DOKUZ EYLUL UNIVERSITY GRADUATE SCHOOL OF
NATURAL AND APPLIED SCIENCES

ULTRASONIC DISINTEGRATION OF SEWAGE SLUDGE

by
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ULTRASONIC DISINTEGRATION OF SEWAGE SLUDGE

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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **“ULTRASONIC DISINTEGRATION OF SEWAGE SLUDGE”** completed by **ÇİMEN GÜNDÜZ** under supervision of **PROF. DR. AYŞE FİLİBELİ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ULTRASONIC DISITEGRATION OF SEWAGE SLUDGE

ABSTRACT

The production of excess sludge is one of the most serious challenges in biological wastewater treatment plants. Treatment and disposal of excess sludge in a biological wastewater treatment system requires high cost which has been estimated to be 50–60% of the total expense of wastewater treatment plant (Metcalf & Eddy, 2004; Egemen et. al., 2001). A common method for the biodegradation of excess sludge is biological treatment by anaerobic digestion. Anaerobic digestion is commonly used for stabilization and solid reduction of treatment plant sludges. Anaerobic digestion is a slow process because of the hydrolysis stage which is the rate-limiting step of the sludge degradation. That disadvantage is prominanced for the treatment of excess sludge which is the final product of the treatment of meat processing sludge due to its high oil and high organic material contents. In order to improve hydrolysis and anaerobic digestion performance, disintegration was developed as the pretreatment process of sludge to accelerate the anaerobic digestion and to increase degree of stabilization (Bougrier et. al., 2005)

The main purpose of this thesis was to investigate the effects of ultrasonic pre-treatment on excess sludge disintegration at different specific energy inputs with low ultrasound frequency (20 kHz). Meat processing sludge containing high organic materials and oil content was chosen as sludge sample for the experimental studies which disintegration degree (DD) that used as the main parameter for evaluation of disintegration performance of sludge. Solid reductions with the ultrasonic pre-treatment were monitored total solids (TS), total organic solids, suspended solids (SS), and volatile suspended solids (VSS) measurements. Effects of ultrasonic disintegration on supernatant characteristics on meat processing industry sludges were also investigated. Biochemical methane potential (BMP) assay was carried out in order to monitor methane production as the indicator of improvement anaerobic biological degradation preceding ultrasonic treatment. In addition, the effect of ultrasonic pre-treatment on sludge filterability was evaluated depending on CST measurements of raw and pre-treated sludge samples.

The experimental results showed that 30000 kJ/kgTS of supplied energy is efficient for disintegration of meat processing sludge. Higher specific energy inputs then 30000 kJ/kgTS led to a mineralization phenomenon preceding a solubilization phenomenon and because of that disintegration degree (DD) decreased. The protein results showed that sludge solids were hydrolyzing during the ultrasonic pre-treatment. Biochemical methane potential (BMP) results obtained in this study suggest that ultrasonic pre-treatment significantly enhanced the biodegradability of biological sludge than sludges that not pre-treated. Maximum methane production was observed for 30000 kJ/kgT and 136% higher biogas production in pre-treated sludge was obtained comparing to the raw sludge at the end of the 40 days of incubation period. Sludge’s supernatant characteristics were also affected by the ultrasonic pre-treatment. For 30000 kJ/kgTS, the soluble chemical oxygen demand (SCOD), dissolved organic carbon (DOC), total nitrogen (TN), total phosphorus (TP) in sludge’s supernatant increased by 487%, 290%, 3230%, and 870%, respectively. Depending on CST data, there was a negative effect of ultrasonic pre-treatment on sludge filterability even for very low specific energy levels.

Keywords: anaerobic digestion, sewage sludge, ultrasonic pre-treatment, disintegration

ARITMA ÇAMURLARININ ULTRASONİK DEZENTAGRASYONU

ÖZ

Biyolojik atıksu arıtma tesisleri için atık çamur en önemli sorunlardan biridir. Biyolojik atıksu arıtma tesisileri için atık çamurun arıtımı ve bertarafı arıtma tesisi toplam işletim masrafının % 50- 60'ını oluşturacak kadar yüksek maliyetler gerektirmektedir. (Metcalf ve Eddy, 2004; Egemen ve diğerleri, 2001) Anaerobik çürüme ile atık çamurun biyolojik arıtımı biyolojik ayrışma için yaygın bir metottur. Anaerobik çürüme arıtma tesisi çamurlarında stabilizasyon ve katı azaltımı için yaygın olarak kullanılmaktadır. Anaerobik çürüme çamur indirgenmesi hız sınırlayıcı adımı olan hidroliz aşaması nedeniyle yavaş bir prosestir. Entegre et tesisi atıksuları gibi yağ ve yüksek organik madde içeriğine sahip atıksuların arıtımından kaynaklanan çamurlarda bu dezavantaj daha da öne çıkmaktadır. Hidroliz aşamasını ve anaerobik çürüme işlemini geliştirmek, anaerobik çürümeyi hızlandırmak ve stabilizasyon derecesini yükseltmek için, çamur ön arıtma prosesi olarak dezentegrasyon yöntemi geliştirilmiştir. (Bougrier, 2005)

Bu tezin temel amacı, ultrasonik ön arıtımın düşük ultrasonic frekans (20 kHz) ile değişik spesifik enerji değerlerinde atık çamur dezentagrasyonunun etkilerinin araştırılmasıdır. Organik madde ve yağ içeriği yüksek olan et işleme tesisi çamur numuneleri kullanılarak yapılan deneysel çalışmalarda, çamurun dezentegrasyon performansının belirlenmesi için Dezentegrasyon Derecesi (DD) ana parametre olarak kullanılmıştır. Toplam katı madde, toplam organik katı madde, askıda katı madde ve uçucu askıda katı madde ölçümleri ile ultrasonic ön arıtma ile katı madde indirgenmesi izlenmiştir. Ayrıca ultrasonic dezentegrasyonun et işleme çamuru üstsuyu karakteristiğine olan etkileri incelenmiştir. Ultrasonik ön arıtımın anaerobik biyolojik indirgenme üzerindeki indikator etkisinin izlenmesi amacıyla biyokimyasal metan potansiyeli deneyleri (BMP) gerçekleştirilmiştir. Ayrıca, ham ve ön arıtımdan geçmiş çamur örneklerinde kapiler emme süresi (KES) ölçüm değerlerine dayanarak ultrasonic ön arıtımın çamur filtrelenebilirliği üstündeki etkisi değerlendirilmiştir.

Elde edilen deneysel sonuçlar, et işleme çamurunun dezentegrasyonunda 30000 kJ/kgTS spesifik enerji değerinin verimli olduğunu göstermiştir. 30000 kJ/kgTS spesifik enerji değerinden daha yüksek spesifik enerji değerleri solibilizasyon olayını takiben mineralizasyon olayının gerçekleşmesine sebep olduğundan dezentegrasyon derecesi (DD) düşmüştür. Protein deneyi sonuçları ise, ultrasonic ön arıtım esnasında çamur katı maddesinin hidroliz olduğunu göstermiştir. Bu çalışmada elde edilen biyokimyasal metan potansiyeli ölçüm sonuçları, ultrasonik ön arıtmanın biyolojik çamurların anaerobik parçalanmasını ön arıtım uygulanmamış olan biyolojik çamurlara göre önemli derecede geliştirdiğini göstermiştir. Maksimum metan üretimi 30000 kJ/kgTS spesifik enerji değeri için bulunmuş ve 40 günlük inkübasyon periyodu sonunda ham çamura göre ultrasonik ön arıtımdan geçmiş çamurun biogaz üretiminin % 136 daha yüksek değerde olduğu belirlenmiştir. Ultrasonik ön arıtma ayrıca çamur üstsuyu özelliklerini de etkilemiştir. 30000 kJ/kgTS specifik enerji değeri için, çamur üstsuyunda kimyasal oksijen ihtiyacı, çözünmüş organik karbon, toplam azot, toplam fosfor değerleri sırasıyla %487, %290, %3230 ve %870 yükselmiştir. KES değerlerine göre ise çok düşük spesifik enerji değerlerinde ultrasonic ön arıtım, çamur filtrelenebilirliği üzerinde olumsuz etki göstermiştir.

Anahtar sözcükler: anaerobik çürüme, atık çamur, ultrasonic ön arıtma, dezentegrasyon

CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 Introduction

Treatment technologies can be classified as aerobic and anaerobic systems. Anaerobic treatment processes have some advantages and disadvantages over aerobic processes. The main advantages of anaerobic digestion in comparison with aerobic treatment are; the lower energy requirement, the production of biogas and the lower production of excess sludge and it is necessary to reduce sludge production to the source that is to say in the wastewater treatment plant. These advantages have led researchers to investigate ways of minimizing the limitations of anaerobic digestion (Speece, 1996).

Water/wastewater treatment processes have produced sludge in different characteristics and quantities. The sludges should be processed and disposed of in accordance with the environmental health criteria for environmental reasons. For many authorities and engineers, the effective sludge management is still a big challenge since the investment and operational costs of sludge processing have an important part of overall plant's costs. Sludge dewatering process has a central role in sludge management for many operations like storage and transport. But, the dewaterability characteristics of sludges can vary depending on their sources and the applied treatment processes. The methods for effective processing cover the methods -thickening, stabilization, conditioning, dewatering-, and the final disposal alternatives- incineration, land application (Metcalf & Eddy, 2004).

Anaerobic digestion is widely used for sewage sludge stabilization, resulted with reduction of sludge and the production of biogas. This treatment, which allows a reduction of sludge quantity of about 40–50%, has become one common method of sludge stabilization. Anaerobic digestion is accomplished through 3 steps: hydrolysis, acidogenesis and methanogenesis. The hydrolysis step of the digestion is the rate limiting step (Bougrier et al.,2005, Wang et. al., 2005). Hence, classical anaerobic digestion requires long duration time and very large tank volumes. Other difficulties due to anaerobic digestion are low biogas production, poor volatile solids (VS) destruction and poor degradation of refractory materials leading to operational problems and foaming (Bartholomew, R., 2002). Therefore disintegration was developed to eliminate the hydrolysis step and to improve anerobic biodegradability of sludge. Several processes like mechanical (G. Zhang et al.(2009), X. Feng et al. (2009)), chemical (S.G. Schrank et al.(2005)), biological (Mayhew et al., 2002, 2003) and thermal disintegration (Vlyssides and Karlis (2004), Ferrer et al. (2006)) were investigated in both lab-scale and full scale studies. These pre- treatment methods cause disintegration of sludge cells. Intracellular matter is released and becomes more accessible by anaerobic microorganisms (Muller et al., 2004).

Ultrasonic energy can be applied as pre-treatment to disintegrate sludge flocs and disrupt bacterial cells' walls, and the hydrolysis can be improved, so that the rate of sludge digestion and methane production is improved (Wang et. al., 2005). Ultrasound treatment as sludge disintegration results in increase of chemical oxygen demand in the sludge supernatant and size reduction of sludge solids (Tiehm et. al., 1997). Ultrasonic process leads to cavitation bubble formation in the liquid phase. These bubbles grow and then violently collapse when they reach a critical size. Cavitational collapse produces intense local heating and high pressure on liquid–gas interface, turbulence and high shearing phenomena in the liquid phase. Because of the extreme local conditions, OH•, HO_2•, H• radicals and hydrogen peroxide can be formed. Thus, three mechanisms (hydro-chemical shear forces, thermal decomposition of volatile hydrophobic substances in the sludge, and oxidizing effect of free radicals produced under the ultrasonic radiation) are responsible for the ultrasonic activated sludge disintegration (Wang et. al., 2005, Riesz et.al., 1985, Bougrier et. al., 2005). Among the four mechanisms mentioned above, hydro-chemical shear forces have the predominant effect on floc disintegration (Wang et. al., 2005). Mechanisms of the ultrasonic process are influenced by supplied energy, ultrasonic frequency, and nature of the influent (Bougrier et. al., 2005). The effects of initial total solids content of sludge, power density, and sonication time on floc disintegration were investigated by several researchers (Chu, et.al., 2001; Show et. al., 2007; Pham et. al., 2008; Xie et. al., 2009). Previous studies showed that low density and long duration sonication is more efficient than high density and short duration (Zhang et. al., 2008, Huan et. al., 2009).

The main purpose of this thesis was to investigate the ultrasonic pre-treatment of meat processing sludge for disintegration purpose. The effects of specific supplied energy levels on ultrasonic floc disintegration performances were examined. Besides, the potential for improving anaerobic digestion through ultrasonic pre-treatment was investigated. In addition, the effect of ultrasonic pre-treatment on filterability characteristics of sludge was evaluated using lab-scale experiments.

CHAPTER TWO
BACKGROUND INFORMATION AND LITERATURE REVIEW

2.1 ANAEROBIC DIGESTION

2.1.1 General Review

Compared to forest and agricultural biosolids, waste water biosolids are mainly composed of highly putrescible volatiles. It is necessary to treat the raw sewage sludge biologically assuring an ensuing environmentally safe utilisation and disposal. The standard stabilisation process for waste water solids is the anaerobic fermentation. In this process a net reduction of the biosolids mass and volume is realised. A portion of the volatile solids is microbiologically converted into methane and carbon dioxide that we call biogas. This biogas is used energetically. The final product are stable, harmless biosolids, that can be used as a fertiliser.

2.1.2 Mechanisms of anaerobic digestion

Anaerobic digestion is a series of processes in which microorganisms break down biodegradable material in the absence of oxygen (Filibeli, A., Büyükkamacı, N., Ayol, A., 2000). It is widely used to treat wastewater sludges and organic waste because it provides volume and mass reduction of the input material. As part of an integrated waste management system, anaerobic digestion reduces the emission of landfill gas into the atmosphere. Anaerobic digestion is widely used as a renewable energy source because the process produces a methane and carbon dioxide rich biogas suitable for energy production helping replace fossil fuels. Also, the nutrient-rich digestate can be used as fertiliser (Residua, 2003, Metcalf & Eddy, 2004, Speece, 1996).

The digestion process begins with bacterial hydrolysis of the input materials in order to break down insoluble organic polymers such as carbohydrates and make them available for other bacteria. Acidogenic bacteria then convert the sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acids. Acetogenic bacteria then convert these resulting organic acids into acetic acid, along with additional ammonia, hydrogen, and carbon dioxide. Methanogens, finally are able to convert these products to methane and carbon dioxide (Metcalf & Eddy, 2004).

There are a number of microorganisms that are involved in the process of anaerobic digestion including acetic acid-forming bacteria (acetogens) and methane-forming archaea (methanogens). These organisms feed upon the initial feedstock, which undergoes a number of different processes converting it to intermediate molecules including sugars, hydrogen & acetic acid before finally being converted to biogas (Speece, 1996).

