication and this argument also seems to be correct according to CST result obtained in this study.

Heavy Metals

There is a concern of concentrating heavy metals after the sludge is pretreated and total solids and volatile solids contents are decreased. This is the main motivation to measure the heavy metals in sludge after pretreatment. Table 4.6 is the tabulated form of the effluent heavy metal concentrations both for control and pretreatment reactors and as seen in the table, there is a trend of slight increase in the pretreatment part of the table. This increase was investigated by checking the allowable metal concentrations for land applications from Soil Pollution and Control Regulations Table B-1 (which is available in the Appendix) and found that even the increased concentrations are too low compared to the limit values. To sum up, sonication does not seem to elevate the heavy metal concentrations of digested sludge. Practical reasons caused the Hg analysis of Control reactors conducted with no replication and reported with no error values.

Calcium and magnesium are the bridging elements of a sludge floc, mainly participating in the reaction of extracellular polymeric substances and the disintegration of these EPS, increase in the supernatant concentrations (Sanin and Vesilind, 2005). “At a level of 0.33 W/mL, however, the release of the Ca^{2+} and Mg^{2+} ions was noted during 20–40 min of ultrasonication prior to major floc structure deterioration” (Chu *et al.*, 2001).

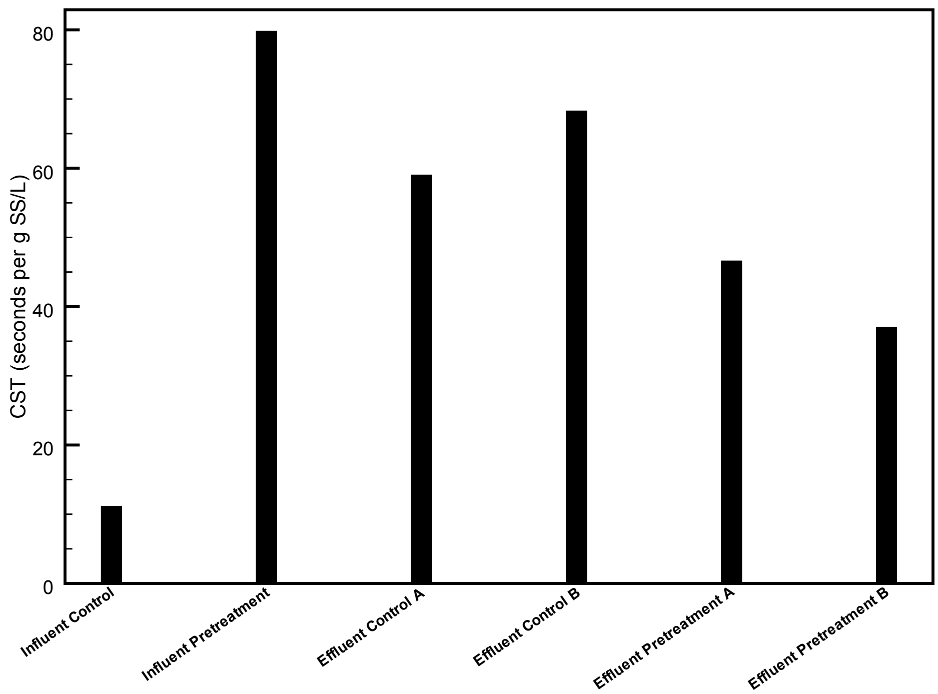

Figure 4-33. Normalized CST values of final analysis

Table 4.6. Metal concentrations of final analysis

	C_A (mg/kg)	C_B (mg/kg)	PR_A (mg/kg)	PR_B (mg/kg)
Cd	0	0	0	0
Pb	3.45 ± 0.01	3.28 ± 0.31	4.14 ± 0.28	4.24 ± 0.39
Zn	308 ± 4.82	306 ± 26.8	391 ± 15.7	377 ± 10.8
Cu	18.3 ± 0.10	17.3 ± 2.24	22.7 ± 1.0	23.4 ± 0.09
Ni	5.86 ± 0.01	5.53 ± 0.15	7.72 ± 0.4	7.27 ± 0.87
Cr	29.0 ± 1.06	27.3 ± 2.47	37.2 ± 0.10	36.3 ± 1.08
Hg	2.99	3.92	0.92 ± 0.44	5.47 ± 4.01
Ca	1064 ± 53.4	969 ± 61.0	1428 ± 120	1143 ± 82.4
Mg	403 ± 2.25	378 ± 41.3	509 ± 46.6	400 ± 3.07

4.3.2 Set II

At the end of 64 days of operation of first set, new set of experiments was initiated as described in the materials and methods part. Instead of starting a new set-up, conditions of *Set I* were changed to new operational conditions for *Set II*. This change was initiated on day 65 of *Set I* reactor operation. The advantage of working continuously was shortening the initial start-up period for each set.

VS Content

As seen in Figure 4-34 the theoretical influent VS content line does not change since SRT was halved only by reducing the volume of the digester. The pretreatment is evaluated in a 50% reduced-volume digester with the same feed characteristics as *Set I*. With this operational scheme, the reactors had an SRT of 7.5 days and an OLR of 1 kg VS/m^3.d; a set of condition corresponding to the limiting edge of a typical anaerobic digester. The data shows that effluent VS concentrations show fewer variations than *Set I*, the lack of start-up period and practical gatherings on reactor operation are the main reasons for this stable set of data.

Two replicate reactors show significant consistency with each other, pointing the confidence of the data produced.

The summary of *Set II* in terms of VS reductions is tabulated in Table 4.7 according to steady state influent and effluent concentrations. Control reactors have 38.03% VS reduction whereas pretreatment reactors have 53.11% VS reduction. These average values show a relative enhancement of 39.65% in VS reduction by pretreatment.

If the results of *Set I* and *Set II* are separately investigated, it is seen that there is a decrease in VS reduction from 44 % to 38 % for control reactors when SRT is halved, whereas, there is no such significant decrease for pretreatment reactors.

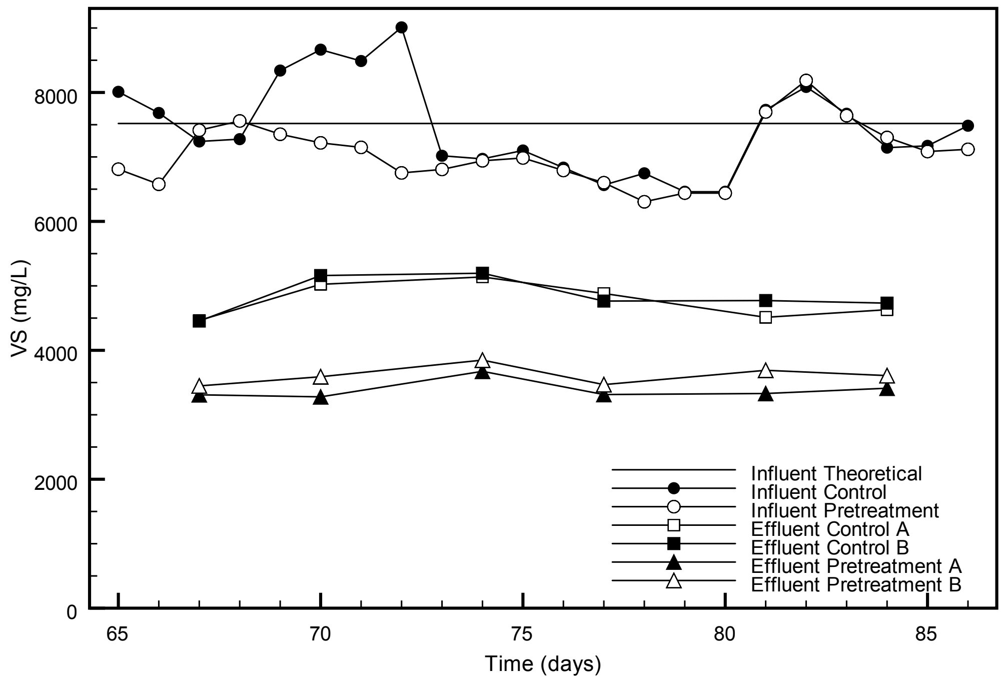

Figure 4-34. Influent and effluent VS concentrations for *Set II*

At 7.5 days of SRT, control reactors show a smaller VS reduction than at 15 days of SRT since the rate limiting step (hydrolysis) limits the overall efficiency of digestion. For pretreatment reactors, the reason for stable VS reduction both for 7.5 and 15 days of SRT directly shows the effect of pretreatment. Since the rate-limiting step is overcome by sonication, an average of 53% VS reduction can be achieved at a sludge age of 7.5 days as compared to 55% at 15 days.

According to Tiehm *et al.* (1997), a conventional digester operated at 22 days of SRT has 45.8% reduction of VS, where 47.3% reduction of VS was achieved at 12 days SRT by ultrasonic pretreatment. Study underlines that; ultrasonic pretreatment is a promising method to reduce the digester volume.

Table 4.7. Influent and effluent VS concentrations and relative VS reduction of *Set II*

	C_A	C_B	Pr_A	Pr_B
Influent VS (mg/L)	7548 ± 360	7547 ± 359	7504 ± 421	7504 ± 421
Effluent VS (mg/L)	4744 ± 203	4822 ± 144	3403 ± 105	3629 ± 92.9
VS reduction (%)	39.0	37.02	54.77	51.45

Biogas Production and Content

In this set, total gas production for all reactors vary daily more than in reactors at 15 days SRT, because the volume used for digestion is smaller and the reactors are more sensitive to any change such as feed characteristics. When steady state was reached there was an obvious gas production difference between pretreated and control reactors as seen in Figure 4-35.

To see the daily gas production at steady state conditions the data was replotted in Figure 4-36. The replica reactors showed similar responses as can be seen in Figure 4-36.

