Effects of low frequency ultrasound pretreatment on anaerobic digestion of sludge

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Effects Of Low Frequency Ultrasound Pretreatment On Anaerobic Digestion Of Sludge

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ABSTRACT

Arising from escalating wastewater sludge quantity and disposal cost, research work has been initiated to explore improvement of sludge digestion through pretreatment techniques. Amongst possible pretreatment methods, sonication treatment exhibits a greater potential for being environmentally and economically sound. However, many aspects pertaining to this ultrasound pretreatment, such as the optimal operating conditions, the influence of pretreatment on bioconversion process, the feasibility of sonicated sludge for continuous anaerobic digestion and the mechanism of sludge sonication, have not been explored in much detail.

This study examines the effects of sonication treatment on sludge characteristics using sonication generated at a low frequency of 20 kHz. The influences of sonication pretreatment of sludge on the subsequent anaerobic digestion were investigated by using batch cultures and upflow anaerobic sludge blanket (UASB) digesters. The results indicated that the sonication resulted in a reduction of sludge particle size from 47-51 μm to 7-15 μm , and an increase in the soluble chemical oxygen demand (SCOD) to total COD (TCOD) ratio from 3-9% to 17-25%, indicating effective disruption of sludge solids and transformation of organic substances into soluble form.

Anaerobic digestion in batch culture indicated that sonication pretreatment of sludge could boost anaerobic bioconversion by increasing the first order hydrolysis rate from 0.0384 d^{-1} to 0.0456-0.0672 d^{-1} . Comparing with the control UASB digester, the TCOD removal improved by 1-17%, 1-31% and 1-32% in the digesters fed with sludge sonicated sludge at densities of 0.18W/mL, 0.33W/mL and 0.52W/mL, respectively. The improved organics removal efficiency corresponded with significant increase in biogas production by 45-175%.

40-220% and 86-220% in the respective digesters, as well as an overall increase in methane content by 2-17%.

This study demonstrates that ultrasonic pre-treatment is a promising method to improve the anaerobic digestion of wastewater sludge. The suspected mechanisms of ultrasonication include the formation and collapse of cavitation bubbles, the behaviour of transient and stable bubbles, as well as acoustic energy adsorption phenomena. Ultrasonication thus destroys the bounded structures of biosolids, flocs or cells, resulting in 1) the release of more degradable components, 2) an increased surface area for enzyme-adsorption, and 3) enhanced mass-transfer conditions. The limiting stage analysis from the batch culture study unveiled that the accelerated bioconversion of sludge is predominantly attributed from the increased rate of first-order hydrolysis and the promoted growth of methanogenic biomass. The experimental study indicated that sonication pretreatment of sludge could bring about several benefits in treatment plant operation. These include capital cost saving out of smaller unit digester, operating cost savings in downstream sludge treatment and disposal, and increase in energy yield derived from improved biogas production.

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CHAPTER 1 INTRODUCTION

1.1 BACKGROUND

Wastewater sludge is an unavoidable byproduct of wastewater treatment. Raw sludge is not only rich in organic carbon and pathogens but also rich in heavy metals and other environmental pollutants. The sludge must be stabilized in order to enable an environmentally safe disposal or utilization. Anaerobic digestion is the most commonly applied process for stabilization of wastewater sludge. There are many positive features of anaerobic treatment which include mass reduction, stable products, and improvement of dewatering properties of the fermented sludge. Anaerobic digestion is unique among other sludge stabilization methods, because it has the ability to produce a net energy gain in the form of methane gas leading to cost effectiveness.