Different species of bacteria are able to survive at different temperature ranges. Ones living optimally at temperatures between 35-40°C are called mesophiles or mesophilic bacteria. Some of the bacteria can survive at the hotter and more hostile conditions of 55-60°C, these are called thermophiles or thermophilic bacteria. Methanogens come from the primitive group of archaea. This family includes species that can grow in the hostile conditions of hydrothermal vents. These species are more resistant to heat and can therefore operate at thermophilic temperatures, a property that is unique to bacterial families (Davies, 2007). As with aerobic systems the bacteria in anaerobic systems the growing and reproducing microorganisms within them require a source of elemental oxygen to survive.

In an anaerobic system there is an absence of gaseous oxygen. Gaseous oxygen is prevented from entering the system through physical containment in sealed tanks. Anaerobes access oxygen from sources other than the surrounding air. The oxygen source for these microorganisms can be the organic material itself or alternatively may be supplied by inorganic oxides from within the input material. When the oxygen source in an anaerobic system is derived from the organic material itself, then the 'intermediate' end products are primarily alcohols, aldehydes, and organic acids plus carbon dioxide. In the presence of specialised methanogens, the intermediates are converted to the 'final' end products of methane, carbon dioxide with trace levels of hydrogen sulfide. In an anaerobic system the majority of the chemical energy contained within the starting material is released by methanogenic bacteria as methane. Populations of anaerobic microorganisms typically take a significant period of time to establish themselves to be fully effective. It is therefore common practice to introduce anaerobic microorganisms from materials with existing populations. This process is called 'seeding' the digesters and typically takes place with the addition of sewage sludge or cattle slurry. (Metcalf & Eddy, 2004, Speece, 1996)

2.1.3 Anaerobic Digestion Stages

In anaerobic digestion, there are three main stages: hydrolysis, acetogenesis and methanogenesis.

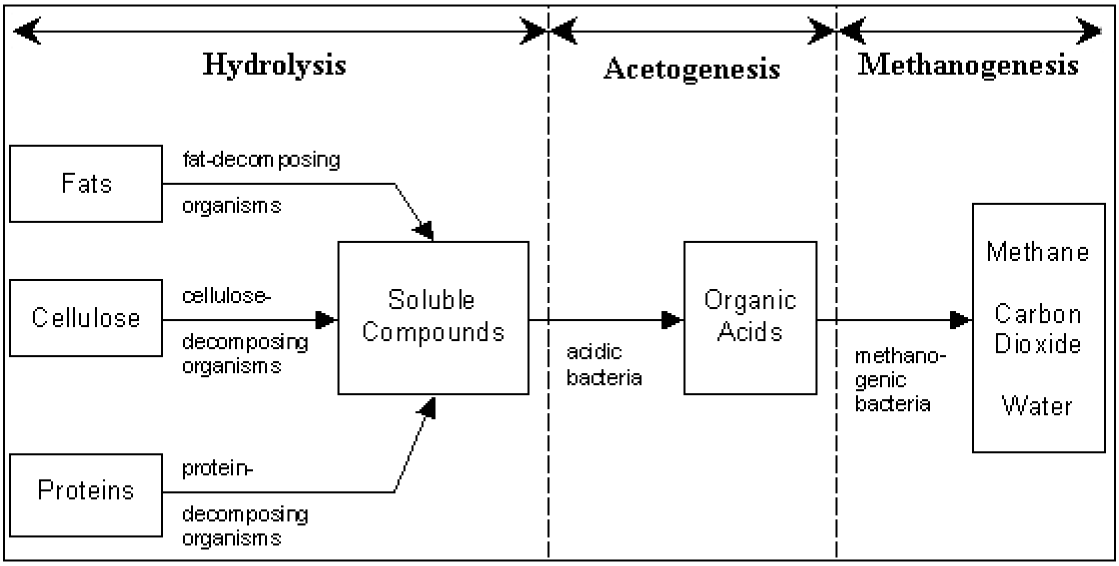

Figure 2.1 Path of Anaerobic Digestion (Metcalf & Eddy, 2004)

2.1.3.1 Hydrolysis Stage

Most waste compounds have non biodegradable properties so it is not possible to treat directly by microorganisms. Because of that, hydrolysis of these complex and insoluble organics are very important in order for them to be used by bacteria as an energy and nutrient source. For example, cellulose should pass through hydrolysis stage to form fats and methane. During hydrolysis, stabilization of the organic material is not possible. In this stage only, transformation of the organic material to a structure that can be used by microorganisms is accomplished. Hydrolysis stage is carried out by enzymes produced and given to the environment by bacteria groups (Filibeli, A., Büyükkamacı, N., Ayol, A., 2000, Metcalf & Eddy, 2004).

It is not possible for the bacteria to completely assimilate the organic matter, because the organic connections in these materials are not easily disturbed. As a result, the total rate of stabilization and methane fermentation depends on the completion of hydrolysis stage which is the beginning of stabilization. Complex organic matter is decomposed into simple soluble organic molecules using water to split the chemical bonds between the substances.

Hydrolized complex organic materials, carbohydrates, fats and proteins are fermented to fatty acids, alcohol, carbon dioxide, ammonium, formic acid and hydrogen produced by ferrodoxine oxidation (Toprak, 1990).

2.1.3.2 Acid Production Stage

In this stage, products formed as a result of hydrolysis stage, are oxidized to H_2 and acetate. After this formation, hydrogen is used as an energy source by some bacteria for acetate production and for the reduction of carbon dioxide to methane. But, hydrogen sulphur in the system carries inhibitory properties for acid forming bacteria. As a result, organic acid concentration decreases and methane production is inhibited (Speece, 1996; Öztürk, 1987). Consequently, hydrogen can be used as an efficiency indicator because of its regulating effect in acid production and consumption.

2.1.3.3 Methane Production Stage

Stabilization of wastewater is completed during methane production phase. In methane production stage, two different groups of organisms are active. These are; methane bacteria that use molecular hydrogen to form methane and methane bacteria that produce methane and bicarbonate by acetate dicarboxylation. This stage prevents accumulation of acids and alcohol and as a result prevents reduction of system efficiency (Metcalf & Eddy, 2004; Speece, 1996).

All methane bacteria can not consume hydrogen. Some of them can also use formic acid and methanol. At first, the compound is transformed to CO_2 and H_2 and if there are H_2 and CO_2 present in the system together with methanol, then reproduction of methanol reducing bacteria increases.

The source of 70 % of the methane produced during anaerobic degradation of organic material is acetate. But, since transformation rates of acetic acid to methanogenes and adaptation of microorganisms to the wastewater are slow, this stage causes the start-up period getting longer.

In anaerobic treatment of wastewater, hydrogen and acetic acid are used by methane bacteria for methane formation as the main substrates. Since the transformation of organic acids to methane, phase needs very little energy, their growth rates are slow and synthesizing organism efficiency is also low (Özer & Kasırga, 1987).

$$CH_3COOH \longrightarrow CH_4 + CO_2 \qquad (1)$$

In the part of 28 % which is left in the system; its 13 % is propionic acid and 15 % is the other intermediate products. These are formed as a result of CO_2 reducing methane bacteria by using hydrogen as an energy source.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad (2)$$

Gas quantity produced during anaerobic treatment depends on the degredated organic material quantity. In calculating organic matter mass balance of the system, this fact makes estimation of the system efficiency easier. CH_4, CO_2 and H_2S are main gas components produced.

Continuous monitoring of CO_2 and H_2S percentages of the produced gas and also volatile acid, H_2 and pH are important parameters in early estimation of any disturbance possible in the treatment.

pH decrease in anaerobic treatment unit effects the system negatively. As a result, CO_2 quantity in the produced gas should be controlled, continuously. CO_2 concentration is important in determining the process phase. For example, normally 31-35% of the produced biogas is CO_2 and this percentage shows that degradation is in a good phase.

The anaerobic process only takes place under strict anaerobic conditions. It requires specific adapted bio-solids and particular process conditions, which are considerably different from those needed for aerobic treatment. (Metcalf & Eddy, 2004, Speece, 1996)

2.1.4 Advantages and disadvantages of Anaerobic Digestion

Advantages and disadvantages of the anaerobic digestion are given below:

2.1.4.1 Advantages of anaerobic digestion

- In treatment of medium and high strength wastewater (Chemical oxygen demand COD $\geq$ 1500 mg/l), usage of anaerobic treatment is cheaper than aerobic treatment
- Biological solid material production is very low
- Dewatering of waste biological sludge is very easy because this sludge is highly stabilized
- Nutrient requirement is low
- There is not any energy requirement for aeration
- A useful final product, methane is produced
- It is possible to apply relatively high loading rates under appropriate conditions
- Treatment is not limited with oxygen transfer

- When compared with aerobic treatment systems, they need small area
- Anaerobic digestion has a relatively low cost technology with respect to the equipment's used
- It is appropriate for seasonal and batch operation
- It is possible to apply anaerobic treatment systems both for big and small scales. (Filibeli, A., Büyükkamacı, N., Ayol, A., 2000 chap. 1)

2.1.4.2. Disadvantages of Anaerobic Digestion

- It needs high temperature (25°C - 40°C)
- Methane bacteria reproduce very slowly and they are very sensitive to environmental conditions
- Even though it is very efficient for high strength wastewater (Biochemical oxygen demand BOD $\geq$ 1000 mg/l), it has some disadvantages for less concentrated wastewater
- Anaerobic degradation is a highly sensitive process to the presence of some chemical compounds such as $CHCL_3$, CCI and CN^-
- Since the growth rate of anaerobic bacteria is slow, start-up period of the process takes a relatively long time
- Anaerobic degradation process is mainly a pretreatment method. Consequently, before giving the treated water to the receiving media an appropriate final treatment is required. (Filibeli, A., Büyükkamacı, N., Ayol, A., 2000 chap. 1)

2.2 Characterization of Meat Processing Sludge

One of the most important kinds of agro-food industries is meat industry, which produces million tons of meat products. The meat industry wastewater contents proteins, fats, carbohydrates from meat, blood, skin and feathers. The water is also polluted with a fair amount of grit and other inorganic matter (Xu et al., 2009).

The organic wastes generated in a meat industry are manure (high solid content), slurry (low solid content), paunch waste from slaughterhouses, meat and bone meals considered as waste products due to the Creutzfeldt–Jakob syndrome, animal fats and sludge generated in the meat industry wastewater treatment plant. Anaerobic treatment of animal wastes such as manure has been reported by several researches (Buendia et al., 2008).

However, meat industry wastes have a very complex composition and to optimize the biological treatment conditions it is necessary to make a thorough analysis of the properties of these organic wastes in terms of their different biodegradable fractions and degradation kinetics. Many of these wastes are solids and either not biodegradable or very slow to degrade (Rico et al., 2007).

The presence of high strength oil and grease (O&G) in industrial wastewaters poses serious challenges for biological treatment systems, often necessitating costly modifications by inclusion of physio-chemical processes such as flotation, sedimentation, flocculation and membrane filtration. In aerobic systems, high oil and grease has a detrimental impact on oxygen transfer efficiency. Under anaerobic conditions, long-chain fatty acids, such as oleic acid, the product of lipid hydrolysis are well-known inhibitors of anaerobic systems (Nakhla et al., 2003). Anaerobic treatment alone is not very efficient at eliminating oil and grease (Wahaab et al., 1999).

Anaerobic treatment processes can favorably compete with aerobic processes for the treatment of high O&G food industry wastewater provided that the wastewater is high in strength and is at high temperatures, particularly at thermophilic ranges where the solubility of oils is high. Batch scale anaerobic treatability studies were conducted to evaluate the feasibility of using a biosurfactant, It can thus be concluded that anaerobic treatment of high oil and grease wastewater can be accomplished by the use of biosurfactants (Nakhla et al., 2003).

Some by-products from meat-processing industry, such as grease trap sludge, are lipid-rich, small particles and pasties, have little fibrous structure and high water content which makes them suitable substrate for anaerobic digestion. On the other hand, digestive tract content consists of partly digested fodder with carbohydrates and lignin. Lipid-rich materials have high methane production potential, but their degradation products, long chain fatty acids (LCFAs), can be inhibitive in high concentrations. LCFA inhibition was long believed to be irreversible, but recent studies have shown the contrary, though recovery takes a long time. Also, high concentration of ammonia is inhibitive and may pose problems when digesting protein-rich materials. Pre-treating organic materials prior to anaerobic digestion aims at enhanced hydrolysis and thus more complete degradation, as bacterial cells are only able to uptake small molecules. Several pre-treatments have been attempted with meat-processing industry residues and slaughterhouse wastewaters. Five different pre-treatments (thermal, ultrasound, base, acid and bacterial product) were used in order to hydrolyze by-products from meat-processing industry. Ultrasound was the most effective pre-treatment with the lipid-rich materials, dissolved air flotation (DAF) sludge and grease trap sludge. Ultrasound and also bacterial product increased CODsol/VS of DAF sludge by 76%, while with grease trap sludge, ultrasound and thermal treatments increased it by 121 and 98%, respectively, compared to the CODsol/VS of untreated material. Ultrasound was found the most versatile pre-treatment, as it effectively solubilized all the studied materials (32–536% increase in CODsol/VS and 27–408% increase in CODsol compared to untreated materials). This is comparable or higher than the 40 and 89% increase in CODsol when sonicating (20 kHz) raw sewage sludge and waste activated sludge. The studied physical (ultrasound and thermal) pre-treatments showed good potential for pre-treating meat-processing industry by-products rapidly, and they have already been reported as the most potential pretreatments for sewage sludge (Luste et al., 2009).

2.3 Sludge Disintegration

2.3.1 Sludge Disintegration Mechanisms

Sewage sludge disintegration can be defined as the destruction of sludge by external forces. These forces can be of physical, chemical or biological nature. A result of the disintegration process is numerous changes of sludge properties, which can be grouped in three main categories:

- destruction of floc structures and disruption of cells
- release of soluble substances and fine particles
- biochemical processes (Müller et. al., 2003, Müller et. al., 2004)

The applied stress during the disintegration causes the destruction of floc structures within the sludge and/or leads to the break-up of micro-organisms. If the energy input is increased, the first result is a decrease in particle size within the sludge. The destruction of floc structures is the main reason for this behavior. The disruption of microorganisms is not as easily determined by the analysis of particle size because disrupted cell walls and the original cells are of similar size. Floc destruction and cell disruption will lead to the following changes in sludge characteristics:

Disintegrated micro-organisms are much more easily hydrolyzed than undisrupted ones. The reduction in particle size generally allows an easier hydrolysis of solids within the sludge due to larger surface areas in relation to the particle volumes.

All micro-organisms are affected by the disintegration process. Higher organisms are disrupted easiest because of their size and gram-positive bacteria are the most difficult organisms to be disrupted due to their strong cell wall. Depending upon the treatment a partial up to a complete disinfection of the sludge is possible since pathogenic micro-organisms are also disintegrated (Barjenbruch, M., et al, 2003).

In case of a strong disintegration a large amount of organic solid material is transferred into the liquid phase. The remaining solid sludge particles contain a higher percentage of inorganic substance. The result is a higher content of dry substance after dewatering (Müller, 2003). The reduction of particle size and therefore the increase of the specific surface causes a higher amount of surface charges that need to be neutralized when the sludge is conditioned. Consequently, disintegrated sludges use more flocculant.