The large deviation observed on day 79 and 80 are the result of a mis-feeding of the reactors. The reactors responded with a decrease in daily gas production, as well as the daily methane production shown on Figure 4-37.

Figure 4-37 shows the daily methane production volumes at steady state. The difference between control and pretreatment reactors are larger in terms of methane production because the content of sonicated reactors are also richer in methane as well as higher in volume.

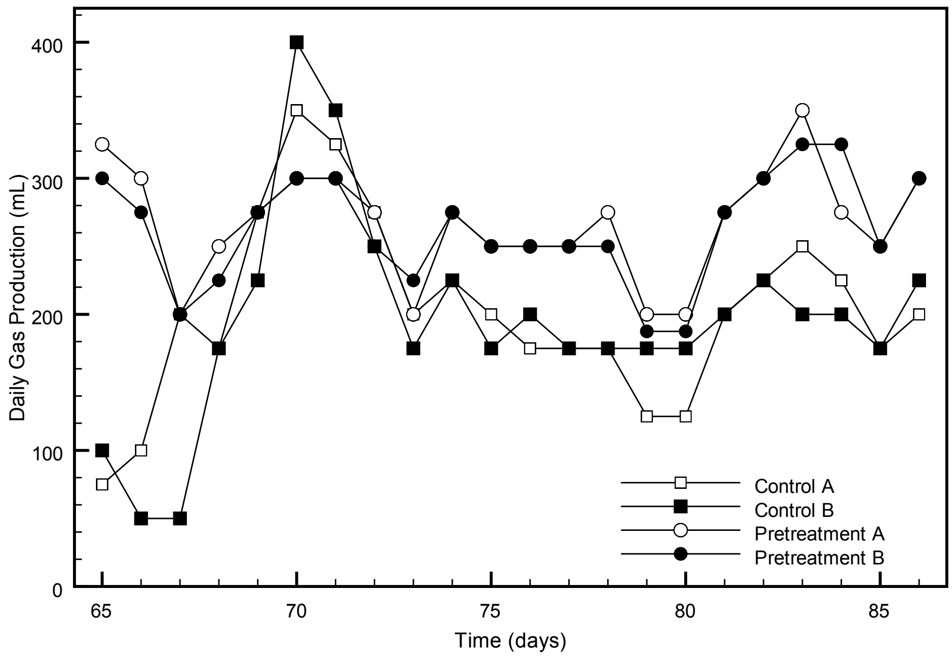

Figure 4-35. Daily biogas production of *Set II*

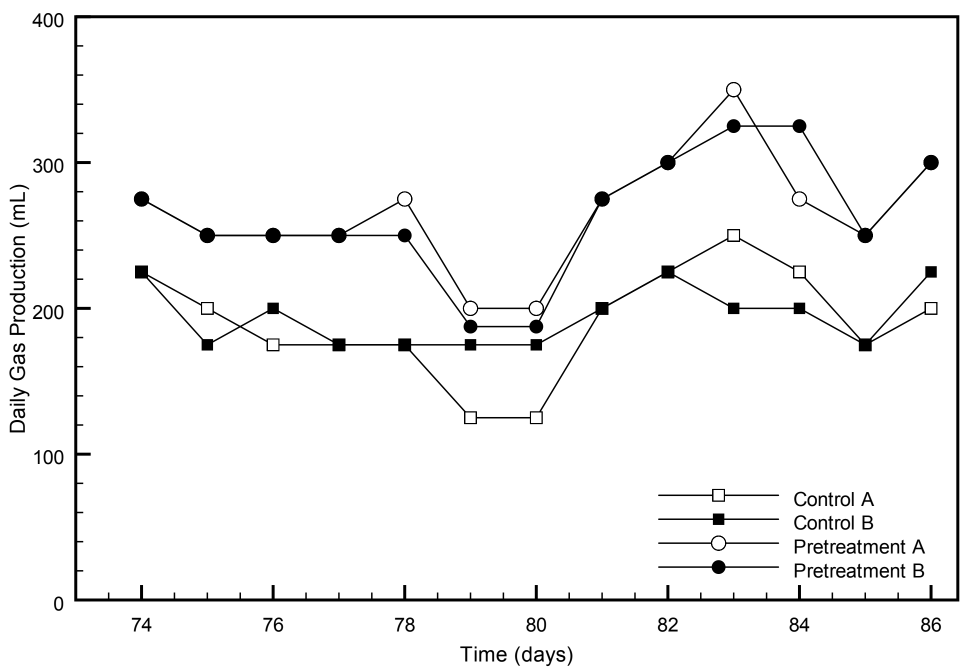

Figure 4-36. Daily biogas productions of *Set II* at steady state

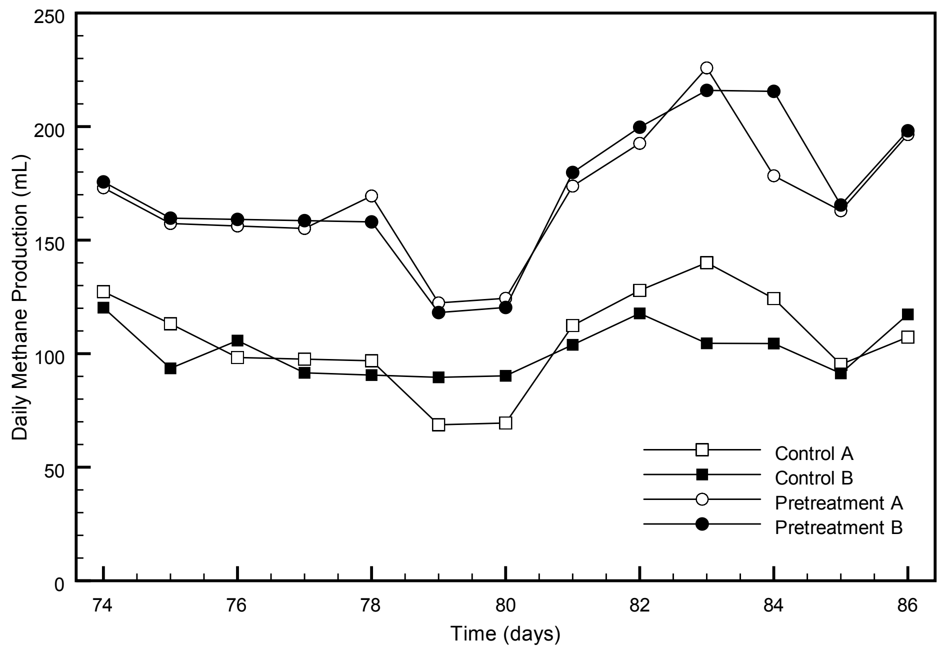

Figure 4-37. Daily methane productions of *Set II* at steady state

The amount and content of biogas produced can be seen in Table 4.8. The overall efficiency both in terms of volume and content of biogas decreased with decreasing SRT, however sonication still cooperated with anaerobic digestion because sonicated reactors' methane production improved by approximately 65% and total gas production increased by 39% compared to non-sonicated reactors. The methane rich content is also another obvious output of sonication in 7.5 days of SRT.

Although the sludge age is in the edge of washout, pretreatment seems to be promising method with encouraging biogas production results.

As seen in Table 4.8 the methane production per unit amount of VS destructed improved by 15.5% relatively. Comparing with SRT of 15 days, this value is quite small.

Table 4.8. Daily average biogas production and methane content of *Set II*

	C_A	C_B	Pr_A	Pr_B
Daily Gas Production (mL)	202 ± 26.1	198 ± 20.8	277 ± 40.2	277 ± 30.5
Methane Percentage (%)	55.6 ± 0.92	52.3 ± 0.66	63.3 ± 1.42	64.8 ± 1.39
Daily Methane Production (mL)	113 ± 15.3	104 ± 11.1	176 ± 21.4	181 ± 23.0
mL CH_4/g VS removed	302	286	324	350

According to Navaneethan, (2007) 192 and 328 mL CH_4 per grams of VS removed, was produced when SRT was decreased from 20 to 15 days respectively. In this study similarly, the methane production per VS removed increased from 275 to 294 when SRT is decreased from 15 to 7.5.

tCOD Content

The average COD reduction increased from 36.64 % to 49.87 %, which was a relative 36.11 % improvement of COD removal in an anaerobic digester (Table 4.9). This may seem better improvement compared to about 11 % improvement for 15 days SRT. However, results show that sonication does not work extremely efficient in lower SRT values but control reactors work less efficiently at lower SRT values. Sonication still helps greatly.

Table 4.9 also shows the methane volumes with respect to COD removal. These results show 22.69 % enhancement in methane production per grams of COD removed after sonication. As discussed in the volatile solids removal efficiencies these results show similar improvements indicating the consistency of the obtained results.

Table 4.9. Influent and effluent COD concentrations and relative COD reduction of *Set II*

	C_A	C_B	Pr_A	Pr_B
Influent COD (mg/L)	13141 ± 847	13141 ± 847	13000 ± 973	13000 ± 973
Effluent COD (mg/L)	8293 ± 541	8360 ± 912	6290 ± 198	6743 ± 159
COD reduction (%)	36.9	36.4	51.6	48.1
mL CH_4/g COD removed	174	163	198	217

sCOD Content

Steady state average effluent soluble COD values are tabulated in Table 4.10 and presenting low concentrations as expected, providing no significant sCOD after digestion in the recirculated supernatant to the influent of the treatment plant.

Table 4.10. Average sCOD concentrations for *Set II*

	C_A	C_B	Pr_A	Pr_B
sCOD (mg/L)	226	264	228	441

MLVSS Concentration

Table 4.11 is the effluent MLVSS concentrations for control and pretreatment reactors and a relative 24.67% MLVSS reduction was achieved for pretreatment reactors compared to control on the average.