However, anaerobic digestion is a rather slow process, resulting in long fermentation times, and huge digesters are usually required (Eastman and Ferguson, 1981; Shimizu *et al.*, 1993). Anaerobic digestion of wastewater sludge is usually considered to be a three-stage process consisting of hydrolysis, acidogenesis and methanogenesis. As most substrate in sludge is enclosed within cell membranes (Lin *et al.*, 1997) or sludge flocs (Chu *et al.*, 2001), the bound substrate has to be released in the hydrolysis phase before it can be utilized by methanogenic anaerobes. Due to the low concentration of soluble organic matter contained in sludge, only the partial total chemical oxygen demand (TCOD) or volatile solids (VS) can be degraded even after very long time retention of 20 days (Chiu *et al.*, 1997). Moreover, the slow-growth, sensitive and delicate nature of the methanogens also limits the efficiency of anaerobic digestion of sludge (Show, 1996). Maintaining a satisfactory and consistent digester performance is a challenging task. Arising from escalating wastewater sludge

generation coupled with increasingly stringent legislation, there is an urgent need for improvement in shortening the digestion process and enhancing the degradation efficiency of anaerobic digestion.

Extensive research work has been initiated exploring ways to improve sludge digestion through pre-treatment of sludge. Thermal pre-treatment, high pressure homogenization, enzyme treatment, chemical solubilization by alkali, acid or base addition, mechanical disintegration and ultrasound treatment are methods that have been investigated. Comparing with other pre-treatment methods, ultrasound treatment exhibits a greater potential for being environmental sound and economically competitive (Tiehm *et al.*, 1997).

High-power ultrasound could generate intensive cavitation which results in sludge disintegration releasing intracellular materials (Harrison, 1991; Neis *et al.*, 2000). In the sonication stage, a certain portion of the insoluble organic particulates could be transformed into a soluble state (Jorand *et al.*, 1995; Chiu *et al.*, 1997; Gonze *et al.*, 2003; Bougrier *et al.*, 2005). It had been reported that sonication treatment could alter sludge characteristics in terms of increased soluble chemical oxygen demand (SCOD) and reduced biosolids particle size (Tiehm *et al.*, 1997; Mao *et al.*, 2004; Grönroos *et al.*, 2005).

In spite of its proven effectiveness and potential development, use of sonication pre-treatment technique is yet to be accepted. This is mainly due to limited information on disintegration mechanism of sludge and on feasibility of anaerobic digestion of sonicated sludge in continuous operation.

Sonication pre-treatment of sludge is an exploration of applying ultrasound technique in environment engineering. This interdisciplinary nature implies that the mechanism of sonication treatment sludge must be derived from a good understanding of the behaviour of ultrasound waves in sludge disintegration. Although it is believed that ultrasonic sludge disintegration is mainly attributed to the effects of cavitation bubbles caused by sonication, studies of correlations of cavitation bubbles, sonication parameters and sludge disintegration are yet to be established. As a result, optimal conditions of ultrasonic pre-treatment are still

not clear and it remains a complex compromise to balance the energy cost and efficient sonication. To shed a light on the mechanisms of sludge disintegration, this study attempts to derive a good understanding on the role and significance of sonication variables on the formation and behaviour of cavitation bubbles.

Previous studies have shown that sludge disintegration upon ultrasonication is beneficial for the subsequent anaerobic digestion. It had been reported that sonication treatment could improve anaerobic sludge digestion in terms of solids degradation and biogas production (Tiehm *et al.*, 2001; Wang *et al.*, 1999; Onyeche *et al.*, 2002). Based on a presumption that hydrolysis was the rate-limiting stage, the improvement was assumed to be attributed to the accelerated hydrolysis by sonication pre-treatment. However, no quantitative indication or fundamental hypothesis has been provided to justify and explain the hydrolysis acceleration due to sonication. As anaerobic digestion is accomplished through interactive and dynamic actions of hydrolytic, acidogenic and methanogenic microbial groups, any of which may play a crux if the balance between the microbial consortium and substrate is disturbed (Valentini *et al.*, 1997). However, information on correlations between sonication treatment of sludge and the individual response of anaerobic degradation pathways is limited. It is therefore important to establish sufficient knowledge addressing how and to what extents ultrasound treatment could influence each dynamic step for digester performance improvement.