The destruction of floc structures and disruption of cells result in the release of organic sludge components into the liquid phase. These components exist in a dissolved phase already, e.g. components of the intracellular water, or can be liquefied. Particle size or colloidal components may still be present within the solution because they cannot be separated from the liquid phase. Their microscopic particle size and only a slight difference in density of particle and surrounding water are the cause. But the components are easily biodegradable on the other hand. Since they are already liquefied or offer a large surface in comparison to their volume, the hydrolyzing process is simple.

Carbon compounds are easily accessible and can be digested much faster in later biological processes than sludge in a particular phase. The results are shorter degradation times and higher degrees of degradation during the aerobic and anaerobic stabilization. The wastewater has to be cleaned from released nitrogen and phosphorus compounds before leaving the treatment plant. If this happens by returning the water into the waste activated sludge-process, additional capacities have to be taken into account. Disintegration within the sludge pre-treatment has advantages in combination with selective recycling processes due to the increased nitrogen and phosphorus concentrations.

During or immediately after the disintegration, biochemical reactions may appear. The influence of these reactions on the degradability of the sludge is contrary:

- Continuing formation or release of easily degradable compounds
- Formation of hardly degradable compounds

The formation of problematically biodegradable, humic-like reaction products if sludges are disintegrated at higher temperatures can be explained by the "Maillardreaction". At lower temperature ranges this effect is less strong, but it is suspected that problematically biodegradable compounds are produced in any thermal disintegration process. Many times proven is the transformation of problematic compounds to easily degradable compounds by partial oxidation. This effect has been found especially in the treatment of industrial wastewaters, but it is not fully verified in sludge treatment through ozone or other oxidation partners. The formation of hardly degradable compounds was found as well and degradation processes only performed well after an adaptation of the micro-organisms (Müller et. al., 2004). The possible objectives of sludge disintegration is summarized in Table 2.1.

Table 2.1 Possible objectives of sludge disintegration (Müller et. al., 2003)

Reduction of sludge	**Improvement of sludge characteristics**
Improvement of the anaerobic degradation performance of surplus sludge	Improvement of the settling performance of bulking and floating sludge
Halogen donor for the denitrification	Reduction of foam production
Improvement of the recycling options of phosphorus and nitrogen	Improvement of sludge conditioning
	Reduction of pathogens

Large amount of wastewater sludge is generated in the biological wastewater treatment processes. The treatment of wastewater sludge presents high cost and imposes great risks to the public health once the treatment system fails. Therefore, the preferred solution is to minimize wastewater sludge production. Cryptic growth of microorganisms has been found very effective to reduce wastewater sludge. However, cryptic growth is very slow due to the stable structure of wastewater sludge. Solid granules, the core of sludge, adsorb a great deal of microorganisms to form small flocs, which further absorb organic macromolecule including saccharides, organic acids, nucleic acids, proteins and fats to make up a loose three-dimensional structure utilizing the bridging effects of positive ions such as Ca^{2+} and Mg^{2+}. Microorganisms can hardly utilize particulates and liquefaction of wastewater sludge is required for effective cryptic-growth. Various methods have been proposed to facilitate the sludge liquefaction and the best one was found to be ozonation.

Pre-treatment processes, namely mechanical disintegration, thermal and thermo-chemical hydrolysis, advanced oxidation processes have been applied in various sludge treatment processes, such as dewatering, digestion, and reutilization to improve treatment efficiency. Most of these processes improved sludge dewaterability characteristics by disrupting extracellular polymeric substances (EPS), which is one of the main components of sludge.

On the other hand, the pre-treatment processes break up sludge flocs, destroying cell walls and membranes, resulting in release of intracellular organics in liquid phase and change in sludge compositions. This enhances the overall solubilization and biodegradability for stabilization and reutilization processes.

2.3.2 Sludge Disintegration Methods

In recent years, for the purpose of wastewater sludge (WWS) minimization and more biogas production than classical anaerobic digestion, several disintegration methods have been investigated. The methods can be classified as;

- Chemical disintegration (Ozone treatment, Alkaline treatment, Fenton process etc.)
- Mechanical disintegration (Stirred ball-mill, High-pressure homogenizer, Ultrasonic Homogenizers, Lysatcentrifuge, Jet Smash Technique, The High Performance Pulse Technique etc.)

- Thermal disintegration
- Biological disintegration (High temperature sludge stabilization with thermophilic bacteria, Enzymatic lysis) (Ayol, A., et al, 2007; G. Erden Kaynak, A. Filibeli, 2007; Salsabil et al., 2009; Lehne, G.A., et al, 2001).

As a technique of chemical disintegration, Fenton oxidation process and ozone treatment are widely used in experimental studies. In Fenton oxidation process, organic substances react with hydrogen peroxide in the presence of inexpensive ferrous sulfate to reduce toxicity and organic load. The oxidation mechanism by Fentons reagent is due to the reactive OH generated in an acidic solution by the catalytic decomposition of hydrogen peroxide. Although the Fenton reaction has been widely studied, there is no agreement on the ratio $[H_2O_2]/[Fe^{2+}]$ that gives the best results. The same occurs with H_2O_2/UV reactions, where an excess of H_2O_2 can act as a hydroxyl scavenger instead of a HO source and which in addition interferes with the determination of the chemical oxygen demand (COD) (G. Erden Kaynak, A. Filibeli, 2007; Schrank et al.,2005).

The application of ozone for sludge solubilization has been demonstrated within aerobic and anaerobic sludge digestion systems. The hydrolysis of sludge can be accomplished by exposing it to highly oxidative conditions (ozone) which rupture cell walls releasing soluble COD. Mechanistically, ozone reacts with polysaccharides, proteins, and lipids (which are components of cell membranes), transforming them into smaller molecular-weight compounds. In doing so, the cellular membrane is ruptured, spilling the cell’s cytoplasm. (Elliott,A., Talat,M., 2007)

The hydrolysis of cellular membranes can also be achieved by mechanical disintegration techniques. The two predominant techniques used are the Kady mill, which uses two counterrotating plates to produce shear, and the wet milling, which is more of a grinding method. The use of a Kady mill for the disintegration of waste activated sludge for its return to the front end of a fullscale aerobic municipal activated sludge treatment system is described in Springer and Higgins (1999). There was a 25% increase in soluble COD after processing the waste activated sludge through the mill. This technology can also be readily used as a pretreatment of sludge to anaerobic digesters (Elliott,A., Talat,M., 2007).

Stirred Ball Mills (SBM) consist of a cylindrical grinding chamber of up to 1 m3 of volume which is almost completely filled with grinding beads. An agitator forces the beads into a rotational movement. The micro-organisms are disintegrated in between the beads by shear- and pressure-forces. For a continuous operation the beads are held back by a sieve while the suspension can flow through the grinding chamber. *High Pressure Homogenizers (HPH)* basically consist of a multistep high-pressure-pump and a homogenizing valve. The pump compresses the suspension to pressures up to several hundred bar, realising a flow of up to several cubic meters per hour. The suspension passes through the homogenizing gap while the pressure drops below the vapour pressure of the fluid. The fluid velocity increases up to 300 m/s. When the occurring cavitation bubbles implode, pressure gradients are induced into the fluid causing temperatures of several hundred degrees Celsius and pressure peaks of 500´105 Pa locally. *Ultrasonic Homogenizers (UH)* consist of three major components. Agenerator supplies a high frequent voltage of 20 to 40 kHz. A ceramic-crystal of piezo-electrical material transforms electrical into mechanical impulses, which are transmitted by a sonotrode into the fluid. Cavitation bubbles are created by alternating overpressure and underpressure. *The Mechanical Jet Smash Technique (MJS)* pressurizes the sludge up to 50´105 Pa and then releases the sludge through a nozzle. The accelerated sludge (30 to 100 m/s) smashes onto a plate where the disintegration takes place. *The High Performance Pulse Technique (HPP)* is an electro-hydraulic method. The sludge is treated by high voltage of up to 10 kV. So a sudden disruption and release of organic substances takes place. The pulse period is only 10 ms, inducing shockwaves in the sludge which lead to disintegration. *The Lysat-Centrifugal-Technique (LC)* uses a decanter equipped with a disintegration device located at the discharge of the dewatered sludge. Tools on either the rotor or the stator stress the sludge by shear forces (Muller, 2000a).

Most investigations involving thermal pretreatment have used exposure temperatures ranging between 150 and 200 °C. It was founded that the thermal hydrolysis of primary and secondary municipal sludges at a very high temperature of 270 °C (for 25 min) prior to digestion in a temperature phased anaerobic digester (TPAD) allowed higher organic loading and increased VS destruction and gas production (Elliott,A., Talat,M., 2007).

Ferrer et al. (2006) found at low temperatures thermal pretreatment was advantageous in terms of gas production from thermophilic anaerobic digestion. In their study, the municipal sludge was conditioned at 110–134 °C (for 20–90 minutes) and at 70 °C (for 9–72 hours) before thermophilic anaerobic digestion. Additional samples of sludge were also conditioned with ultrasound (300W at 20 kHz) to provide a comparison with thermal treatment. Though all pretreatments increased soluble organic content of the sludge, only the low temperature (70 °C) treatment showed a positive effect on biogas production.

The use of microbial enzymes for the enhancement of degradation of waste activated sludge is the basis for another process called the Enzymic Hydrolysis (EH) Process. The primary benefit described by the developers of this process is the pathogen kill; however, a further benefit is the enhancement of biogas production in anaerobic digestion. During laboratory trials, a 10% improvement in biogas production was found. (Ayol, A., et al, 2007).

2.4 Mechanisms of Ultrasonic Disintegration

Ultrasonic energy can be applied as pre-treatment to disintegrate sludge flocs and disrupt bacterial cells' walls, and the hydrolysis can be improved, so that the rate of sludge digestion and methane production is improved (Wang et. al., 2005). Ultrasound treatment as sludge disintegration results in increase of chemical oxygen demand in the sludge supernatant and size reduction of sludge solids (Tiehm et. al., 1997).

There are four paths, which are shown as following, responsible for the ultrasonic activated sludge disintegration:

- hydro-mechanical shear forces;
- oxidizing effect of •OH, •H, •N and •O produced under the ultrasonic radiation;
- thermal decomposition of volatile hydrophobic substances in the sludge;
- increase of temperature during ultrasonic activated sludge disintegration (Wang et. al., 2005).

Ultrasonic process leads to cavitation bubble formation in the liquid phase. These bubbles grow and then violently collapse when they reach a critical size. Cavitational collapse produces intense local heating and high pressure on liquid–gas interface, turbulence and high shearing phenomena in the liquid phase. Because of the extreme local conditions, OH•, HO_2•, H• radicals and hydrogen peroxide can be formed. Thus, sonication is a combination of different phenomena: chemical reactions using radicals, pyrolysis, and combustion and shearing. Mechanisms of the ultrasonic process are influenced by three factors:

- supplied energy,
- ultrasonic frequency and,
- nature of the influent.

Specific energy (SE) is defined using ultrasonic power (P), ultrasonic time (t), sample volume (v) and initial total solid concentration (TS_0):

$$SE = (Pt)/(vTS_0) \qquad (3)$$

Cell disintegration is proportional to supplied energy. High frequencies promote oxidation by radicals, whereas low frequencies promote mechanical and physical phenomena like pressure waves. With complex influents, radical performance decreases. It has been shown that degradation of excess sludge is more efficient using low frequencies (Bougrier et. al., 2005).

The effects of initial total solids content of sludge, on floc disintegration were investigated by several researchers (Bartholomew, 2002, Neis, 2000, Lafitte-

Trouque, 2002, Nickel, 2007). Results show that low solids content of sludge is more efficient than high solids content.

Ultrasound frequencies range from 20 kHz to 10 MHz. Particularly at low frequencies from 20 kHz to 40 kHz cavitations occur when the local pressure in the aqeous phase falls below the evaporating pressure resulting in the explosive formation of small bubbles. These bubbles oscillate in the sound field over several oscillation periods, grow by a process termed rectified diffusion, and collapse in a nonlinear manner. Cavitation is accomplished by high pressure gradients, an extreme increase of the temperature inside the bubbles, and in the region around the bubble. Therefore, cavitations lead to strong mechanical forces.

Reported advantages of ultrasonic technologies are;

- average payback period of the installed plants is below two years; This is mainly due to the high cost of recycling of sludge. (the main influences on payback time would consist of local legislation, treatment type, land availability, electricity price and views on renewable energy)
- improves degradation of organic material (30-45%)
- increases yield in digester biogas (30-45%); The increase in biogas production could produce as much as 240 million m^3 of gas or 480 GWh/yr of "green" electricity.
- reduces sludge solids content (5-25%)
- increases dry solids with dewatering with or without prior digestion (5-10%)
- reduces polymer and other flocculant use (15-45%)
- minimizes sludge cake quantity (25-40%)
- eliminates sludge bulking
- Less sludge, improved sludge stabilization, and enhanced dewaterability result in an improved C/N ratio for denitrification. (Bartholomew,R., 2002)

2.5 Literature Review

Bougrier et. al., 2005 was studied solubilization of waste activated sludge by ultrasonic treatment. Different ultrasonic energy supplies (ranged from 0 to 15,000 kJ/kg TS) were applied to the activated sludge in their study with a constant operating frequency of 20 kHz and a constant supplied power of about 225W. As conclusions of that study, COD, organic matter, biogas production and nitrogen solubilisation increased with supplied energy. The ultrasonic process led to floc size reduction and cells lysis. For specific supplied energy lower than 1000 kJ/kg TS, energy was used in order to reduce flocs size. Then, supplementary energy was used to break flocs or cells. That permitted the release of organic substances into the liquid phase. Organic substances were more available, so biodegradability was improved. In term of biogas production, it did not seem interesting to have a supplied energy higher than 7000 kJ/kg TS. Indeed, when the supplied energy was higher than 7000 kJ/kg TS, biogas generation was constant and solubilisation was less marked.

Tiehm et al., 1997 showed that applying ultrasound (3.6kW, 31 kHz, 64 s) to sludge disintegration can release the organic substances into the sludge, so that the soluble chemical oxygen demand (SCOD) in the supernatant increases from 630 to 2270 mg/L. Moreover, the digestion time reduces from 22 days to 8 days.

Nickel et al., 2007, used a pilot-scale ultrasound reactor (maximum power consumption: 3.6 kW and Ultrasonic frequency is fixed at 31 kHz) for biosolids sonication. Nickel et al., 2007 showed that volatile solids (VS) degradation rate of the sonicated biosolids at 16 days SRT increased by more than 30% compared to conventional digestion. The final concentration of VS in the digested sludge was reduced by 14%. At an SRT of 8 days, ultrasonic disintegration of waste activated sludge enhanced the degree of anaerobic degradation by more than 40%. The highest rate of VS degradation was obtained at the shortest SRT (4 days). Compared to the 16-day SRT control digester the specific volumetric degradation rate increased by a factor of 3.93. The data demonstrate that the anaerobic degradation process is considerably accelerated by ultrasonic sludge pre-treatment. Therefore, ultrasonic disintegration is a promising method to reduce the volume of new biosolids digesters or enables operators to maintain undisturbed biosolids digestion of overloaded systems. Ultrasound disintegration of biological cell mass improves the reaction rate of the anaerobic digestion process of waste activated sludge by a factor of two. The portion of non-degradable matter that exists in each type of biosolids is reduced from 60% to 52% or, in other words, more organic mass is made available for biological digestion when biosolids are sonicated.