Table 4.11. Average MLVSS concentrations for *Set II*

	C_A	C_B	Pr_A	Pr_B
MLVSS (mg/L)	4440	4600	3360	3450

pH

Table 4.12 shows the pH values that were tracked during the operation of *Set II* starting from day 65 until day 86 indicating the proper operation conditions for all reactors showing no or little variations of pH with time. The low SRT selected as 7.5 days had the risk of washout of methanogens and accumulation of VFAs in the reactors. So possible drop of the pH was a threat for this set but it did not happen.

Table 4.12. Average pH values for *Set II*

	C_A	C_B	Pr_A	Pr_B
pH	7.80	7.83	7.86	7.98

4.3.3 Set III

Initiation of *Set II* and *Set III* are similar in terms of operation, therefore *Set III* is also expected to have very short start-up period compared to *Set I* due to this methodology. *Set III* was initiated from *Set II* reactors. In *Set III,* conditions were pushed even more to extreme conditions by reducing the OLR by half and keeping the SRT at 7.5 days.

As discussed in 'Materials and Methods' chapter, before switching to *Set III* no wasting or feeding was done for 7 days but the first day of operation of *Set III* was plotted as no such waiting was done for the good of logical sequence.

VS Content

The influent VS concentration was halved and the theoretical influent concentration was plotted as a straight line. This divergence from the theoretical line is due to inconsistencies during the dilution of influent sludge to satisfy the new OLR of 0.5 at 7.5 days SRT. The VS removal was calculated relatively by considering the measurements of influent concentrations therefore, these variations will not effect the discussions about the efficiency of pretreatment. Figure 4-38 is the plot of influent and effluent VS concentrations of the reactors at specific conditions of *Set III*.

According to data gathered from steady state a relative 28% enhancement of VS reduction with respect to control was achieved after pretreatment. The overall reduction values were low compared to *Set I* and Set *II.* The reason for low efficiency of the reactors was low feed organic content and short sludge age provided. Even in very dilute feed streams approximately 40% of VS reduction can be achieved by pretreatment. This value can be improved with concentrated influent streams. The related data was tabulated and can be seen in Table 4.13 in details.

Table 4.13. Influent and effluent VS concentrations and relative VS reduction of *Set III*

	C_A	C_B	Pr_A	Pr_B
Influent VS (mg/L)	3633 ± 142	3633 ± 142	2908 ± 195	2908 ± 195
Effluent VS (mg/L)	2479 ± 74	2560 ± 118	1797 ± 68.2	1727 ± 33.5
VS reduction (%)	31.7	29.5	38.0	40.4

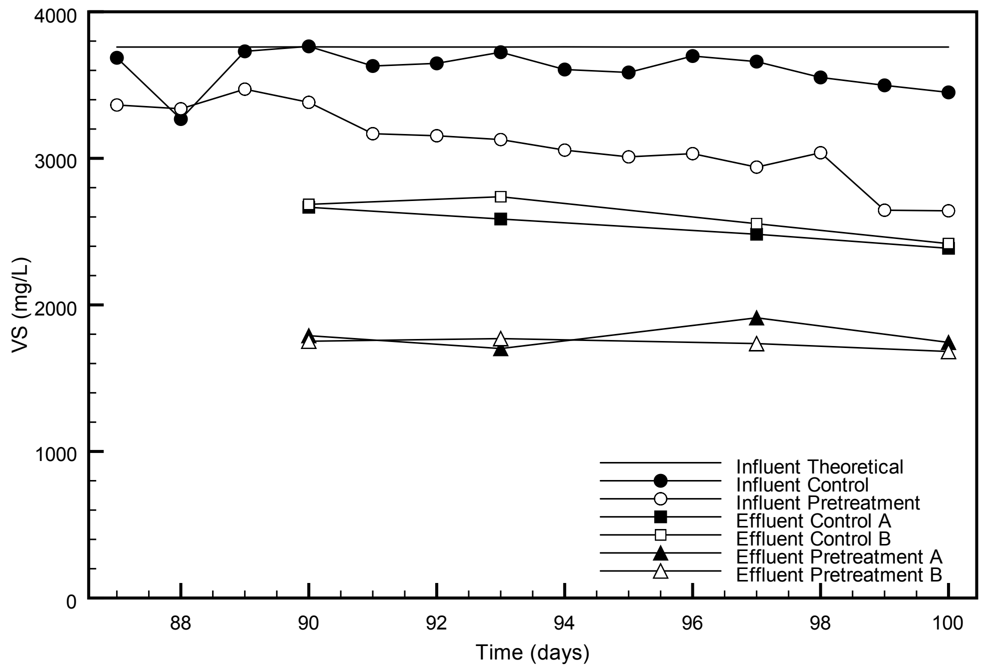

Figure 4-38. Influent and effluent VS concentrations for *Set III*

Biogas Production and Content

Biogas production fluctuated for a short time period at start-up and came to steady state at day 92 as seen in Figure 4-39. Results show that there is still an improvement in biogas production with dilute feeding also.

Figure 4-40 is the replotted version of previous graph that focuses on the steady state gas production underlining the enhancement of total daily gas production difference between control and pretreatment reactors.

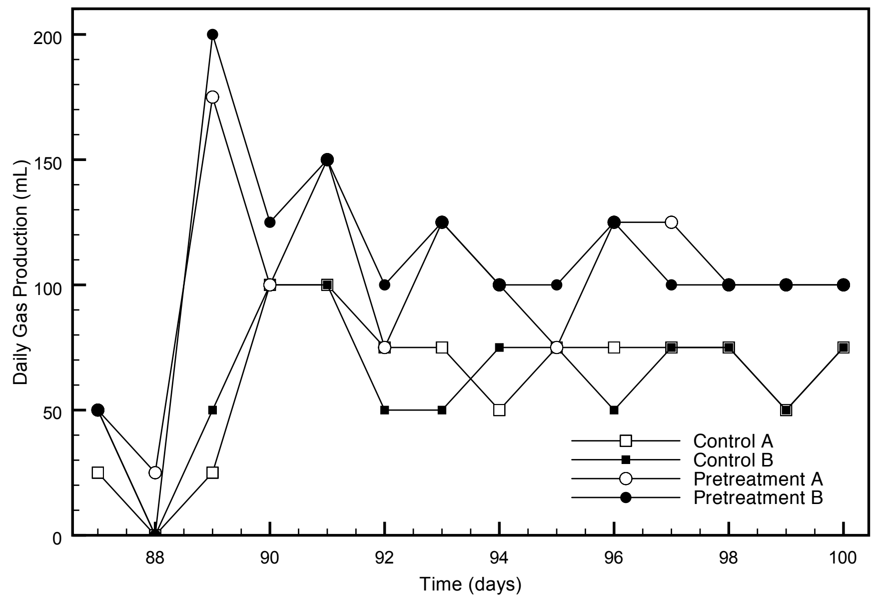

Figure 4-39. Daily biogas productions of *Set III*

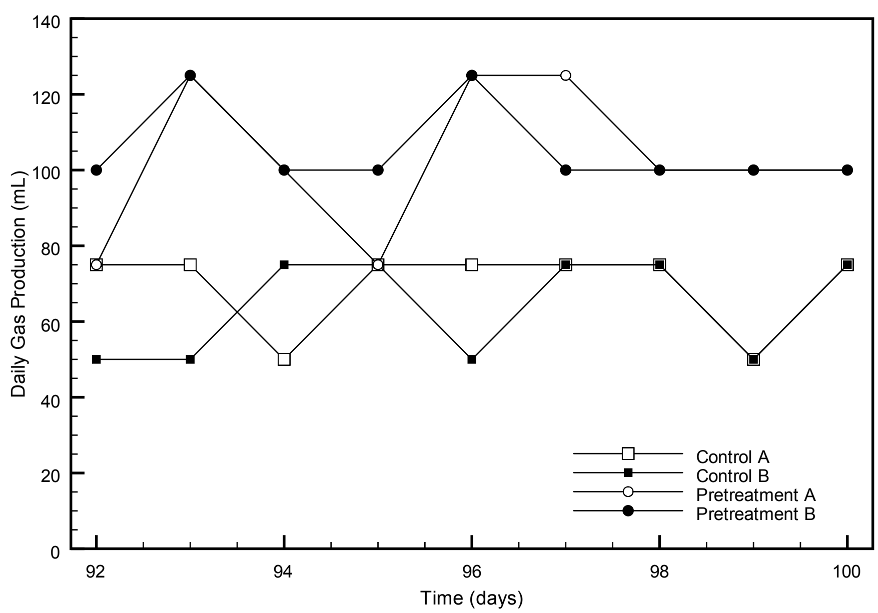

Figure 4-40. Daily biogas productions of *Set III* at steady state

Figure 4-41 is representing the daily methane production of control and pretreatment reactors calculated from the content and volume of biogas. The highest daily variation up to 20% coefficient of variation in daily biogas production was stated by Rivero, (2005) as “the variation observed in the volume of biogas produced for reactors operated at 5 days SRT was significantly higher than the one for reactors operated at 40 days SRT.”

Our experience is also similar with SRT 7.5 day reactors; we observed larger fluctuations in methane amounts compared to SRT 15 day reactors. These fluctuations made the difference between the control and pretreatment reactors became smaller. But one thing obvious was the larger fluctuations of data in control reactors than in the pretreatment reactors.