A majority of the studies on sonication pre-treatment had been focused on fermentation by batch operation (Wang *et al.*, 1999; Tiehm *et al.*, 2001; Chu *et al.*, 2002; Onyeche *et al.*, 2002) and a few cases in semi-continuous operation mode (Tiehm *et al.*, 1997). No study has been reported on the performance and stability of digester treating sonicated sludge under continuous operation mode (continuous feeding), which is usually applied by large-scale wastewater treatment plants. The significance and impacts of sludge disintegration with respect to system operating conditions under both steady-state and transient-state have not been well-defined and examined in detail. Successful implementation of pre-treatment technique is possible only when sufficient knowledge on reliability of digester performance has been established. Therefore, it remains imperative to

examine to what extent the anaerobic microbial community can optimally adapt to the sonicated sludge under continuous feeding conditions.

Moreover, ultrasonication implies high energy consumption. Since the process optimization of sludge sonication has not been established in detail, there is a need to investigate the optimal operating conditions in terms of ultrasonic variables, sludge qualities, digester loading and operation, in deriving a cost-effective operation.

1.2 OBJECTIVES OF WORK

Research has been conducted in an attempt to answer fundamental questions in areas relevant to ultrasound pre-treatment of sludge for anaerobic digestion.

Specific objectives include:

1. To examine the effects of sonication treatment on sludge characteristics and to investigate significance of sonication time, sonication density, sludge type and solids concentration in providing guidelines for variables selection in sonication pre-treatment of sludge.
2. To investigate influence of sonication pre-treatment on anaerobic bioconversion in steps of hydrolysis, acidogenesis and methanogenesis in the anaerobic digestion.
3. To examine the feasibility of sonication pre-treatment in continuous digester operation and to investigate the relationships between organic loading, sonication treatment level, and system performance in identifying optimum operating conditions.
4. To explore mechanism of sludge disintegration in sonication treatment with respect to formation and behaviour of cavitation bubbles and to study the correlations between sludge modification and sludge digestion efficiency.

1.3 SCOPE OF WORK

The scope of study was limited to the effects of ultrasound treatment on sludge and the effects of sonicated sludge on the subsequent anaerobic digestion. The

ultrasonic frequency used was fixed at 20 kHz; the sonication density and sonication time were varied. The maximum sonication level used in this project was limited to 0.52 W/ml by the ultrasonic processor; the sonication time was adjustable and ranged from 0.5 - 15 min. Sonication power levels reported were based on the actual power levels delivered at probe tip.

In preliminary investigation, the effects of sonication pre-treatment on both primary and secondary sludge characteristics were examined in terms of temperature, particle size and distribution, soluble chemical oxygen demand (SCOD), dissolved organic carbon (DOC), volatile fatty acids (VFA), pH, oxidation-reduction potential (ORP), turbidity and sludge volume index (SVI). Optimal sonication conditions were established on the basis of marker parameters of SCOD and particle size in terms of sonication time, sonication density, solids concentration and sludge type.

Four lab-scale batch digesters were used to examine the effects of sonication pretreatment of sludge on respective steps of hydrolysis, acidogenesis and methanogenesis. The feasibility and reliability of anaerobic digestion of sonicated sludge under continuous system operation were investigated by four identical upflow anaerobic sludge blanket (UASB) digesters operating at five HRT of 20, 14, 8, 4 and 2 days. Digester performance was evaluated in terms of biogas production, methane content, TCOD removal, solids removal and volatile fatty acids.

Results obtained from sonication pretreatment of sludge were compared with the digester performance in practice (one municipal wastewater plant in Singapore), including increased biogas revenue and savings in construction and operation. A multi-variable linear correlation approach was used to develop an empirical model to address the relationship between sonication treatment of sludge and anaerobic digester efficiency.