Neis et al., 2000, used a pilot- scale plant consisting of a 3.6 kW ultrasound reactor and five stirred tank fermenters. The average waste activated sludge (WAS) retention time is 16 days. The dry solids (DS) content of the thickened WAS varied between 0.7 and 2.6% and the volatile solids (VS) concentration was 78%. The pilot-scale reactor was developed for operation at a low frequency of 31 kHz. Two control fermenters were operated with untreated sludge at sludge residence times (SRT) of 16 and 8 days. Three fermenters were fed with ultrasonically treated sludge at SRT of 16, 8 and 4 days. The enhanced degradation rates resulted in a significant increase of biogas production. Specific biogas yields ranged between 520 and 730 L/kg VS degraded. The methane concentration of the biogas varied between 67 to 72%. In that study demonstrate that ultrasonic cell disintegration is a suitable method to overcome the slow biological sludge hydrolysis. Consequently the fermentation rate is significantly increased. Higher removal rates allow shorter sludge residence times. A decrease in sludge residence time from 16 to 4 days showed no loss in degradation efficiency. Ultrasound treatment of waste activated sludge is a reliable method to reduce the necessary volume of sludge digesters. Higher removal rates lead to higher degree of volatile solids degradation. An increased production of biogas is also observed.

Salsabil et al., 2009, was studied ultrasonic treatment of sludge at different specific energies 3600, 31,500, 108,000 kJ/kgTS led to solubilisation (disintegration) of matter. Experimental results showed that TS, VS, Total Nitrogen, and COD solubilisation increased with increasing specific energy supplied. Poor solubilisation results (10%) could correspond to good disintegration degree (47%). In the conditions of the study (*f* = 20 Hz, power supply = 60W, TS: 17.8 g/L), flow cytometry experiments showed that organic matter solubilisation was not due to cell membrane breakage but more probably to floc breakage.

Some other examples of full- scale plant usage and technology verifications of ultrasonic treatment are given below. All of the ultrasound technology is of patented design and ISO 9001-approved. Ultrasound has been successfully used at full-scale installations for several years in Europe. Currently, there are 8 full-scale plants in Europe (most in Germany) using ultrasound. Some of these plants are described below. An additional eight plants are in the construction phase.

Süd Treatment Works in Germany anaerobically digests a waste stream consisting of *100% secondary sludge*. Since operation of the ultrasound plant began in May 2000, the digesters have experienced an average of 50% improvement in volatile solids destruction. This has resulted in a 45% increase in biogas production. Also, during dewatering, 11% less polymer was needed. An other full- scale plant in Germany is The Darmstadt plant, treats a *mixture of primary and secondary sludge* in a ratio of 35:65. Since operation of the plant began in November 2000, improvements have been made to volatile solids destruction from 44% to 55%. This resulted in an average increase in biogas of approximately 50% prior to treatment. Improvements were also found in the dewatering plant where cake solids content increased by up to 5% in spite of using one third less polymer. Improved dewatering and volatile solids destruction resulted in 20% less cake leaving the works (Bartholomew,R., 2002).

At the Mannheim Sewage Treatment Works in Germany, sludge is composed of *50% primary and 50% secondary sludge* and thickened to 10% dry solids prior to high-rate digestion. Since start-up of the plant, the volatile solids destruction has risen to 70%. This resulted in an increase in biogas production of 45%. Improvements were also noticed in the dewatering operation with a reduction in polymer consumption. Work is currently taking place to optimize the dewatering output. An average improvement of 3 % has been noted so far. The additional biogas produced by ultrasound treatment has resulted in an electricity generation of 1.2MW and this enabled savings to be made of €285,000 ($443,754) per year. The required drying capacity has also dropped by 25%. These benefits have enabled Mannheim to pay for the plant in the first 8 months of operation. Another plant is in operation that uses ultrasound on secondary treatment without digestion. The benefits in this case include the complete elimination of sludge bulking, improved biological nutrient removal, improved denitrification and reduced sludge production. Preliminary results from the plant have shown a decrease in activated sludge production of 20 – 25% (Bartholomew,R., 2002).

Ultrasound design consists of two components: the switchboard and the disintegration system. With the configuration of the ultrasound plant, sewage sludge is led through a flow-through vessel. (Larger systems may have an arrangement of parallel or series lines or both.) In each cell an ultrasound processor generates longitudinal mechanical oscillations. The sonotrode transmits these oscillations on the streaming sewage sludge.

The ultrasound plant has a modular design so it can be easily adapted to cater to different sludge quantities. For example, the plant can be easily expanded in size if future sludge quantities increase or decrease. If sludge quantities are reduced, individual ultrasonic probes can be shut down until required. The entire installation consists of: ultrasound processor, pipe-work and fittings, and the required interface for the implementation of the process control system. Ultrasound treatment units are available in multiples of 1 kW, 2 kW, 4 kW, 8 kW, and 16 KW per probe. Capital and O&M costs for the Ultrasound Treatment vary by the type and size of facility.

In general, capital costs for the ultrasound process are roughly $30,000/kW (One kW of the ultrasound process treats approximately 10,000 population equivalents.). O&M costs are minimal and generally include the need to replace the probes once every 1.5 to 2 years. (Bartholomew,R., 2002)

Ultrasonic energy was applied as pre-treatment to disintegrate sludge flocs and disrupt bacterial cells' walls and the hydrolysis step of anaerobic digestion can be improved, so that the rate of sludge digestion and methane production is improved (Wang et. al., 2005)

Ultrasound treatment as sludge disintegration results in increase of chemical oxygen demand in the sludge supernatant and size reduction of sludge solids (Tiehm et. al., 1997).

The most important results of ultrasonic sludge disintegration are:

- Ultrasonic sludge disintegration is most effective at low ultrasound frequencies.

- Hydromechanical shear forces produced by ultrasonic cavitation are predominantly responsible for sludge disintegration.

- Ultrasonic pretreatment enhances the subsequent anaerobic digestion resulting in a better degradation of volatile solids and an increased production of biogas.

- Preliminary results from a plant that is in operation that uses ultrasonic systems for sludge treatment have shown a decrease in activated sludge production of 20 – 25%.

- Xie et al., 2009, studied with municipal wastewater treatment sludge, was disposed by the anaerobic sludge with/without ultrasonic treatment. The result showed that the COD removal efficiency increased 3.60% after ultrasonic treatment and the effluent COD was about 30% lower than that of the control.

- The SCOD value increases accompanied with the reduction in the microbial density levels.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Introduction

This chapter gives the information on the materials and methods used in this thesis.

3.2 Materials

3.2.1 Sludge

Waste sludge used in the study was obtained from Tanet Inc (Izmir) aerobic wastewater treatment facility. The sludge total solids (TS) was found 1.1 % (w/v) and the supernatant was discarded. Maximum storage period of sludge was 1 week at 4±1 °C to minimize microbial degradation.

Inoculum Sludge used in BMP Assay was taken from a full scale Upflow Anaerobic Sludge Blanket (UASB) reactor treating beer industry wastewater of Anadolu Efes Inc., Izmir.

3.2.2 Basal Medium Used in BMP Assay

Basal medium for BMP Assay contains 0.4 g/L $MgSO_4$, 0.4 g/L NH_4Cl, 0.4 g/L KCl, 0.3 g/L Na_2S, 0.08 g/L $(NH_4)_2HPO_4$, 0.05 g/L $CaCl_2$, 0.04 g/L $FeCl_2$, 0.01 g/L $CoCl_2$, 0.01 g/L KI, 0.01 g/L $Na(PO_3)_6$, 0.5 mg/L $AlCl_3$, 0.5 mg/L $MnCl_2$, 0.5 mg/L $CuCl_2$, 0.5 mg/L $ZnCl_2$, 0.5 mg/L NH_4VO_3, 0.5 mg/L $NaMoO_4$, 0.5 mg/L H_3BO_3, 0.5 mg/L $NiCl_2$, 0.5 mg/L $NaWO_4$, 0.5 mg/L Na_2SeO and 0.01 g/L sistein, and for methane measurements 3% NaOH (w/v) was used. For each of the chemical, a stock solution was prepared.

3.3. Methods Used in Experimental Studies

3.3.1 Analitical methods

Disintegration degree (Muller, 2000a) parameter based on soluble COD calculations was considered as the main parameter for evaluation of sludge disintegration. Soluble part of sludge was obtained with centrifugation carried out at 10 000 rpm and 4°C for 20 min. Dissolved organic carbon (DOC) concentrations were measured using a Shimadzu, ASI-V model TOC analyzer for disintegration evaluation. Dry solids content (DS,%), volatile solids content (VS, %), suspended solids (SS, mg/L), volatile suspended solids (VSS,mg/L), temperature, pH, capillary suction time (CST), chemical oxygen demand (COD), were measured according to procedure given in Standard Methods (APHA, 2005). Nitrogen (N), and phosphorus (P) in sludge supernatant were measured using spectroquant Merck kits numbered 14537, and 00616 respectively, in a Merc Photometer SQ 300 photometer. Particle size distributions of sludge were monitored using Malvern Mastersizer 2000QM analyzer. CST values were analyzed with a Triton A-304 M CST-meter. Extracellular polymeric substances (EPS) were extracted from the samples using the heat extraction technique. Protein contents of EPS samples were analyzed using protein assay kits (Procedure No. TP0300 Micro Lowry, Sigma).

3.3.1.1 Disintegration Degree

DD parameter is calculated as following equation:

$$DD = [(COD_1 - COD_2) / (COD_3 - COD_2)]. 100 \qquad (4)$$

where;

COD_1 = COD concentration of sludge centrate after disintegration,

COD_2 = COD concentration of raw sludge centrate,

COD_3 = COD concentration of sludge centrate after chemical disintegration

Chemical disintegration is processed the sludge at 90 °C for 10 min after the addition of NaOH. Centrate samples were obtained with centrifugation and centrifugation is carried out at 10000 rpm, at 4°C for 20 min.

3.3.1.2 Temperature and pH

Temperature and pH were measured by WTW model 340i multi analyzer (Figure 3.1.).

Figure 3.1 WTW model 340i

3.3.1.3 Particle Size Analysis

Particle size distributions were monitored using a Malvern Mastersizer 2000QM analyzer (Figure 3.2.).

Figure 3.2 Malvern Mastersizer 2000QM analyzer.

3.3.1.4 Total Nitrogen (TN), Total Phosphorus ($PO_4 - P$) Analysis

Total Nitrogen (TN) (Merc cell kit # 14537) and Total Phosphorus (PO_4 – P) (Merc cell kit # 14543) were analyzed by using spectroquant cell test obtained from Merc. For photometric measurement, “Merc Photometer SQ 300” was used.

Figure 3.3 TN and TP cell kits.

3.3.1.5 Dissolved Organic Carbon Analysis

DOC concentrations were measured using a Shimadzu, ASI-V model TOC analyzer. For DOC measurements, ultrasonically pretreated sludge samples were centrifuged at 10000 rpm for 20 minute and filtered by Whatman blue band filter paper. The centrate samples were diluted to 1/20 with pure water before analysis.

3.3.1.6 Protein Analysis

Extracellular polymeric substances (EPS) were extracted from the samples using the heat extraction technique originated by Goodwin and Forster (1985) and Frolund et al. (1996). Protein contents of EPS samples were analyzed using protein assay kits (Procedure No. TP0300 Micro Lowry, Sigma).

3.3.1.7 Capillary Suction Time Test

Capillary Suction Time Test (CST) was also used as another method for the evaluation of the filtration characteristics of conditioned sludge samples. CST values were analyzed using Triton A 304 M CST-meter (Figure 3.3). A standard CST sample cylinder of 1.8 cm diameter was used during experiments with Whatman # 17 filter paper. All CST measurements were conducted in triplicates and average values were taken into consideration for standard deviation to be less than ±1 s.

Figure 3.4 Triton A 304 M CST-meter

3.3.1.8 Chemical Oxygen Demand (COD) Analysis

Chemical oxygen demand was measured in supernatant as soluble COD (SCOD) by centrifuging at 10000 × g for 20 min at 4 ^{o}C, followed by filtration of the sludge supernatant by blue ribbon filter paper.

3.3.2 Biochemical Methane Potential (BMP) Assay

In order to see the effect of ultrasonic pretreatment on anaerobic biodegradability, BMP assay was performed (Owen et. al., 1979). BMP test was applied to both raw and sonicated samples for comparison purpose. In BMP test, 1/1 ratio (as volume) of samples and inoculum was added to a 150 mL serum bottle. Then basal medium (Demirer and Speece, 1996) contained all the necessary micro and macronutrients required for an optimum anaerobic microbial growth was added as the 20% of working volume (60 mL). All bottles were purged with a gas mixture of 75% N_2 and 25% CO_2 for 3–4 min to supply anaerobic conditions and cpped with rubber stoper and sealed with aluminum covers. The serum bottles were then incubated at 36±1 ◦C in a temperature-controlled room. Methane gas productions were measured daily with liquid displacement method by using 3% NaOH (w/v) containing distilled water (Razo-Flores et. al., 1997).

Figure 3.5 Incubator used for BMP test

3.3.3 Ultrasonic Pre-treatment

The ultrasonication was carried out using ultrasonic homogenizer. The ultrasonic apparatus was a Sonopuls ultrasonic homogenizer (Bandelin- Sonopuls HD 2200) (Figure 3.4). This apparatus was equipped with a VS 70 T probe with a tip diameter of 2 cm, operating frequency of 20 kHz and a supplied power of 200 W. 250 mL of wastewater sludge sample at ambient temperature (20 ± 1 ^{o}C) was placed in a 600 mL beaker. For each experiment, 250 mL of sludge were filled in a glass beaker without temperature adjustment (no cooling) and ultrasonic probe was submerged into the sludge containing beaker to the depth of 2 cm above the bottom of the beaker. Specific energy was considered as a main variable parameter for evaluation of disintegration performance of sludge. The range of the specific energy (SE) varied from 0 to 100000 kJ/kgTS.

Figure 3.6 The ultrasonic homogenizer (Bandelin- Sonopuls HD 2200).