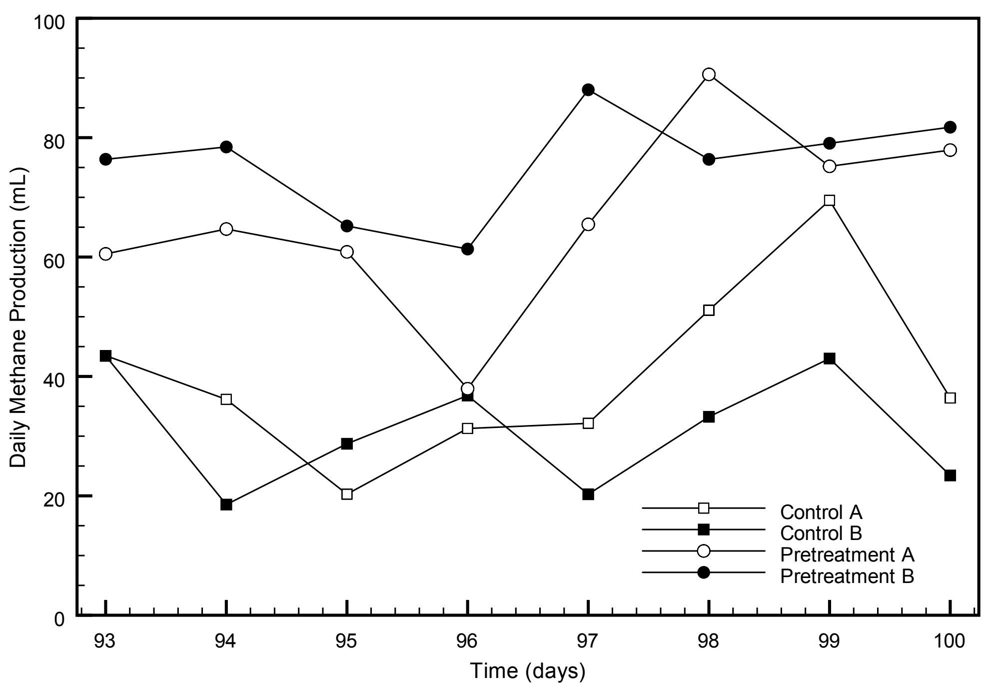

Figure 4-41. Daily methane productions of *Set III* at steady state

Table 4.14 is showing the effect of pretreatment on biogas production. There is a relative improvement of approximately 56 % in biogas production, however both reactors produced quite low amounts of biogas compared to *Set I* and *Set II*. The content of biogas was also rich as expected; sonicated sludge produced 26 % richer biogas in terms of methane than control reactors for the specific set of experiments.

From the standard deviation of data obtained (Table 4.14) it can be seen that control reactor methane production showed larger variation compared to pretreatment reactor. So one can suggest that pretreatment produces a substrate that helps system in cooping with extreme conditions of anaerobic digesters easier and behave more stable.

There is a significant improvement of methane production per grams of VS destroyed. This enhancement is due to the scale of data processed. When the quantities are very small, even a weak enhancement may reflect as an important variation. The yield for methane production seems high, however both the removals and the methane productions are very small and conditions of *Set III* can be qualified as weak conditions generally.

The methane production yield per unit amount of organic matter consumed for sewage sludge digestion was reported to be 250 – 350 mL CH_4/ g organic solids removed (Jingura and Matengaifa, 2008). For this study, control reactors for almost all sets were fitting in the ranges, which are 275, 294 and 239 mL CH_4/g VS removed respectively indicating the consistency of the data produced.

Table 4.14. Daily average biogas production and methane content of *Set III*

	C_A	**C_B**	**Pr_A**	**Pr_B**
Daily Gas Production (mL)	69.4 ± 11.0	63.9 ± 13.2	102 ± 19.5	105 ± 11.0
Methane Percentage (%)	58.1 ± 18.6	53.1 ± 16.3	69.3 ± 12.7	71.6 ± 7.9
Daily Methane Production (mL)	40.0 ± 15.0	30.9 ± 9.8	66.7 ± 15.5	75.8 ± 8.7
mL CH_4/g VS removed	260	217	451	483

tCOD Content

Table 4.15 shows that removal of COD by digestion was improved approximately by 17%. Less effluent COD points to a more stabilized sludge even at very unusual conditions such as *Set III*.

Table 4.15. Influent and effluent COD concentrations and relative COD reduction of *Set III*

	C_A	C_B	Pr_A	Pr_B
Influent COD (mg/L)	6606 ± 257	6606 ± 257	5288 ± 355	5288 ± 355
Effluent COD (mg/L)	3893 ± 67.2	4240 ± 339	2925 ± 269	2910 ± 163
COD reduction (%)	41.1	35.8	44.7	45.0
mL CH_4/g COD removed	111	98	212	240

sCOD Content

Soluble organic concentrations indicate an accumulation in pretreatment reactors. This accumulation is probably due to inadequate operational conditions of *Set III*. The methane production rates and low efficiency of pretreatment in terms of VS reduction was already indicating an inappropriate anaerobic degradation. Table 4.16 shows, pretreatment reactors have much higher soluble COD concentrations than control by 85%.

Similar sCOD concentrations would indicate a better performance of pretreatment free from influent COD concentrations, because pretreatment aims to improve sCOD of feed and if the difference is small this means that, pretreatment reactors operate in a higher rate than conventional reactor.

Results do not show excessive sCOD in either Set of the reactors and can be easily handled by recirculation of digester supernatant with the treatment plant.

Table 4.16. Average sCOD concentrations for *Set III*

	C_A	C_B	Pr_A	Pr_B
sCOD (mg/L)	139	131	262	243

MLVSS Concentrations

Table 4.17 shows a 26% drop in MLVSS concentrations correlated with VS concentrations and MLVSS concentrations are relatively low since the influent is dilute compared to *Set I* and *Set II*.

Table 4.17. Average MLVSS concentrations for *Set III*

	C_A	C_B	Pr_A	Pr_B
MLVSS (mg/L)	2210	2160	1750	1530

pH

Table 4.18 shows the pH values of all reactors, which indicate, proper operating digesters and no extremes were observed just like in *Set I* and *Set II*.

Table 4.18. Average pH values for *Set III*

	C_A	C_B	Pr_A	Pr_B
pH	7.77	7.78	7.70	7.68

Table 4.19 was built in order to summarize the results of the semi-continuous anaerobic reactors. Both control and pretreatment reactors have two replicates, which are C_A, C_B and Pr_A, Pr_B respectively. All quantities used for this table represent the arithmetic average values of these replicates. Since any two reactors were operated in parallel, the standard deviation was not provided. '*% Change*' column was calculated in order to show the relative improvements of pretreatment reactors when compared with control reactors.

When comparing three sets of operation, it can be seen that enhancement of biogas production is highest in *Set III* with 55% but when comparing the volumes of biogas production (or methane production) *Set I* is obviously the highest (211 mL methane per day). Similarly highest VS removal (56%) can be achieved by the conditions of *Set I*. When SRT is decreased, VS removal of control reactors decreases down to 31% depending on the OLR. COD removal is highest (53%) again in *Set I* conditions, however *Set II* presents a 35% relative improvement.

As a summary, *Set I* shows the peak values with pretreatment but when checking the enhancement percentages, highest enhancements obtained may not necessarily be in *Set I*, however the reason behind is the decrease in control reactors due to low SRT and OLR. This study will focus on the real case implementation of the most realistic and most effective scenario, which is *Set I* while working on the cost analysis.

Table 4.19. Summary table for performances of semi-continuous reactors for steady state

	Set I SRT = 15 d OLR = 0.5 kg/m^3d			*Set II* SRT = 7.5 d OLR = 1 kg/m^3d			*Set III* SRT = 7.5 d OLR = 0.5 kg/m^3d		
	Control	Pretreatment	% Change	Control	Pretreatment	% Change	Control	Pretreatment	% Change
Daily Biogas Production (mL)	217	324	49	200	277	39	67	104	55
Daily Methane Production (mL)	121	211	74	108	178	65	35	71	103
Methane Percentage (%)	57	66	16	54	64	19	56	70	25
VS Removal (%)	45	56	24	38	53	39	31	39	26
mL CH_4/g VS removed	275	384	40	294	340	16	239	467	95
tCOD Removal (%)	48	53	10	37	50	35	38	45	18
mL CH_4/g COD removed	140	267	91	140	207	48	105	226	115

CHAPTER 5

COST ANALYSIS

Life Cycle Costing

Sludge handling is responsible for 30 - 40% of the capital cost and 50% of operating cost for a treatment plant (Vesilind, 1988). Pretreatment will add an extra cost on both the capital and operating cost of a treatment plant. It will also add some benefits, however the situation is not as shallow as calculating the unit treatment cost, subtracting the biogas production enhancement and concluding as profitable or not. So therefore, *life-cycle costing* (LCC) is used to underline the importance of comprehensive thinking of elements of cost analysis both the present time and the future and external opportunities and threats as well as present strengths and weaknesses of the investment.

The major cost components of pretreatment investment can be grouped into two as costs and revenues. After expanding these elements as concrete terms as possible, profit becomes the difference between the cost and the revenue. Environment oriented investments generally have negative profits, because the revenues are limited and these investments are usually service to public.

Revenues and Costs

Revenue is obviously items bringing in money such as, selling service, end-products or by-products or interest rates (Cheremisinioff, 2002). For a pretreatment add-on; enriched biogas, which is also high in amount and increased wastewater taxes, can be grouped as revenues.

Cost is, contrast to revenue, items consuming money such as construction, operation, maintenance, insurance and the major ones are expenses of labor, land, electricity etc. (Cheremisinioff, 2002). In a sludge pretreatment add-on, expenses are the installation of a new sonication unit, consumption of energy during operation and maintenance of ultrasonic probe.

Apart from revenues, there is an obvious reduction of cost after pretreatment that can also be accounted as revenue, which is reduction of volatile solids in sludge that will be transported and disposed consequently.

Briefly, the major costs are the construction of sonication unit and installation of ultrasonic probe and consumption of extra energy by ultrasound and also major revenues are the enhancement of biogas production, reduction of transportation and sludge disposal costs.

Cost Calculations

To simplify the calculations baseline situation and upgraded new situation was defined as follows.