3.3.4 Specific Energy

The specific energy is defined as the amount of mechanical energy that stresses a certain amount of sludge. (Muller, 2000a) SE was determined by using ultrasonic power (*P*), ultrasonic time (*t*), sample volume (*V*) and initial total solid concentration (TS_0) according to the following equation (Bougrier et. al., 2006) :

$$SE= (P*t) / (V*T*S_0) \qquad (5)$$

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Sludge Characteristics

In this thesis, ultrasonic treatment was applied to meat processing sludge for floc disintegration purpose. Meat processing sludge was sampled from Tanet Inc (Izmir) aerobic wastewater treatment facility. Samples were stored at +4° C in a refrigerator and before the analysis; they were waited in room temperature until their temperature reached to 20 ± 1°C. Inoculum sludge used in BMP assay was taken from a full scale upflow anaerobic sludge blanket (UASB) reactor treating beer industry wastewater of Anadolu Efes Inc., Izmir. The properties of meat processing sludge and anerobic inoculums sludge are given in Table 4.1.

Table 4.1 Characteristics of meat processing sludge and anerobic inoculums sludge

Parameters	Raw sludge characteristics	Anaerobic inoculums sludge
Total solids (TS, %)	1.10	7.35
Volatile solids (VS, %)	76.00	82.2
Suspended solids (SS, mg/L)	10520	72750
Volatile suspended solids (VSS, mg/L)	9100	64225
pH	7.29	7.93
T (°C)	20±1	20±1
Capillary suction time (CST, sec.)	14.50	197
Particle size (µm)		
Surface weighted mean D[3,2]	71.530	93.705
Volume weighted mean D[4,3]	148.584	526.432
d (0.5)	53.228	433.559
d (0.9)	118.103	1202.893
d (0.1)	255.033	37.299
Total Nitrogen (TN, mg/L)	9	95.5
Total Phosphorus (TP, mg/L)	4.8	125
DOC (mg/L)	340.60	-
SCOD (mg/L)	880	1920
Oil and Grease (mg/L)	19478	-
Protein (mg/L)	2530.60	-

4.2 Disintegration Degree

The disintegration degree permits to evaluate the maximum level of sludge solubilization. Increase of DD is determined as the substance that can be readily used to produce methane in the anaerobic digestion (Wang et al., 2005). Variation of disintegration degree with specific energy is given in Figure 4.1. The disintegration degree of biological sludge increased significantly with increasing specific energy in each experiment. The maximum disintegration degree of 47.4 % was obtained for specific energy of 30000 kJ/kg TS. For specific energies above 30000 kJ/kgTS, DD decreased. Decreasing of DD may be explained by high oxidation effects of radicals. High ultrasonic energies promote oxidation by radicals and ultrasonic pre-treatment led to mineralization preceding solubilization of sludge.This result was observed in other study for waste activated sludge (Bougrier et. Al., 2006).

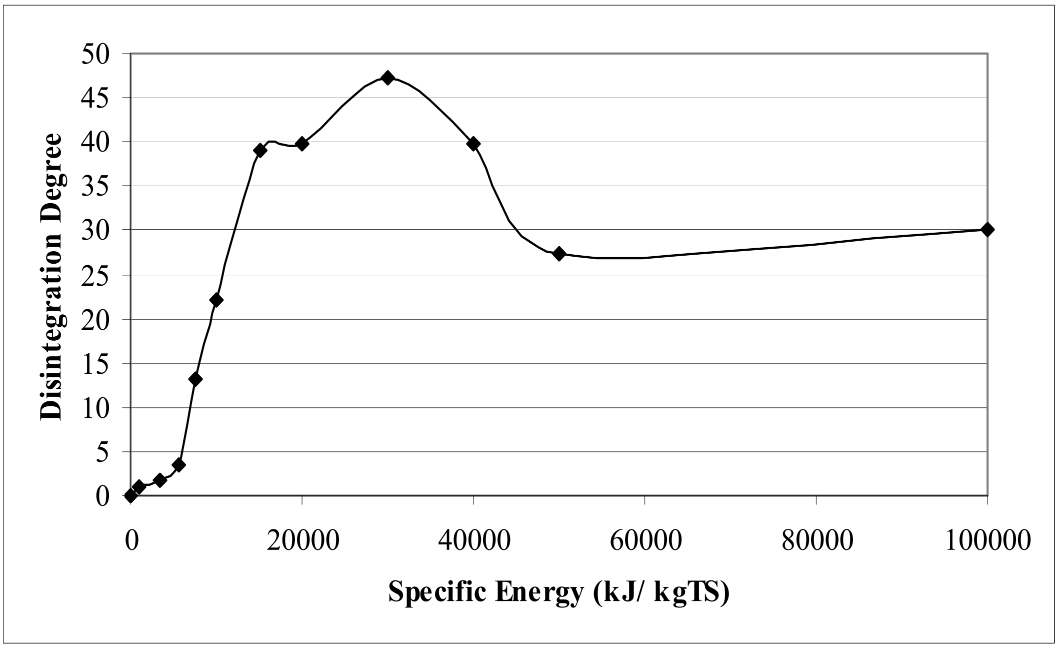

Figure 4.1 Variation of Disintegration Degree with specific energy

4.3 Physico-chemical characteristics

The changes in the particle size distributions of raw and ultrasonically pretreated sludge samples are shown in Table 4.2. and Figure 4.2. Reductions in particle size of ultrasonically pretreated sludge samples can be clearly seen from these results.

The reduction in particle size generally allows an easier hydrolysis of solids within the sludge due to larger surface areas in relation to the particle volumes. The result is an accelerated and enhanced degradation of the organic fraction of the solid phase (Muller, 2003). Although particle size distribution shows the sludge disintegration, this parameter is not efficient for process optimization (Muller et. Al., 2004). Table 4.2 shows the particle size changes for different specific energies. D (0.1), d (0.5), and d (0.9) demonstrate 10 %, 50 %, and 90 % of particles (in volume) having a diameter lower or equal to d (0.1), d (0.5), and d (0.9), respectively. Particle size in sludge reduced due to ultrasonic pre-treatment and higher reductions were obtained in ultrasonic pre-treated sludge with high specific energies comparing to that in raw sludge. Particle size distributions demostrated in Figure 4.2 were also indicated floc disintegration. 70 % of particle size reduction was observed for specific energy of 3500 kJ/kgTS based on volume weighted mean (D[4.3]).

Ultrasonic treatment led to change of physico-chemical characteristics of sludge. For instance, temperature increased almost linearly with increasing specific energy (Fig. 4.3). Temperature increased from 19°C in raw sludge to 84°C for ultrasonic pre-treated sludge with maximum specific energy input of 100000 kJ/kgTS. The rise of temperature helps to ultrasonic disintegration. On the other hand, the high increase in temperature leads to higher saturated vapor pressures, which makes it harder for vapor bubbles to collapse and thus decreases the intensity of cavitation (Huan et. Al., 2009). In contrast, pH decreased during ultrasonic pre-treatment (Fig. 4.3). It decreased from 7.29 in raw sludge to 6.28 for ultrasonic pre-treated sludge at 100000 kJ/kgTS application. Decreasing pH may be explained by acidic compound formation due to the floc disintegration. Lipids were hydrolyzed to volatile fatty acids and these compounds led to decrease pH.

Table 4.2 Particle size changes of raw sludge and ultrasonically pretreated sludge samples

Specific Energy (SE) (kJ/kgTS)	Surface weighted mean D[3.2], µm	Volume weighted mean D[4.3], µm	d (0.1), µm	d (0.5), µm	d (0.9), µm
0	71.53	148.584	53.228	118.103	255.033
1000	24.753	85.78	11,924	64.083	173.924
3500	10.322	44.621	5.238	22.182	96.138
5500	8.625	46.273	4.125	18.735	101.127
7500	8.305	46.354	4.188	17.259	102.622
10000	8.643	42.197	4.615	17.948	95.100
15000	6.054	44.879	2.728	14.475	119.985
20000	6.197	48.734	2.843	14.957	129.621
30000	6.055	46.120	2.758	14.539	122.541
40000	7.477	68.438	3.548	21.039	220.255
50000	6.137	79.301	2.586	22.238	250.519
100000	6.035	63.825	2.515	24.314	155.196

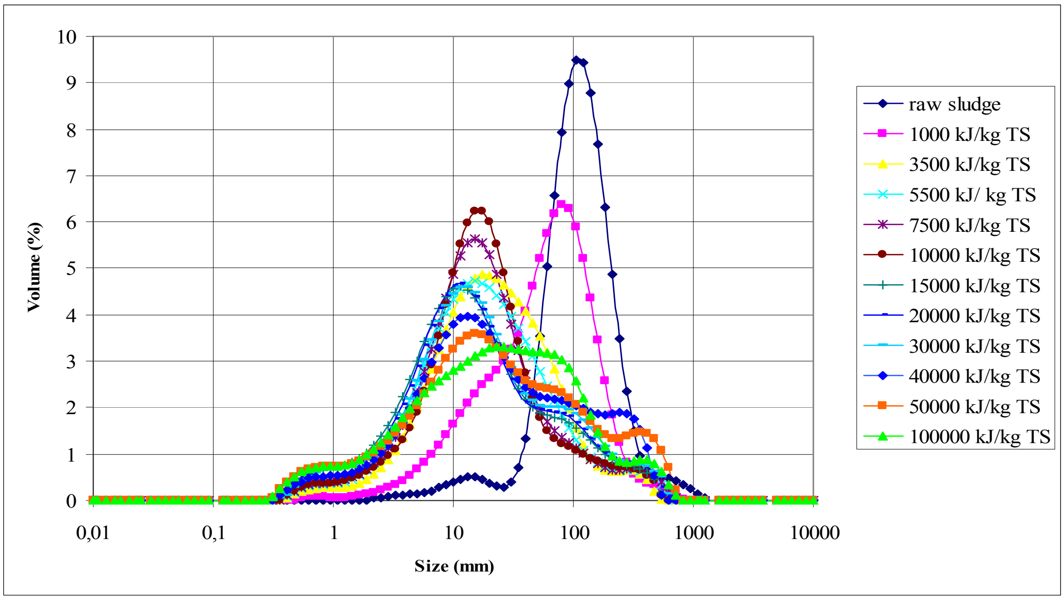

Figure 4.2 Variation of particle size distribution with specific energy

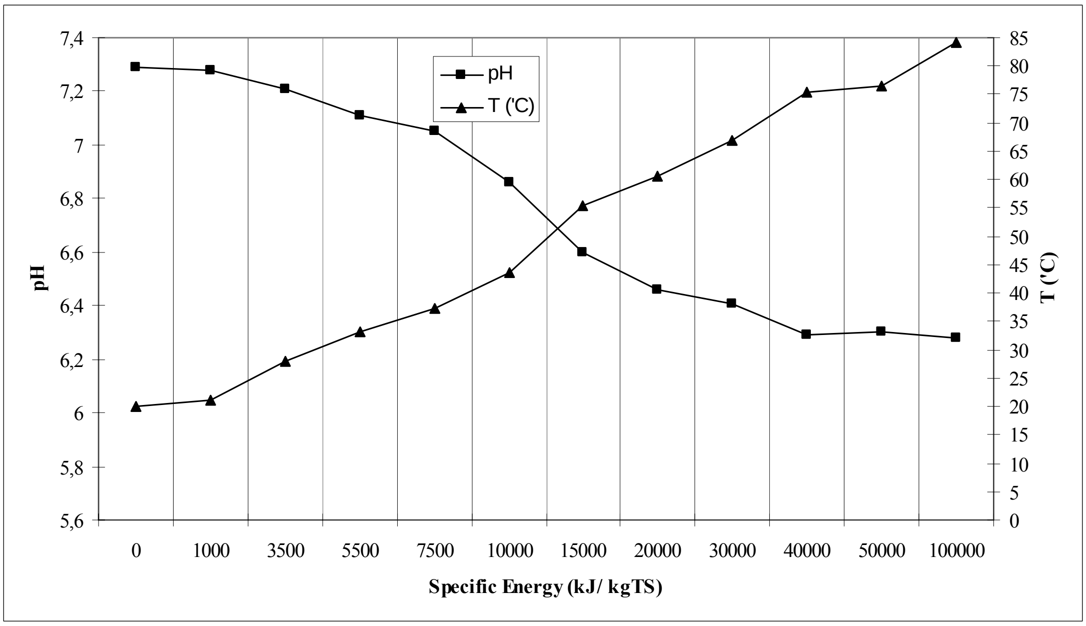

Figure 4.3 The variation of pH and Temperature with specific energy

4.4 Effects of ultrasonic disintegration on supernatant characteristics on meat processing sludge

Disintegration cause disruption of microbial cells in the sludge, thereby destroying the cell walls (Vranitzky et. al., 2005). The destruction of floc structure and disruption of cells results in the release of organic sludge components into the liquid phase. These components exist in a dissolved phase, e.g. components of intracellular water, or can be liquefied (Muller et. al., 2004).

Ultrasonic pre-treatment used for the disintegration process was very effective and contributed to the rapid initial increase of nitrogen and phosphorus. Variation of total nitrogen in sludge’s supernatant with specific energy is given in Figure 4.4. Nitrogen concentration in supernatant increased with increasing specific energy also. Nitrogen concentration in sludge’s supernatant was increased from 9 mg/L to 524 mg/L for specific energy of 100000 kJ/kgTS. As shown in Figure 4.5, phosphorus released to the sludge supernatant due to ultrasonic pre-treatment. Phosphorus increased significantly with increasing SE up to 20000 kJ/kg TS after that it was observed a little improment in phosphorus release. Phosphorus concentration in sludge's supernatant increased from 4,8 mg/L to 58 mg/L for specific energy of 100000 kJ/kgTS. For the optimum specific energy (30000 kJ/kgTS) for DD, TN and TP in sludge's supernatant increased by 3330% and 970%, respectively.