The major elements included as the cost for a conventional plant are the transportation and disposal costs of sludge; furthermore biogas production and the related profiting as revenue can be counted for baseline situation.

The upgrading of the plant will be done by a sonication unit and the new situation will consist of capital and operational costs for a sonication unit additionally. Concurrently, the increased biogas and decreased transportation and disposal costs can be counted for revenues of the upgraded situation. Here since there are conflicting results about the improvement of dewaterability and polymer consumption amounts in literature, even though this study found an improved dewaterability, its effect either or negative was not taken into account during cost calculations.

Baseline Situation

The defined baseline situations have some assumptions and the related calculations are as follows. The cost calculation was conducted for a hypothetical wastewater treatment plant with 75,000-person capacity. The wastewater generation factor was assumed to be 125 L/cap.day. The daily sludge production was calculated as 135 m^3 (7.5 % dry solids). In the calculations, the results obtained in *Set I* was used thinking that it best reflects the usual operational conditions of an anaerobic digester system.

All the calculations will be based on the annual basis and the currency of New Turkish Liras (YTL) in 2008.

Since this is the baseline situation, the capital and operational costs are taken as zero and the digester was assumed to handle 10 tons of dry primary sludge and 10 tons of dry waste activated sludge daily.

The organic content of primary and secondary sludge was taken as 65% and 75% respectively and the organic reduction of primary sludge in the digester was taken as 50% whereas the organic reduction of waste activated sludge was taken as 45% from Table 4.19. The residuals of the organics and the whole inorganic portion were assumed to be wasted (Tchobanoglous *et al.*, 2003).

The cost of disposal was assumed to be 18 YTL; therefore the cost of disposal for primary sludge was calculated as 43,740 YTL/year and for secondary sludge as 42,930 YTL/year (data from MATAB as cited in Doğan, 2008).

Similarly, by assuming a capacity of 13.5 tones for a single truck with a 2.8918 YTL/km transportation cost and a 10 km far disposal site, the cost of transportation for primary sludge and secondary sludge is 10,410 YTL/year and 10,218 YTL/year, respectively. However, additional costs such as worker costs and vehicle maintenances will be added as 10% increase in transportation costs (Doğan, 2008).

After clarifying the costs for baseline situation, the revenue from biogas production was also calculated.

The methane production per VS removed value was taken from Table 4.19 and the potential of methane production for primary sludge was taken as 1.2 times of waste activated sludge (Gavala *et al.*, 2003).

Other important assumptions are the electrical energy potential of digester methane and the cost of energy, which are 6.5 kWh/m^3 (Apples *et al.*, 2008) and 0.15 YTL/kWh (TEDAS, 2008) respectively. By using all the data, profit from primary and secondary sludge digestion were calculated as 112,934 YTL/year and 97,732 YTL/year, respectively.

Table 5.1 shows the tabulated summary of all costs and revenues for both primary and waste activated sludge.

Table 5.1. Summary table for cost analysis of baseline situation

	Primary Sludge	**Waste Activated Sludge**	**Total**
Capital Cost (YTL)	-	0	0
Sonication Cost (YTL/year)	-	0	0
Disposal Cost (YTL/year)	43,740	42,930	86,670
Transportation Cost (YTL/year)	11,451	11,239	22,690
Total Cost (YTL/year)	**55,191**	**54,169**	**109,360**
Biogas Revenue (YTL/year)	**112,934**	**97,732**	**210,666**

Upgraded Situation

The major additional costs for a new system are capital cost which would be initially paid once and energy consumption cost due to electricity consumption.

The capital cost was taken as 4167 €/ton sludge (Nickel, 2002) and 1 € was taken as 1.9598 YTL (ISO, 2008). The power required for 1 ton of sludge was taken as 4.17 kW (Nickel 2002). The initial cost will be paid once and the replacement of the system will be done after ten years (Nickel, 2002).

To calculate the transportation and disposal costs, all the assumptions used in the baseline were held constant nevertheless due to enhanced VS reduction after sonication, disposal and transportation costs reduced accordingly. The VS reduction was taken as 54% for waste activated sludge as in Table 4.19.

The biogas production per VS reduction was increased from 275 m^3/kg VS to 384 m^3/kg VS. Therefore, the energy gained from biogas will be increased proportionally.

Table 5.2 shows the operational costs and revenues of the upgraded system and additionally the first row is the installation cost of the new system.

Table 5.2. Summary table for cost analysis of upgraded situation

	Primary Sludge	Waste Activated Sludge	Total
Capital Cost (YTL)	-	81,665	81,665
Sonication Cost (YTL/year)	-	54,004	54,004
Disposal Cost (YTL/year)	43,740	38,556	82,296
Transportation Cost (YTL/year)	11,451	10,994	21,546
Total Cost (YTL/year)	**55,191**	**103,554**	**157,846**
Biogas Revenue (YTL/year)	**112,934**	**163,763**	**276,697**

Payback Period

Payback period can simply be defined as the length of time for an investment to become even with the capital cost. For this case the capital cost is the investment cost which is 81,665 YTL.

The annual gaining’s from the investment is the difference of annual benefits between the baseline and the upgraded situation. Equation 3 finally becomes as follows and the payback period can be calculated in terms of years.

$$\text{payback period} = \frac{\text{capital cost}}{\left[(\text{revenues - costs})_{upgraded} - (\text{revenues - costs})_{baseline}\right]} \qquad (3)$$

$$\text{payback period} = \frac{81,665}{\left[(276,697 - 157,846)_{upgraded} - (210,666 - 109,361)_{baseline}\right]} = 4.7 \text{ years}$$

This payback period shows that the system will break even after 4.7 years.

CHAPTER 6

CONCLUSIONS

The conclusions of the study will be summarized as follows.

Preliminary studies showed that the most promising acidic pretreatment method in terms of solubilization of organics was the lowest pH, which was pH 1.5 among all the other pH values. Eight hundred percent more soluble COD was measured when compared with untreated sludge.

Dewaterability of sludge samples pretreated with acid were not dramatically decreased, furthermore pH 2.5 enhanced the dewaterability of sludge due to neutralization of surface charges.

Acidic pretreatment did not act as a promising pretreatment method for COD solubilization but could be counted as an effective chemical conditioning technique.

Even mild ultrasonication was able to solubilize more organics than acidic pretreatment. Five minutes of mild sonication increased the sCOD up to 500 % of its original concentration.

Strong sonication experiments showed fluctuating sCOD concentrations with time and the peak value was around 2500 mg/L when the untreated sludge had a sCOD concentrations below 100 mg/L at 15 minutes of sonication.

Combining the acidic and ultrasonic pretreatment methods was expected to show a synergistic effect on each other by both improving the dewaterability and increasing the solubilization, but due probably to the reflocculation with acid addition, the method was not able to solubilize higher amounts of organics.

Strong ultrasonic pretreatment method seems to disintegrate the sludge and is likely the most promising method among other evaluated methods.

The dewaterability and supernatant turbidity show a correlation with each other and sCOD concentrations.

BMP tests showed no significant difference for acidic pretreatment however, 15 minutes of sonication lead the most enhanced anaerobic digestion among 0, 10, 15 and 20 minutes.

15 minutes of strong sonication was decided to be further evaluated and lab scale anaerobic digesters were set to investigate the operational reactions of anaerobic digestion to pretreatment.

Semi-continuous anaerobic reactors that have SRT of 15 days and a corresponding OLR of 0.5 kg/m^{3}d produced approximately 275 mL CH_4 per g VS removed daily, however ultrasonic pretreatment enhanced this value up to 384 mL CH_4 per g VS removed due to enrichment of biogas and the production amounts. Same study with SRT of 7.5 days treating the same amount of waste activated sludge in a half-sized digester was evaluated and found 294 mL CH_4 production per g VS removed daily and increased to 340 mL CH_4 per g VS removed. When the SRT of 7.5 days for a corresponding OLR of 0.5 kg/m^3/d produced 239 mL CH_4 per g VS removed daily and was increased to 467 mL CH_4 per g VS removed. The methane volume was improved from 35 mL to 71 mL per day.

Sonication was able to improve the anaerobic digestion even in extreme operational conditions such as short sludge age and low organic loading. However, these extreme conditions cannot be considered favorable.

Comparing the efficiencies of anaerobic digesters, same waste activated sludge can be treated with a half sized digester with insignificant efficiency decrease.

Ultrasonic pretreatment for all three operational conditions improved the biogas production and methane content of biogas. Moreover the COD and VS removal was enhanced after pretreatment similarly for all operational conditions.

Glucose and protein as major constituents of soluble organics increased after digestion in pretreated reactors as % 48 and % 10 respectively. This increase is not significant and can be minimum with a proper anaerobic digester operation. Similarly, NH_3-N and ortho-P were increased % 31 and % 15 respectively and this increase can also be handled by conventional treatment methods.

Worsening dewaterability as another major disadvantage of sonication was mitigated during anaerobic digestion. Furthermore, CST values decreased by 35 %

indicating a less problematic sludge to disposal compared to conventional excess sludge.

Ultrasound is an energy consuming technology and its investment cost is also high. For a treatment plant, a sonicator handling 10 tons of waste activated sludge daily, costs 82,000 YTL and consumes 54,000 YTL for operation annually. However, the gatherings from pretreatment such as more methane production and less sludge disposal break even after some operation periods with 66,000 YTL more revenue annually. The break even period for the specific case is 4.7 years.

Apart from financial benefits, since the technology is a greener way of sludge treatment that is producing less solid residuals and consuming less electricity than a conventional sludge stabilizing treatment plant, the benefits are more than expected. Quantifying these environmental benefits are somehow difficult in short term but obviously human specie is the main beneficiary of environmentally friendly technologies.

CHAPTER 7

RECOMMENDATIONS FOR FUTURE WORKS

The findings of this study point the effectiveness of ultrasonication on disintegration of sludge. On the other hand, the cost of sonication can be comparatively high for larger treatment plants therefore; minimization of cost by additional modifications should be studied on. Not only combination of two different pretreatment methods but also combination of different sludge stabilization methods and optimization of conditions can be studied.

Modeling of ultrasonic pretreatment can also be studied depending on critical variables and the degree of disintegration and/or anaerobic digestion may be the output of the model.

Pilot/Full scale implementation of ultrasonic pretreatment in Turkey can draw attention and lead to the usage of pretreatment widespread with unnumbered advantages for the economy of the country. The detailed life cycle costing for ultrasonic pretreatment before anaerobic digestion can lead to more comfortable design and implementation for real cases.

Thermophilic anaerobic digestion can be favored with the heat exhausted during continuous sonication instead of mesophilic digestion.

Another important factor is the conditioning effect of acidic pretreatment. Simply by dropping the pH of the media down to 2.5 solves the dewaterability problem, as a result acidic pretreatment can be separately studied for solving the operational problems due to high amounts of water.

Application of ultrasonication as a pretreatment method can also enhance the efficiency of an aeration tank since; hydrolysis is the common step for both anaerobic or aerobic digestion. Pretreatment of influent wastewater by ultrasonication can be a promising way of building more compact treatment plants in costly lands.

Ultrasonication of solid waste before anaerobic digestion or composting can be studied in order to enhance the solid waste stabilization.

Radicals are very precious compounds for the environment and ultrasonication is known to produce these radicals in specific frequencies, the conscious production of these radicals can degrade hazardous and persistent pollutants (Pétrier and Francony, 1997) and sonication can propose an alternative treatment for hazardous chemicals.

To conclude, pretreatment of sludge is not an extraordinary treatment technology contrastingly seems will be the conventional way of sludge handling in the following years therefore research could better converge to the area as soon as possible.

REFERENCES

Andreasen, K., Petersen, G., Thomsen, H. and Strube, R. (1997) "Reduction of Nutrient Emission by Sludge Hydrolysis." *Water Sci. Technol*. **35** (10), 79-85.

APHA (2005). “Standard Methods for the Examination of Water and Wastewater.” 21st Edition. *American Public Health Association (APHA)*, *American Water Work Association (AWWA)*, Washington D.C: Water Environment Federation (WEF).

Appels, L., Baeyens, J., Degreve, J. and Dewil, R. (2008) “Principles and Potential of the Anaerobic Digestion of Waste-Activated Sludge.” *Prog. Energ. Combust.* **34** (6) 755–781.

ASKI (2008) “Official Web Site of Ankara Su ve Kanalizayon Isleri Dairesi Baskanligi” *www.aski.gov.tr* visited on 02/12/2008.

Blume, T. and Neis, U. (2004) "Improved Wastewater Disinfection by Ultrasonic Pre-treatment." *Ultrason. Sonochem*. **5** (11)**,** 333-336.

Bolzonella, D., Pavan, P., Battistoni, P. and Cecchi, F. (2005) "Mesophilic Anaerobic Digestion of Waste Activated Sludge: Influence of the Solid Retention Time in the Wastewater Treatment Process." *Process Biochem*. **40** (3-4), 1453-1460.

Bougrier, C., Carrere, H. and Delgenes, J.P. (2005) "Solubilisation of Waste-Activated Sludge by Ultrasonic Pretreatment." *Chem. Eng. J*. **106** (2), 163-169.

Brodersen, J., Juul, J. and Jacobsen, H. (2002) “Review of Selected Waste Streams: Sewage Sludge, Construction and Demolition Waste, Waste Oils, Waste from Coal-fired Power Plants and Biodegradable Municipal Waste.” *European Environment Agency, Technical Report No: 69.*

Chen, Y., Chen, Y.S. and Gu, G. (2004) "Influence of Pretreating Activated Sludge with Acid and Surfactant Prior to Conventional Conditioning on Filtration Dewatering." *Chem. Eng. J.* **99** (2), 137-143.

Chen, Y., Yang H. and Gu, G. (2001) "Effect of Acid and Surfactant Treatment on Activated Sludge Dewatering and Settling." *Water Res*. **35** (11), 2615-2620.

Chen, Y., Jiang, S., Yuan, H., Zhou, Q. and Gu, G. (2007) "Hydrolysis and Acidification of Waste Activated Sludge at Different pHs." *Water Res*. **41** (3), 683-689.

Cheremisinioff, N.P. (2002) “Handbook of Water and Wastewater Treatment Technologies.” Washington D.C: Butterworth-Heinemann.

Chu, C.P., Chang, B., Liao, G.S., Jean, D.S. and Lee, D.J. (2001) "Observations on Change in Ultrasonically Treated Waste Activated Sludge." *Water Res.* **35** (4), 1038-1046.

Chu, C.P., Lee, D.J., Chang, B.V., You, C.S. and Tay, J.H. (2002). " 'Weak' Ultrasonic Pre-treatment on Anaerobic Digestion of Flocculated Activated Biosolids." *Water Res.* **36** (11), 2681-2688.

De Franchi, G.B.I. (2005) "Effect of Acid and Base Pretreatment on the Anaerobic Digestion of Excess Municipal Sludge" *M.Sc. Thesis*, Department of Civil and Environmental Engineering, College of Engineering, University of Cincinnati, USA.

Doğan, I. (2008) "Combination of Alkaline Solubilization with Microwave Digestion as a Sludge Disintegration Method: Effect on Gas Production and Quantity and Dewaterability of Anaerobically Digested Sludge" M.Sc. Thesis, Department Environmental Engineering, The Graduate School of Natural and Applied Sciences, Middle East Technical University, Turkey.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F. (1956) "Colorimetric Method for Determination of Sugars and Related Substances." *Anal. Chem.* **28** (3), 350-356.

Erdinçler, A. and Vesilind, P.A. (2003) "Effect of Sludge Water Distribution on the Liquid–Solid Separation of a Biological Sludge" *J. Environ Sci. Heal. A.* **A38** (10), 2391-2400.

Eurostat (2008) "Official Web Site of Eurostat" *ec.europa.eu/eurostat* visited on 02/01/2009.

Forster, C.F. (1971) "Activated Sludge Surfaces in Relation to the Sludge Volume Index." *Water Res.* **5** (10), 861-870.

Frostell, B. (1985) "Process Control in Anaerobic Wastewater Treatment." *Water Sci. Technol.* **17** (1), 173-189.

Gavala H.N., Yenal U., Skiadas I.V., Westermann P. and Ahring B.K. (2003). “Mesophilic and Thermophilic Digestion of Primary and Secondary Sludge. Effect of Pre-treatment at Elevated Temperature.” *Water Res.*, **37** (19), 4561-4572.

Gogate, P.R. (2002) "Cavitation: An Auxiliary Technique in Wastewater Treatment Schemes." *Adv. Environ. Res.* **6** (3), 335-358.

Grönroos, A., Kyllönen, H., Korpijarvi, K., Pirkonen, P., Paavola, T., Jokela, J. and Rintala, J. (2005) "Assisted Method to Increase Soluble Chemical Oxygen Demand (sCOD) of Sewage Sludge for Digestion." *Ultrason. Sonochem.* **12** (1-2), 115-120.

Hatziconstantinou, G.J., Yannakopoulos, P. and Andreadakis, A. (1996) "Primary Sludge Hydrolysis for Biological Nutrient Removal." *Water Sci. Technol.* **34** (1-2), 417-423.

Hogan, F., Mormede, S., Clark, P. and Crane, M. (2004) “Ultrasonic Sludge Treatment for Enhanced Anaerobic Digestion” *Water Sci. Technol.* **50** (9), 25-32

Hua, I. and Hoffman, M.R. (1997) "Optimization of Ultrasonic Irradiation as an Advanced Oxidation Technology." *Environ. Sci. Technol.* **31** (8), 2237-2243.

ISO. (2008) “Ekonomik Durum Tespit Anketi Sonuclari 2008-I” Istanbul: Istanbul Sanayi Odasi Yayinlari.

Jingura, R.M. and Matengaifa, R., (2008) “Optimization of Biogas Production by Anaerobic Digestion for Sustainable Energy Development in Zimbabwe.” *Renew. Sustain. Energy Rev.* doi:10.1016/j.rser.2007.06.015

Jirka, A.M. and Carter, M.J. (1975) “Reactor Digestion Method; USEPA Approved for Reporting” *Anal. Chem.* **47** (8), 1397. Approved by United Stated Environmental Protection Agency (1980) *Federal Register* **45** (78), 26811-26812

Jyoti, K.K., and Pandit, A.B. (2004) "Effect of Cavitation on Chemical Disinfection Efficiency." *Water Res.* **38** (9), 2249-2258.

Khanal, S.K., Grewell, D., Sung, S. and Van Leeuwen, J.H. (2007) "Ultrasound Applications in Wastewater Sludge Pretreatment: A Review." *Crit. Rev. Env. Sci. Tec.* **37** (4), 277-313.

Kim, J., Park, C., Kim, T.H., Lee, M., Kim, S., Kim, S.W. and Lee, J. (2003) "Effects of Various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge." *J. Biosci. Bioeng.* **95** (3), 271-275.

King, R.O. and Forster, C.F. (1990) "Effects of Sonication on Activated Sludge." *Enzyme Microb. Technol.* **12** (22), 109-115.

Kouloumbis, P., Rigas, F. and Mavridou, A. (2000) "Environmental Problems from the Disposal of Sewage Sludge in Greece." *Int. J. Environ. Heal. R.* **10** (1), 77-83.

Lafitte-Trouque, S., and Forster, C.F. (2002) "The Use of Ultrasound and γ-irradiation as Pre-treatments for the Anaerobic Digestion of Waste Activated Sludge at Mesophilic and Thermophilic Temperatures." *Bioresource Technol.* **84** (2), 113-118.