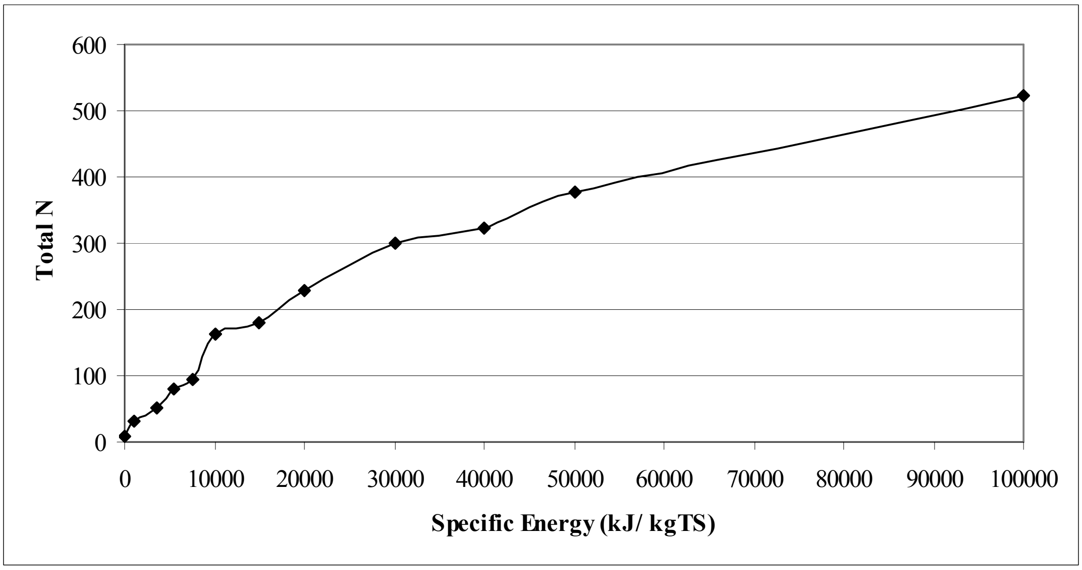

Figure 4.4 Variation of total nitrogen in sludge's supernatant with specific energy

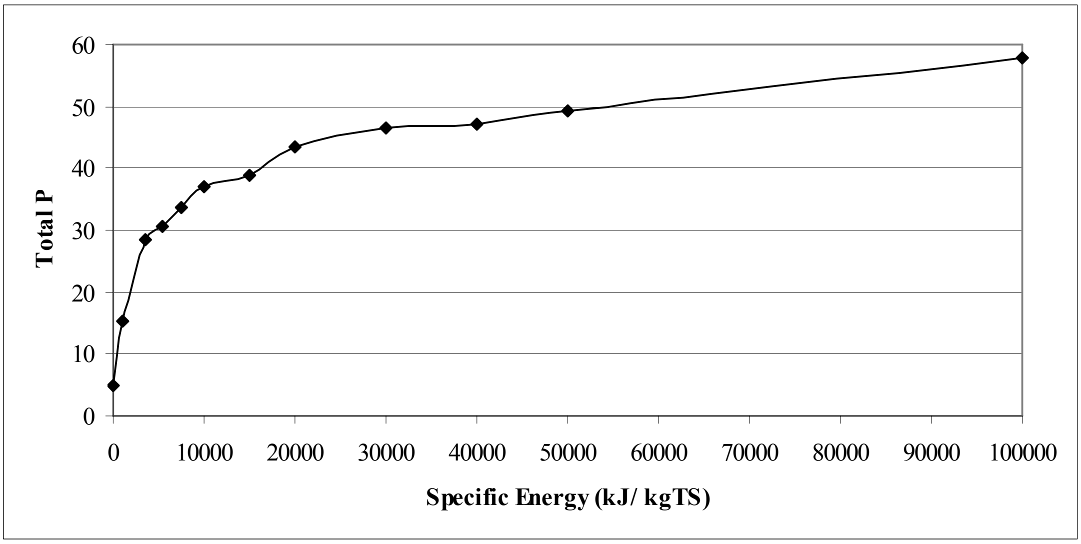

Figure 4.5 Variation of total phosphorus in sludge's supernatant with specific energy

The effect of ultrasonic pre-treatment on solubilization may be monitored depending on the dissolved organic substance. As a result of the ultrasonic pre-treatment, bacterial cells disintegrate because of shear forces generated by low frequency ultrasound. Thus, the quantity of dissolved organic substrate is increased.

Consequently, the degradation rate and the biodegradability of organic biosolids mass are improved (Nickel & Neis, 2007). Increasing oil concentration in sludge's supernatant may be a good indicator of solubilization. As shown in Figure 4.6 oil concentration in sludge's supernatant increased due to ultrasonic pre-treatment and higher increases were obtained in pre-treated sludge with high specific energies comparing to that in non-sonicated sludge. Particle sizes reduced due to ultrasonic pre-treatment and higher reductions were obtained in pre-treated sludge samples with high specific energies comparing to that in non-sonicated sludge. After 40000 kJ/kgTS application, slight increase was observed in oil concentration.

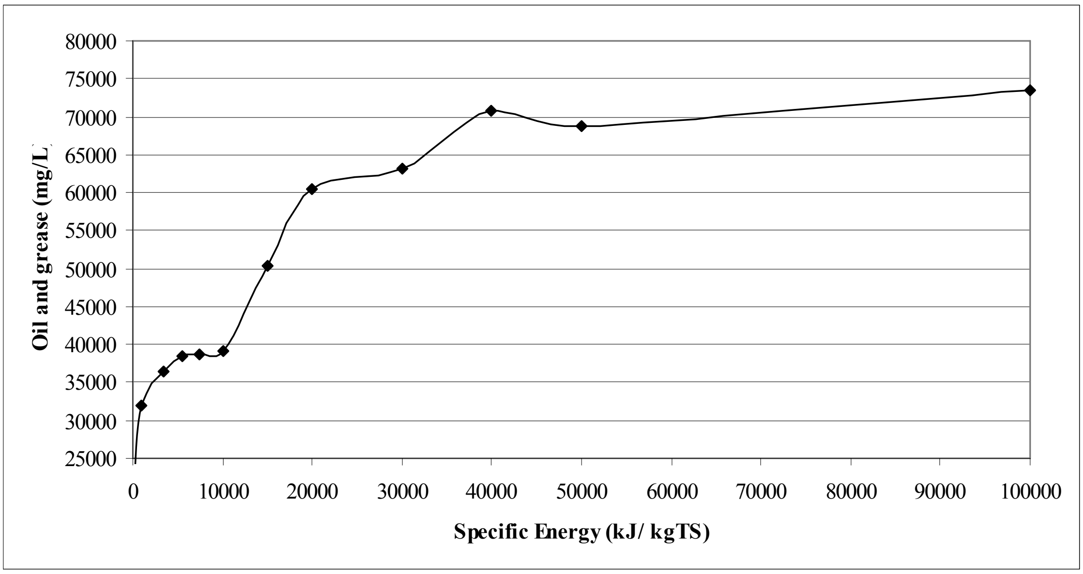

Figure 4.6 Variation of oil and grease concentration with specific energy

The variation of DOC with specific energy is given in Figure 4.7. DOC of sludge increased with increasing specific energy. Increase of DOC with ultrasonic pre-treatment demonstrate that sonicated sludge stabilize higher degree in biological digestion processes than non-sonicated sludge. DOC value of 2050 mg/L was obtained for specific supplied energy of 100000 kJ/kg TS.

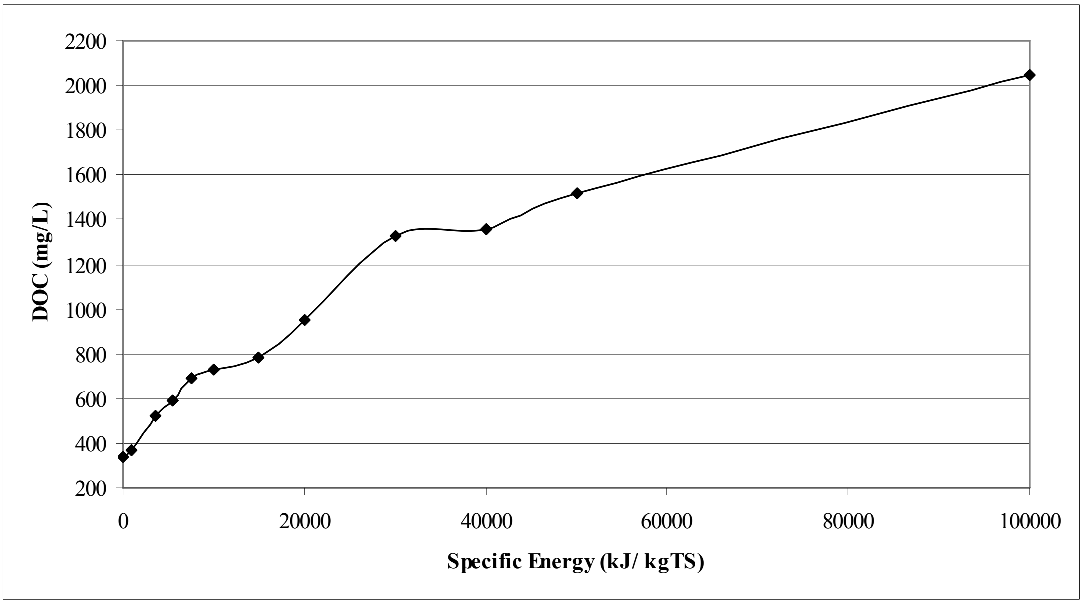

Figure 4.7 Variation of DOC with Specific Energy

The variation of SCOD with specific energy is given in Figure 4.8. SCOD increased significantly with increasing specific energy, also. Maximum SCOD was achieved for the specific energy of 30000 kJ/kg TS and SCOD increased from 880 mg/L to 5160 mg/L.

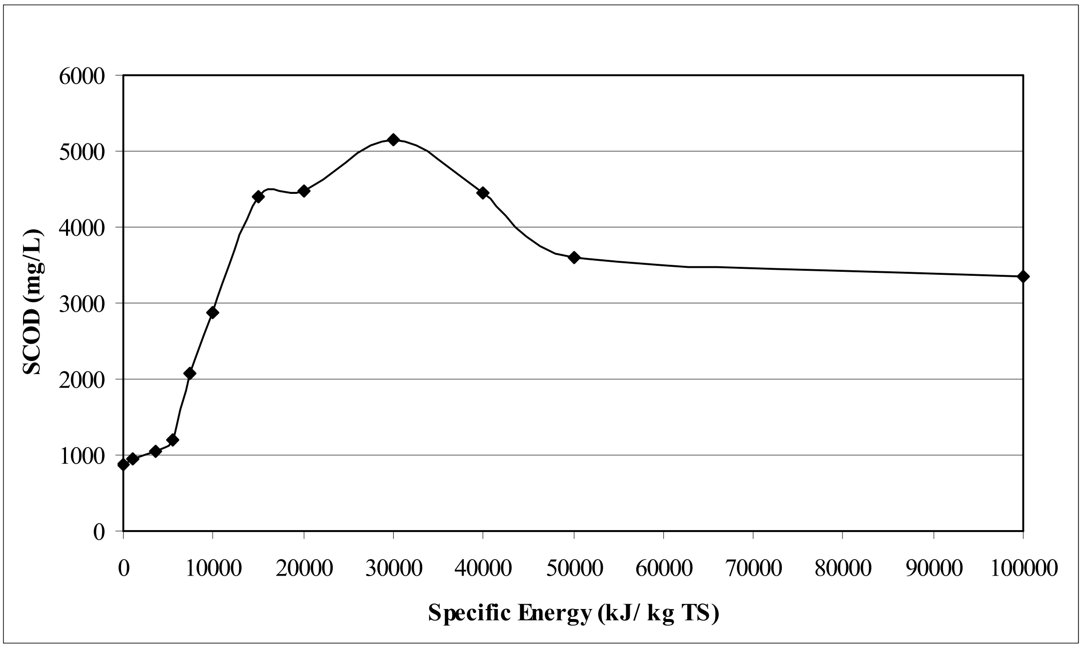

Figure 4.8 Variation of SCOD with Specific Energy

4.5 Effects of Ultrasonic Pretreatment on meat processing sludge reduction

The variation of total solid (TS) concentrations is shown in Figure 4.9. Using ultrasonic pre-treatment did not change significantly dried solids quantity for specific energy (SE) lower than 20000 kJ/kg TS. At higher specific energy inputs, ultrasonic pre-treatment induced sludge reduction due to the solubilization of sludge's solids. Dried solids concentration decreased from 1.1% to 0.67% for maximum specific energy of 100000 kJ/kg TS. Higher solubilization degree of volatile solids in sludge is important for the elimination of hydrolysis phase of anaerobic biodegradation further. The variation of volatile solid (VS) concentrations is shown in Figure 4.10. Ultrasonic pretreatment of sludge did not improve the volatile solid reductions.

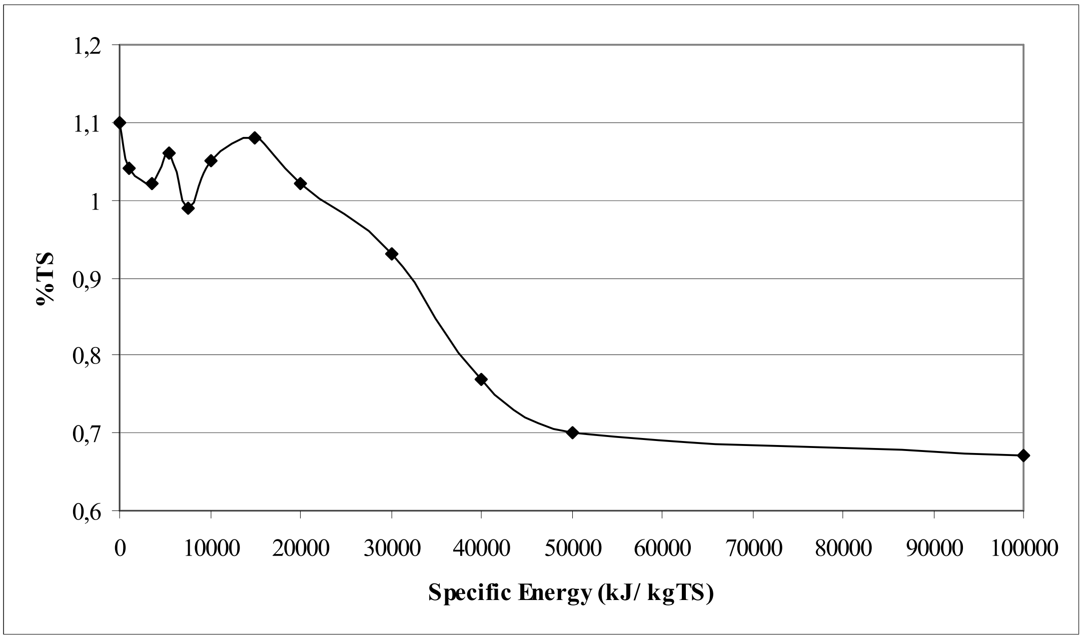

Figure 4.9 Variation of Total Solids with Specific Energy

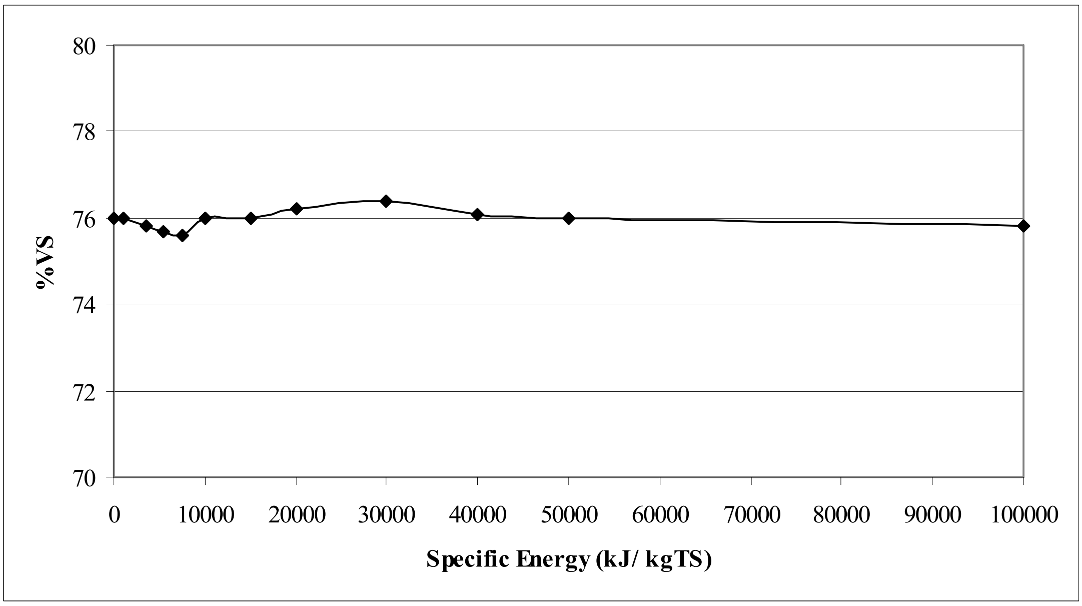

Figure 4.10 Variation of Volatile Solids with Specific Energy

The disintegration of the sludge cells was also reflected in the decreasing SS and VSS-contents of the sludge. SS and VSS results given in Figure 4.11 showed that ultrasonic pre-treatment played an important role in sludge destruction and solubilization. SS and VSS content of sludge decreased with increasing SE. 48% of the SS and 40% of the VSS-concentration was oxidized and solubilized for 100000 kJ/ kg TS.

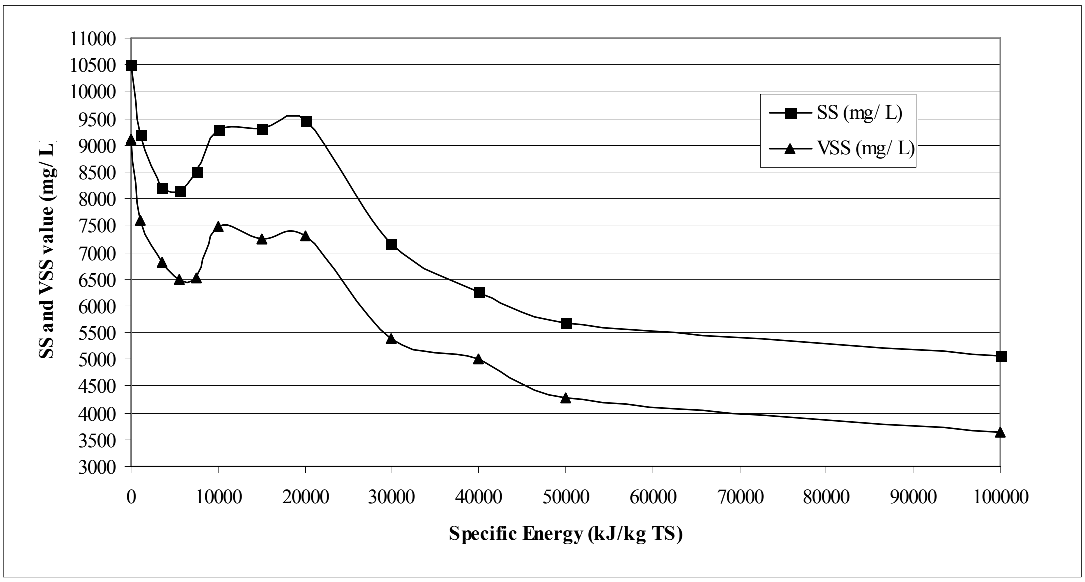

Figure 4.11 Variation of SS and VSS with Specific Energy

4.6 Effects of ultrasonic pre-treatment on anaerobic processing of meat processing sludge

Anaerobic digestion process is achieved through several stages: hydrolysis, acidogenesis, and methanogenesis. Hydrolysis is the rate-limiting stage for waste activated sludge degradation. In order to improve the rate of hydrolysis and anaerobic digestion performance, disintegration was developed as the pre-treatment process of sludge to accelerate the anaerobic digestion and to increase degree of stabilization (Bougrier et. al., 2005). Increasement of stabilization degree of sludge with disintegration process provides less sludge production, more stable sludge, and more biogas production comparing the classical anaerobic digestion.

The main purpose of pre-treatment of waste sludge is eliminate the hydrolysis step in anaerobic digestion. The decreases in the protein value clearly seen at Figure 4.12. According to protein values of ultrasonically pretreated sludge samples it can be said that the hydrolysis step of anaerobic digestion was eliminated.

Cell lysis transforming cell content into the medium is the first, and breakdown of extracellular polymeric substance (EPS) fraction in the sludge is the second stage of floc disintegration. Cell lysis in the first stage causes to release of protein content into the liquid phase of sludge. In the second stage, disintegration enhances the degradation of extracellular polymeric substances (EPS) and protein content of sludge decreases. The variation of protein concentration with the specific energy is given in Figure 4.12. Protein concentration decreased with increasing SE. Ultrasonic pre-treatment enhanced the degradation of protein content of sludge. The main purpose of disintegration is the elimination of hydrolysis step to accelerate the anaerobic degradation. Results show that protein hydrolysis was performed successfully by ultrasonic pre-treatment.

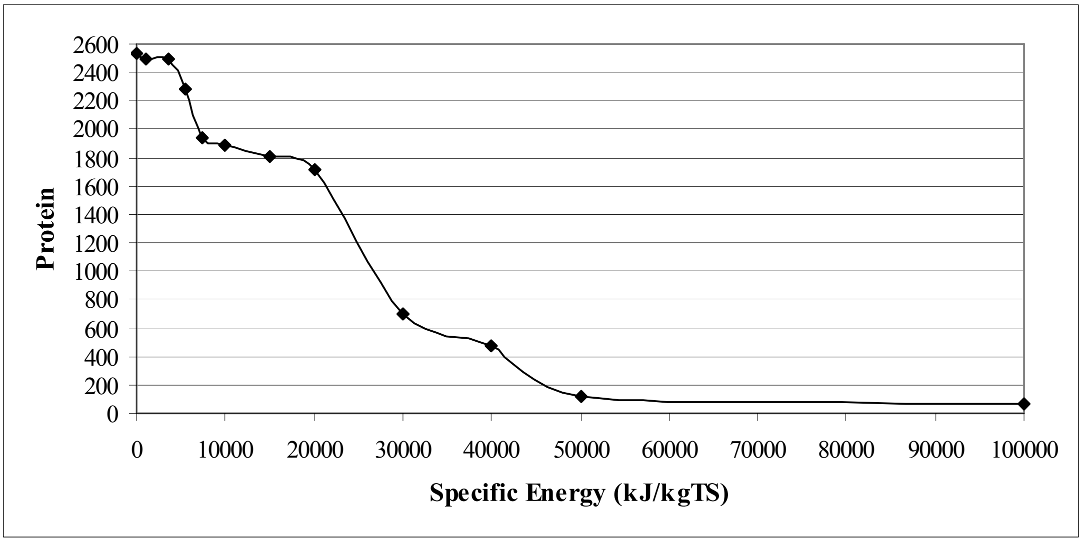

Figure 4.12 Variation of Protein Content of Sludge with Specific Energy

BMP assay was carried out to assess the feasibility of using ultrasonic pre-treatment in order to improve the anaerobic biological degradation of biological sludge. BMP assay, in which cumulative methane production was monitored, were applied to both raw biological sludge and pre-treated sludges for comparison purpose. Cumulative methane productions in serum bottles were monitored at 40 days (continued until the gas production ceased) and the results show that ultrasonic pre-treatment of biological sludge may be good alternative for improving the anaerobic degradation (Fig. 4.13). Maximum cumulative methane production was achieved for 30000 kJ /kg TS.

At the end of the 40 days of incubation, cumulative methane production of raw sludge was found as 121.40 mL, while methane production was found as 286.50 mL for 30000 kJ /kg TS application(2.36 times higher than raw sludge).

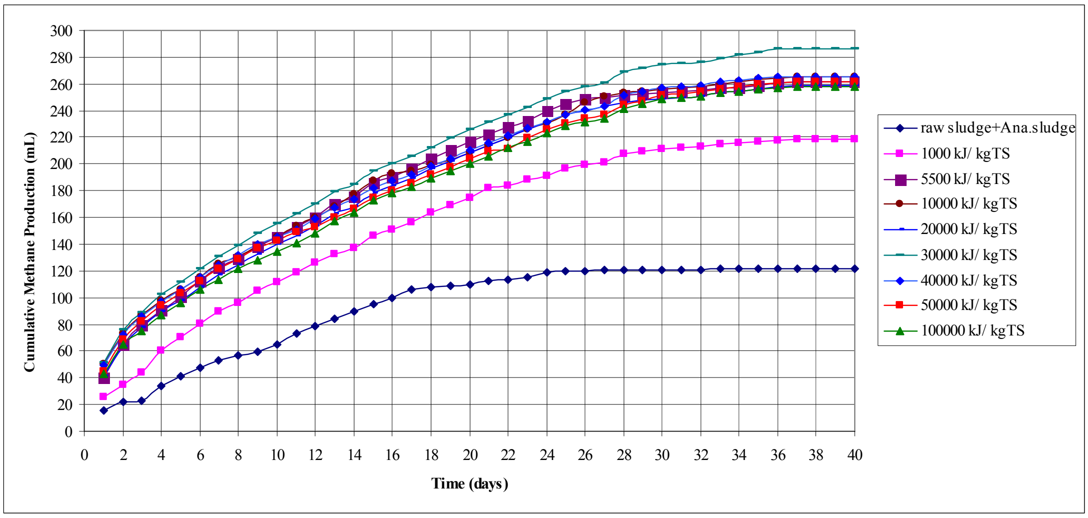

Figure 4.13 Results of BMP Tests.

4.7 Filtration characteristics of meat processing sludge

CST is a quick and simple method to evaluate the filterability of sludge. This method neglects the shear effect on sludge, and it can not determine dewaterability differences between dewatering processes but gives an approach dewatering capacity of sludge (Meeten et. al., 1995). CST variations versus applied specific energy are given in Figure 4.14. CST gradually increased during the ultrasonic pre-treatment. CST results showed that ultrasonic pre-treatment deteriorates the filterability of meat processing sludge.

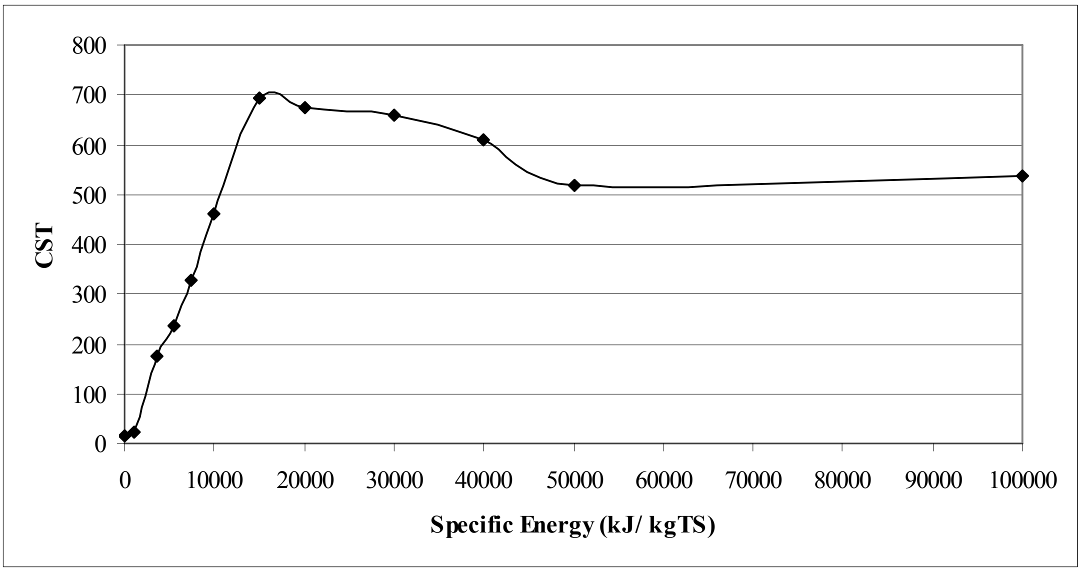

Figure 4.14 Variation of CST with SE values.

CHAPTER FIVE

CONCLUSIONS and RECOMMENDATIONS

5.1 Conclusions

As a new approach ultrasonic pre-treatment effects on anaerobic digestion of meat processing waste sludge were examined in this study. Experimental results showed that using an ultrasonic homogenizer as a disintegration method improved processing of the sludges. The concluding remarks from this study can be given as follows:

- Experimental studies showed that the disintegration degree (DD) of biological sludge increased significantly with increasing specific energy (SE) and the maximum disintegration degree of 47.4 % was obtained for specific energy of 30000 kJ/kg TS. For specific energies above 30000 kJ/kgTS, DD decreased. For the maximum SE input of 100000 kJ/kgTS disintegration degree was found 30.1%. Decreasing of DD may be explained by high oxidation effects of radicals. High ultrasonic energies promote oxidation by radicals and ultrasonic pre-treatment led to mineralization preceding solubilization of sludge.

- Temperature increased almost linearly with increasing SE. Temperature increased from 19 °C in raw sludge to 84 °C for ultrasonic pre-treated sludge with maximum SE input of 100000 kJ/kgTS. In contrast, pH decreased during ultrasonic pre-treatment. It decreased from 7.29 in raw sludge to 6.28 for ultrasonic pre-treated sludge at 100000 kJ/kgTS application. Decreasing pH may be explained by acidic compound formation due to the floc disintegration.

- Experimental studies showed that the particle size changes for different specific energies. Particle size in sludge reduced due to ultrasonic pre-treatment and higher reductions were obtained in ultrasonic pre-treated sludge with high specific energies comparing to that in raw sludge. 70 % of particle size reduction was observed for specific energy of 3500 kJ/kgTS based on volume weighted mean (D[4.3]). After that, particle size of sonicated sludge kept almost constant.
- DOC of sludge increased with increasing SE. Increase of DOC with ultrasonic pre-treatment demonstrate that sonicated sludge stabilize higher degree in biological digestion processes than non-sonicated sludge. The maximum DOC value of 2050 mg/L was obtained for SE of 100000 kJ/kg TS. For the optimum SE value of 30000 kJ/kg TS DOC value was found 1326.8 mg/L.
- SCOD increased significantly with increasing SE. Maximum SCOD was achieved for the SE of 30000 kJ/kg TS and SCOD increased from 880 mg/L to 5160 mg/L.
- Phosphorus concentration in sludge's supernatant increased significantly with increasing SE up to 20000 kJ/kg TS after that it was observed a little improment in phosphorus release. Phosphorus concentration in sludge's supernatant increased from 4,8 mg/L to 58 mg/L for SE of 100000 kJ/kgTS.
- Nitrogen concentration in supernatant increased with increasing SE also. Nitrogen concentration in sludge's supernatant was increased from 9 mg/L to 524 mg/L for SE of 100000 kJ/kgTS. For the optimum SE (30000 kJ/kgTS) for DD, TN and TP in sludge's supernatant increased by 3330% and 970%, respectively.
- For 30000 kJ/kgTS, the soluble chemical oxygen demand (SCOD), dissolved organic carbon (DOC), total nitrogen (TN), total phosphorus (TP) in sludge's supernatant increased by 487%, 290%, 3230%, and 870%, respectively.