Lehne, G., Müller, A. and Schwedes, J. (2001) "Mechanical Disintegraton of Sewage Sludge." *Water Sci. Technol.* **43**, (1), 19-26.

Lowry, O.H., Rosebrough, N.J., Farr, A.L. and Randall, J.R. (1951) "Protein Measurement with the Folin Phenol Reagent." *J. Biol. Chem.* **193** (1): 265-275.

Mason, T.J. and Lorimer P. (2002) “Applied Sonochemistry the Uses of Power Ultrasound in Chemistry and Processing.” Weinheim: Wiley-VCH Verlag GmbH.

McCarty, P.L. (1964a) "Anaerobic Waste Treatment Fundemantals Part One: Chemistry and Microbiology." *Public Works* **95** (9), 107-112.

McCarty, P.L. (1964b) "Anaerobic Waste Treatment Fundementals Part Two: Environmental Requirements and Control." *Public Works* **95** (10), 123-126.

McCarty, P.L. (1964c) "Anaerobic Waste Treatment Fundementals Part Four: Process Design." *Public Works*, **95** (12), 95-99

Meuner, N., R.D. Tyagi, and J.F. Blais. (1996) "Acid Treatment for Stabilisation of Sewage Sludge." *Can. J. Civil Eng.* **23** (1), 76-85.

Ministry of Environment and Forestry (MoEF). (2001) “Regulation on Control of Soil Pollution.” *Official Gazette* no:24609.

Müller, J.A. (2001) "Prospects and Problems of Sludge Pre-Treatment Processes." *Water Sci. Technol.* **44** (10), 121-128.

Müller, J.A., Winter, A. and Stünkmann, G. (2004) "Investigation and Assessment of Sludge Pre-treatment Processes." *Water Sci. Technol.* **49** (10), 97-104.

Navaneethan, N. (2007) “Anaerobic Digestion of Waste Activated Sludge with Ultrasonic Pretreatment.” *M.Sc. Thesis*, Department of Environmental Engineering and Management, Asian Institute of Technology School of Environment, Resources and Development, Thailand.

Neyens, E., Baeyens, J., Dewil, R. and De Heyder, B. (2004) "Advanced Sludge Treatment Affects Extracellular Polymeric Substances to Improve Activated Sludge Dewatering." *J. Hazard. Mater.* **106** (2-3), 83-92.

Neyens, E., Baeyens, J., Weemas, M. and De Heyder, B. (2003) "Hot Acid Hydrolysis as a Potential Treatment of Thickened Sewage Sludge." *J. Hazard. Mater.* **98** (1-3), 275-293.

Nickel K., (2002) "Ultrasonic Disintegration of Biosolids – Benefits, Consequences and New Strategies." TU Hamburg: Harburg Reports on Sanitary Engineering.

Oles, J., Ditchtl, N. and Niehoff, H. (1997) "Full Scale Exprience of Two Stage Thermophilic/Mesophilic Sludge Digestion." *Water Sci. Technol.* **36** (6-7), 449-456.

Onyeche, T.I., Schlafer, O., Bormann, H., Schröder, C. and Sievers, M. (2002) "Ultrasonic Cell Disruption of Stabilised Sludge with Subsequent Anaerobic Digestion." *Ultrasonics* **40** (1-8), 31-35.

Owen, W.F., Stuckey, D.C., Healy, J.B., Young, Jr. L.Y. and McCarty, P.L. (1979) "Bioassay for Monitoring Biochemical Methane Potential and Anaerobic Toxicity." *Water Res.* 1**3** (6), 485-492.

Özsoy, G. (2006) "An Investigation of Agricultural Use Potential of Wastewater Sludges in Turkey With Respect To Heavy Metals and Pathogens." M.Sc. Thesis, Department of Environmental Engineering, The Graduate School of Natural and Applied Sciences, Middle East Technical University, Turkey.

Parkin, G.F. and Owen, W.F. (1986) "Fundementals of Anaerobic Digestion of Wastewater Sludges." *J. Environ. Eng.* **112** (5), 867-920.

Pavlostathis, S.G. and Giraldo-Gomez, E. (1991) "Kinetics of Anaerobic Treatment: A Critical Review." *Crit. Rev. Environ. Control* **21** (5-6), 411-490.

Pétrier, C. and Francony, A. (1997) “Ultrasonic Waste-water Treatment: Incidence of Ultrasonic Frequency on the Rate of Phenol and Carbon Tetrachloride Degradation.” *Ultrason. Sonochem.* **4** (4), 295-300.

Perez-Elvira, S.I., Diez P.N. and Fdz-Polanco, F. (2006) "Sludge Minimisation Technologies." *Rev. Environ. Sci. Biotechnol.* **5** (4), 375–398.

Reynolds, T.D. and Richards, P.A. (1995) “Unit Operations and Processes in Enviromental Engineering. 2”. Boston: PWS Publishing Company.

Rivero, J.A.C. (2005) “Anaerobic Digestion of Excess Municipal Sludge. Optimization for Increased Solid Destruction.” *Ph.D. Thesis*, Department of Civil and Environmental Engineering, College of Engineering, University of Cincinnati, USA.

Roy, R.A., Atchley, A.A., Crum, L.A., Fowlkes, J.B. and Reidy, J.J. (1985) “A Precise Technique for the Measurement of Acoustic Cavitation Thresholds and Some Preliminary-Results.” *J. Acoust. Soc. Am.* **78** (5), 1799-1805.

Salihoglu, N.K., Pinarli, V. and Salihoglu, G. (2007) "Solar Drying in Sludge Management in Turkey." *Renew. Energ.* **32** (10), 1661-1675.

Sanin F.D. and Vesilind P.A. (2005) “Rheology of wastewater sludge - A review” *J. Residuals Sci. Tech.* **2** (2), 71-78.

Show, K.Y., Mao, T. and Lee, D.J. (2007) "Optimisation of Sludge Disruption by Sonication." *Water Res.* **41** (20), 4741-4747.

Show, K.Y., Mao, T., Tay, J.H. and Lee, D.J. (2006) "Effects of Ultrasound Pretreatment of Sludge on Anaerobic Digestion." *J. Residuals Sci. Tech.* **3** (1), 51-59.

Smith, G. and Göransson, J. (1992) "Generation of an Effective Internal Carbon Source for Denitrification Through Thermal Hydrolysis of Pre-precipitated Sludge." *Water Sci. Technol.* **25** (4-5), 211-218.

Song, Y., Kwon, S.J. and Woo, J.H. (2004) "Mesophilic and Thermophilic Temperature Co-Phase Anaerobic Digestion Compared with Single-Stage Mesophilic- and Thermophilic Digestion of Sewage Sludge." *Water Res.* **38** (7), 1653-1662.

Speece, R.E. (1996) “Anaerobic Biotechnology for Industrial Wastewaters.” Nashville: Archea Press.

Strünkmann, G.W., Müller, J.A., Albert, F. and Schwedes, J. (2006) "Reduction of Excess Sludge Production Using Mechanical Disintegration Devices." *Water Sci. Technol.* **54** (5), 69-76.

Tanaka, S., Kobayashi, T. Kamiyama, K. and Bildan, M.L.N.S. (1997) "Effects of Thermochemical Pretreatment on the Anaerobic Digestion of Waste Activated Sludge." *Water Sci. Technol.* **35** (8): 209-215.

Tchobanoglous, G., Burton F.L. and Stensel H.D. (2003) “Wastewater Engineering: Treatment, Disposal and Reuse.” Edited by Metcalf and Eddy. New York: McGraw-Hill Inc.

TEDAS (2008) “Official Web Site of Turkiye Elektrik Dagitim Anonim Sirketi (TEDAS) Geneli 2008 Yili Fonsuz Tarifesi” *www.tedas.gov.tr*, visited on 20/12/2008.

Tiehm, A., Nickel, K. and Neis, U. (1997) "The Use of Ultrasound to Accelerate the Anaerobic Digestion of Sewage Sludge." *Water Sci. Technol.* **36** (11), 121-128.

Tiehm, A., Nickel, K., Zellhorn, M. and Neis, U. (2001) "Ultrasonic Waste Activated Sludge Disintegration for Improving Anaerobic Stabilization." *Water Res.* **35** (8), 2003-2009.

Ultrawaves (2007) “Official Website of Ultrawaves Company.” *www.ultrawaves.de*, visited on 28/12/2008.

US EPA (1999) ”Biosolids Generation, Use and Disposal in the United States.” United States: Environmental Protection Agency, *Report No: EPA/530/R-99-009*.

Vesilind, P.A. (1974) “Treatment and Disposal of Wastewater Sludges.” Ann Arbor: Ann Arbor Science Publishers Inc.

Vesilind, P.A. (1988) "Capillary Suction Time as a Fundamental Measure of Sludge Dewaterability." *J. Water Pollut. Control Fed.* **60** (2), 215-220.

Vesilind, P.A. (1994) “The Role of Water in Sludge Dewatering.” *Water Environ. Res.* **66** (1), 4-11.

Wang, F., Ji, M. and Lu, S. (2006b) “Influence of Ultrasonic Disintegration on the Dewaterability of Waste Activated Sludge.” *Envion. Prog.* **25** (3), 334-338.

Wang, F., Lu, S. and Ji, M. (2006a) "Components of Released Liquid from Ultrasonic Waste Activated Sludge Disintegration." *Ultrason. Sonochem.* **13** (4), 334-338.

Wang, F., Wang, Y. and Ji, M. (2005) "Mechanisms and Kinetics Models for Ultrasonic Waste Activated Sludge Disintegration." *J. Hazard. Mater.* **123** (1-3), 145-150.

Wang, Q.H., Kuninobu, M., Kakimoto, K., Ogawa, H.I. and Kato, Y. (1999) "Upgrading of Anaerobic Digestion of Waste Activated Sludge by Ultrasonic Pretreatment." *Bioresource Technol.* **68** (3), 309-313.

Wang, Q.H., Noguchi, C.K., Kuninobu, M., Hara, Y., Kakimoto, K., Ogawa, H.I. and Kato, Y. (1997) “Influence of Hydraulic Retention Time on Anaerobic Digestion of Pretreated Sludge.” *Biotechnol. Tech.* **11** (2), 105-108.

Weemaes, P.J.M. and Verstraete W.H. (1998) "Evaluation of Current Wet Sludge Disintegration Techniques." *J. Chem. Technol. Biot.* **73** (2), 83-92.

Woodard, S.E., and Wukash, R.F. (1994) "A Hydrolysis/Thickening/Filtration Process for the Treatment of Waste Activated Sludge." *Water Sci. Technol.* **30** (3), 29-38.

WWI (2003) “Water & Wastewater International (WWI).” *ww.pennnet.com/display_article/180581/20/ARTCL/none/none/1/Ultrasound-enhances-sludge-digestion*, visited on 11/11/2008.

Xie, R., Xing, Y., Ghani, Y.A., Ooi, K. and Ng, S. (2007) "Full-scale demonstration of an ultrasonic disintegration technology in enhancing anaerobic digestion of mixed primary and thickened secondary sewage sludge." *J. Environ. Eng. Sci.* **6** (5), 533-541.

Yamaguchi, T., Yao, Y. and Kihara, Y. (2006) "Biological Sludge Solubilisation for Reduction of Excess Sludge in Wastewater Treatment Process." *Water Sci. Technol.* **54** (5), 51-58.

APPENDIX A

CALIBRATION CURVES

Glucose calibration data was fit in a linear curve. R^2 and the equation of the fit curve are 0.99279 and y = 0.0194 x, respectively.

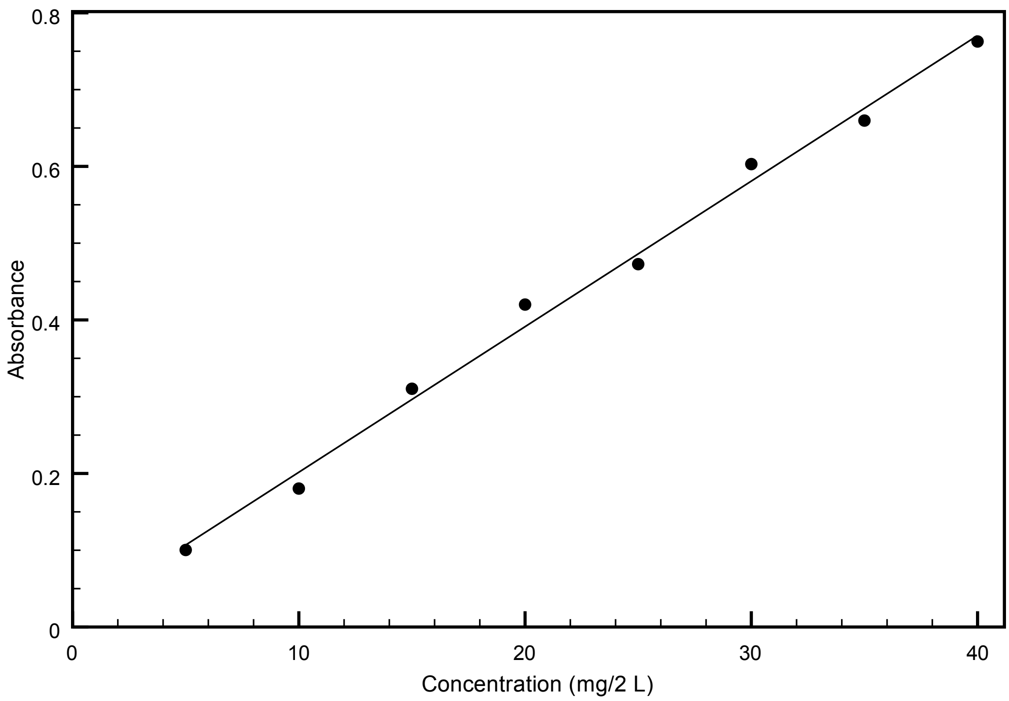

Figure A 1. Glucose calibration curve

Protein calibration data was also fit in a linear curve. R^2 and the equation of the fit curve are 0.99321 and y = 0.035 x, respectively.

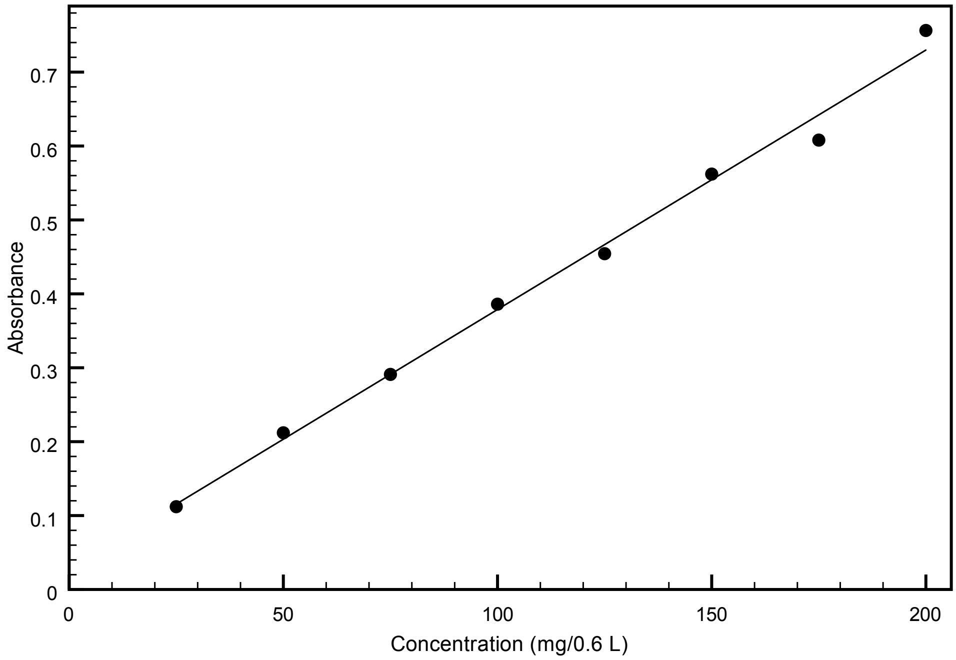

Figure A 2. Protein calibration curve

Ortho-phosphate calibration data was also fit in a linear curve. R^2 and the equation of the fit curve are 0.9972 and y = 0.07039 x, respectively.

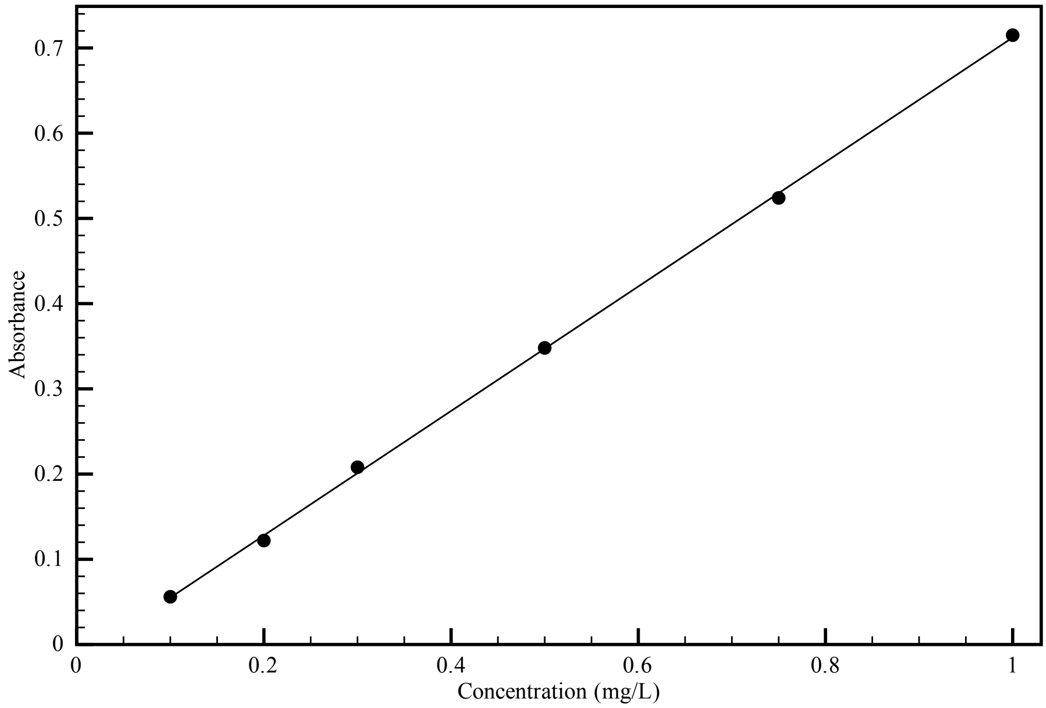

Figure A 3. Ortho-phosphate calibration curve

APPENDIX B

STABILIZED TREATMENT SLUDGE STANDARDS FOR SOIL APPLICATIONS

Table B 1. Maximum concentrations of heavy metals for stabilized treatment sludge on soil applications (MoEF, 2001)

	Ni (mg/kg)	**Cd (mg/kg)**	**Zn (mg/kg)**	**Pb (mg/kg)**	**Cr (mg/kg)**	**Cu (mg/kg)**	**Hg (mg/kg)**
Concentration	400	40	4000	1200	1200	1750	25