- Oil concentration in sludge's supernatant increased due to ultrasonic pre-treatment and higher increases were obtained in ultrasonically pre-treated sludge with high SE comparing to that in non-sonicated sludge. After 40000 kJ/kgTS application, slight increase was observed in oil concentretaion. For non- sonicated sludge oil concentration value was found 19478 mg/L and for the optimum SE (30000 kJ/kgTS) for DD it was found 63170 mg/L.

- Using ultrasonic pre-treatment did not change significantly dried solids quantity for SE lower than 20000 kJ/kg TS. Dried solids concentration decreased from 1.1% to 0.67% for maximum SE of 100000 kJ/kg TS. It was shown that volatile solid (VS) concentrations didn't have a significant changes. Ultrasonic pre-treatment of sludge did not improve the volatile solid reductions.

- The disintegration of the sludge cells was also reflected in the decreasing SS and VSS-contents of the sludge. SS and VSS content of sludge decreased with increasing SE. 48% of the SS and 40% of the VSS-concentration was oxidized and solubilized for 100000 kJ/ kg TS. Experimental results showed that ultrasonic pre-treatment played an important role in sludge destruction and solubilization.

- Maximum cumulative methane production was achieved for 30000 kJ /kg TS. At the end of the 40 days of incubation, cumulative methane production of raw sludge was found as 121.40 mL, while methane production was found as 286.50 mL for 30000 kJ /kg TS application(2.36 times higher than raw sludge).

- CST gradually increased during the ultrasonic pre-treatment. CST values increased from 14.50 in raw sludge , 659.6 for the optimum SE input of 30000 kJ/kgTS for DD and 538 for ultrasonic pre-treated sludge with maximum SE input of 100000 kJ/kgTS. CST results showed that ultrasonic pre-treatment deteriorates the filterability of meat processing sludge.

- According to protein values of ultrasonically pre-treated sludge samples it can be said that the hydrolysis step of anaerobic digestion was eleminated. Protein concentration decreased with increasing SE. It decreased from 2530.60 in raw sludge to 62.50 for ultrasonic pre-treated sludge at 100000 kJ/kgTS application. Ultrasonic pre-treatment enhanced the degradation of protein content of sludge. The main purpose of disintegration is the elimination of hydrolysis step to accelerate the anaerobic degradation. Results show that protein hydrolysis was performed successfully by ultrasonic pre-treatment.

5.2 Recommendations

Experimental studies were done in laboratory scale. To make more conclusive results on ultrasonic pretreatment of meat processing waste sludge, pilot scale and then full–scale trials should be done. As promising technology, ultrasonic pretreatment of the industrial sludges requires comprehensive studies which include costs analysis to show whether the ultrasonic pre-treatment is appropriate in practice or not.

REFERENCES

APHA, (1998). *Standard Methods for the Examination of Water and Wastewater*. 20th ed. American Public Health Association, American Water Works Association and Water Environment Federation, Washington, USA

Ayol, A., Filibeli, A., Sir, D., Kuzyaka, E. (2007). Aerobic and Anaerobic bioprocessing of activated sludge: floc disintegration by enzymes. *Facing Sludge Diversities: Challanges, Risks and Oppurtunities*, Antalya, Turkey, March 28-30, Filibeli, A.; Sanin, F.D.; Ayol, A.; Sanin S.L., Eds.; IWA Publishing: Turkey, 755-765.

Bartholomew, R., (2002). *Ultrasound Disintegration of Sewage Sludge: An Innovative Wastewater Treatment Technology PA Department of Environmental Protection, Bureau of Water Supply and Wastewater Management*. From http://www.dep.state.pa.us/DEP/DEPutate/Watermgt WSM/ WSM_TAO/ InnovTech/ ProjReviews/ Ultrasound- Disintegr. htm

Barjenbruch, M., Kopplow,O., (2003). Enzymatic, mechanical and thermal pre-treatment of surplus sludge. *Advances in Environmental Research , 7*, 715–720.

Bonmati, A., Flotats, X., Mateu, L., Campos, E., (2001). Study of thermal hydrolysis as a pre-treatment to mesophilic anaerobic digestion of pig slurry. *Water Science and Technology 44*, 109–116.

Bougrier, C., Albasi, C., Delgen, J.P., Carrere, H., (2006). Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability. *Chemical Engineering and Processing 45*, 711–718.

Bougrier, C., Delgenes, J.P., Carrere, H., (2005). Solubilisation of waste-activated sludge by ultrasonic treatment. *Chemical Engineering Journal 106*, 163-169.

Buendia, I.M., Fernandez, F.J., Villasenor, J., Rodriguez, L., (2008). Biodegradability of meat industry wastes under anaerobic and aerobic conditions. *Water Research 42*, 3767– 3774.

Chu, C.P., Chang, B., Liao, G. S., Jean, D. S., Lee, D. J., (2001). Observations on changes in ultrasonically treated waste- activated sludge. *Water Res. 35*, 1038–1046.

Davies, M., (2007). Anerobic Digestion And Biogas. *Nuffield Farming Scholarship Trust.*

Egemen, E., Corpening, J., Nirmalakhandan, N., (2001). Evaluation of an ozonation system for reduced waste sludge generation. *Water Sci Technol., 44*, 2–3, 445–52.

Elliott.A., M.Talat, (2007). Pretreatment technologies for advancing anaerobic digestion of pulp and paper biotreatment residues. *Water Research 41*, 4273-4286.

Feng, X., Deng, J., Lei, H., Bai, T., Fan, Q., Li, Z., (2009). Dewaterability of waste activated sludge with ultrasound conditioning. *Bioresource Technology 100*, 1074–1081.

Ferrer, I., Climent, M., Baeza, M.M., Artola, A., Vazquez, F., Font, X., (2006). Effect of sludge pretreatment on thermophilic anaerobic digestion. *Proceedings of the IWA Specialized Conference on Sustainable Sludge Management: State-of-the-Art, Challenges and Perspectives, Moscow, Russia*, 235–241.

Filibeli, A., (1998). *Arıtma Çamurlarının İşlenmesi*. Dokuz Eylül Üniversitesi Yayınları No:225, ISBN 975-441-117-4.

Filibeli, A., Büyükkamacı, N., Ayol, A., (2000). *Anaerobik Arıtma*. Dokuz Eylül Üniversitesi Yayınları No:280, ISBN 975-441-154-9

Huan, L., Yiying, J., Mahar, R.B., Zhiyu, W., Yongfeng, N., (2009). Effects of ultrasonic disintegration on sludge microbial activity and dewaterability. *Journal of Hazardous Materials 161*, 1421–1426.

Kaynak G.E, Filibeli A., (2007). Sludge Disintegration Using Fenton's Peroxidation. *IWA Conferance- Facing Sludge Diversities:Challanges, Risks and Opportunities, Antalya*, 28-30 March 2007.

Kaynak, G. E., Filibeli, A.(2008). Sludge minimization by Fenton process: Effects on anaerobic sludge bioprocessing. *ECSM'08 - European Conference on Sludge Management Liège, Belgium.*

Lafitte-Trouque, S., C.F. Forster, C.F., (2002). The use of ultrasound and c-irradiation as pre-treatments for the anaerobic digestion of waste activated sludge at mesophilic and thermophilic temperatures. *Bioresource Technology 84*, 113-118.

Lehne, G.A., Muller,J. A., Schwedes,J. (2001). Mechanical disintegration of sewage sludge. *Water Science and Technology, 43*, 19–26.

Lettinga, G. (1981). Anaerobic Treatment For Wastewater Treatment And Energy Production. *Inter-American Seminar On Biogas*, 22-25 November, Joao Pessoa, Brasil.

Luste, S., Luostarinen, S., Sillanpaa, M., (2009). Effect of pre-treatments on hydrolysis and methane production potentials of by-products from meat-processing industry. *Journal of Hazardous Materials 164*, 247–255.

Metcalf & Eddy (2004). *Wastewater Engineering: Treatment And Reuse Fourth Edition*. Revised by G. Tchobanoglous, F. L. Burton, H. D. Stensel, The McGraw-Hill Companies, Inc., New York, USA.

Meeten, G.H., Smeulders, J. B. A. F, (1995). Interpretation of filterability measured by the capillary suction time method. *Chemical Engineering Science 50*, 1273-1279.

Muller J.A (2003). Conditioning, thickening and dewatering of mechanically disintegrated excess sludge. *Seperation Science and Technology, 38*(4), 889-902.

Muller J.A, Winter A., Strünkmann G. (2004). Investigation and assessment of sludge pre-treatment processes. *Water Science and Technology*, 49(10), 97-104.

Muller, J.A., (2000a). Disintegration as a Key-Step in Sewage Sludge Treatment. *Water Sci. Technol.*, 41,8, 123–130.

Muller, J., (2000b). Pretreatment processes for the recycling and reuse of sewage sludge. *Water Sci. Technol.*, 42 (9), 167–174.

Mayhew, M., Le, M., Ratcliff, R., (2002). A novel approach to pathogen reduction in biosolids: the enzymic hydrolyser. *Water Sci. Technol.*, 46 (4/5), 427–434.

Mayhew, M., Le, M., Brade, C., Harrison, D., (2003). The United utilities 'enzymic hydrolysis process'—validation of phased digestion at full-scale to enhance pathogen removal. In: *WEF Proceedings of the Residuals and Biosolids Conference, Baltimore.*

Nakhla, G., Al- Sabawi, M., Bassi, A., Liu, V., (2003). Anaerobic treatability of high oil and Grease rendering wastewater. *Journal of Hazardous Materials B102*, 243–255.

Neis, U., Nickel, K., Tiehm, A., (2000). Enhancement of anaerobic sludge digestion by ultrasonic disintegration. *Water Science and Technology Vol 42,* No 9 pp 73–80, IWA Publishing.

Neis, U., Nickel, K., Tiehm, A., Zellhorn, M., (2001). Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. *Water Res. 35 (8)*, 2003-2009.

Nickel, K., (2002). Ultrasonic disintegration of biosolids –benefits, consequences and new strategies. TU Hamburg-Harburg Reports *on Sanitary Engineering 35*, Ultrasound in Environmental Engineering II

Nickel, K., Neis, U., (2007). Ultrasonic disintegration of biosolids for improved biodegredation. *Ultrasonics Sonochemistry 14*, 450–455.

Owen W.F., Stuckey D.C., Healy J.B., Young JR. L.Y.,McCarty P. L., (1979). Bioassay for monitoring biochemical methane potential and anaerobic toxicity. *Water Research, 13*, 485-492.

Özer, A., & Kasırga, E. (1987). *Anaerobik Arıtma Tesislerinde Ekonomi ve Tasarım*. TMH, Ocak-Şubat.

Öztürk, İ. (1987). *Biyoenerji Sistemlerinde İşletmeye Alma ve Proses Kontrolu Problemler. Uluslararası Çevre'87 Sempozyumu Bildiriler Kitabı*, 521-536., İstanbul.

Pham, T.T.H., Brar, S.K., Tyagia, R.D., Surampalli, R.Y., (2008). Ultrasonication of wastewater sludge—Consequences on biodegradability and flowability. *Journal of Hazardous Materials 163*, 891–898.

Razo-Flores, E., Luijten, M., Donlon, B. A., Lettinga, G. ve Field, J.A. (1997). Biodegradation of selected azo dye under methanogenic conditions. *Water Science and Technology, 36*, (6-7), 65-72.

Residua, (2003). *Anaerobic digestion*. Warmer Bulletin.

Rico, J.L., Garcıa, H., Rico, C., Tejero, I., (2007). Characterisation of solid and liquid fractions of dairy manure with regard to their component distribution and methane production. *Bioresource Technology 98*, 971–979.

Riesz, P., Berdahl, D., Christman, L., (1985). Free radical generation by ultrasound in aqeous and nonaqeous solutions. *Environ. Health Perspect*, 64, 233-252.

Salsabil, M.,R., Prorot, A., Casellasa, M., Dagot, C., (2009). Pre-treatment of activated sludge: Effect of sonication on aerobic and anaerobic digestibility. *Chemical Engineering Journal 148*, 327–335.

Schmitz,U., Berger, R. C., Orthm, H., (2000). Protein analysis as a simple method for the quantitative assessment of sewage sludge disintegration. *Wat. Res. Vol. 34*, No. 14, pp. 3682- 3685.

Schrank, S.G., Jose, H.J., Moreira, R.F.P.M., Schroder, H.F., (2005). Applicability of Fenton and H2O2/UV reactions in the treatment of tannery wastewaters. *Chemosphere 60*, 644–655.

Show, K., Mao, Lee, D., (2007). Optimisation of sludge disruption by sonication, *Water Research 41*, 4741 – 4747.

Speece RE. 1996. *Anaerobic biotechnology for industrial wastewater*. Nashville Tennessee, USA: Archae Press.

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

Toprak, H. (1990). *Anaerobik Stabilizasyon Havuzlarının Dinamik Modellemesi*, T.C. Dokuz Eylül Üniversitesi Fen Bilimleri Enstitüsü Doktora Tezi, Yöneten: Prof. Dr. O. Uslu, İzmir.

Vlyssides, A., Karlis, P., (2004). Thermal-alkaline solubilization of waste activated sludge as a pre-treatment for anaerobic digestion. *Bioresource Technology 91*, 201–206.

Vranitzky, R., Lahnsteiner, J., (2005). *Sewage Sludge Disintegration Using Ozone – A Method of Enhancing the Anaerobic Stabilization of Sewage Sludge*. VA TECH WABAH, R&D Process Engineering, Siemensstrasse 89, A-1211 Vienna, Austria.

Wahaab, R.A., El-Awady, M.H., (1999). Anaerobic/ aerobic treatment of meat processing wastewater. *The Environmentalist 19*, 61–65.

Wang, F., Lu, S., Ji, M., (2006). Components of released liquid from ultrasonic waste activated sludge disintegration. *Ultrasonics Sonochemistry 13*, 334–338.

Xie, B., Liu, H., Yan, Y., (2009). Improvement of the activity of anaerobic sludge. *Journal of Environmental Management 90*, 260-264.

Xu, N., Wang, W., Han, P., Lu, X., (2009). Effects of Ultrasound on Oily Sludge Deoiling. *Journal of Hazardous Materials*, 10.1016/j.jhazmat.2009.06.091.

Zhang, P., Zhang, G., Wang, W., (2007). Ultrasonic treatment of biological sludge: Floc disintegration, cell lysis and inactivation. *Bioresource Technology 98*, 207–210.

Zhang, G., Zhang, P., Yang, J., Liu, H., (2008). Energy-efficient sludge sonication: Power and sludge characteristics. *Bioresource Technology 99*, 9029–9031.

Zhang, G., He, J.,, Zhang, P., Zhang, J., (2009). Ultrasonic reduction of excess sludge from activated sludge system II: Urban sewage treatment. *Journal of Hazardous Materials, 164*, 1105–1109.