CHAPTER 2 LITERATURE REVIEW

2.1 ANAEROBIC TREATMENT

2.1.1 Introduction

Wastewater treatment plants use a combination of sedimentation and biological processes to treat the influent wastewater. Large quantities of wastewater sludge are therefore produced everyday worldwide in the process of municipal wastewater treatment. The raw sludge is highly putrescible, not only rich in organic carbon and pathogens but also in heavy metals and other environmental pollutants. Hence, the sludge has to be stabilized in order to enable an environmentally safe disposal or utilization. Anaerobic digestion is the commonly applied process for stabilization of wastewater sludge.

Anaerobic sludge digestion process converts organic materials biologically to methane and carbon dioxide in an environment devoid of oxygen resulting in the reduction of sludge volatile solids and the production of biogas. Although anaerobic treatment in wastewater treatment plants was first used more than a century ago, it was only during the last three decades that due consideration was given to this process. Advances in science along with recent research studies have helped to better understand the complex biochemistry and microbiology of anaerobic process, and this helps to stimulate further interest and application of the process in wastewater treatment industry.

This section gives a brief review of past research on the fundamentals of anaerobic treatment including biochemistry and microbiology, and also gives a description of the environmental requirements and control of the process.

2.1.2 Biochemistry and Microbiology

Dague (1981) presented a historical overview of the process recognising that anaerobic microorganisms were first discovered by Pasteur in 1861 while studying fermentive reactions. The process was not utilized for waste treatment until late in the nineteenth century (Dague, 1981). Since then, anaerobic digestion has been recognized as a useful process for waste treatment from the earliest household septic tanks to modern waste treatment systems.

The mechanisms of anaerobic processes are much more complicated than that of aerobic processes, due to the many pathways available for an anaerobic community. The biochemistry and microbiology responsible for the reactions are not fully understood, but during the last 30 years a broad outline of the processes has been reported by various researchers (McCarty, 1964; Lawrence and McCarty, 1969; Zeikus, 1977).

2.1.2.1 Three-stage of anaerobic digestion process

The biochemistry and microbiology of methane production during anaerobic digestion of complex organic compounds involve various processes used by a number of microbial populations linked by their individual substrate and product specificities (McCarty, 1964; McCarty and Smith, 1986). Usually, anaerobic digestion of complex organic substances is considered to be a three-stage process consisting of hydrolysis, acidogenesis and methanogenesis as depicted in Figure 2.1. To illustrate the pathways of methane fermentation of complex wastes, Figure 2.2 demonstrates the conversion percentage of waste chemical oxygen demand (COD) by different routes.

Figure 2.1 Three-stage process of anaerobic digestion. k_1 = hydrolysis rate constant (time^{-1}), k_2 = acidogenesis rate constant (time^{-1}), k_0 = fermentation rate or the rate for stages of hydrolysis and acidogenesis (time^{-1}), μ = specific growth rate (time^{-1}), k = methanogenesis rate or rate of entire anaerobic digestion process.

Figure 2.2 Pathways of methanogenesis of complex wastes (% represents waste COD) (McCarty and Smith, 1986)

Anaerobic digestion process is performed by two physiologically distinct bacterial populations. In the stage of hydrolysis and acidogenesis, organic materials are converted into simple volatile fatty acids by a group of facultative and obligate anaerobes commonly termed as acid formers. The end products of hydrolytic and acidogenic conversion comprise predominately organic fatty acids, and a small portion of biological cells. Although no waste stabilization is brought about during hydrolysis and acidogenesis, it is normally considered as intermediate reactions to prepare the organic matter in a form amendable for the second stage of fermentation. It is in the third stage of methanogenesis that actual waste stabilization occurs.

2.1.2.2 Hydrolysis of complex organics

Anaerobic digestion sludge starts with the complex organic substances which must initially be hydrolyzed to soluble organics of lower molecular weight. The large complex organics, such as proteins, carbohydrates, and lipids, present in the wastewater sludge cannot be directly utilized by the bacteria since these polymers are too large to diffuse through the cell membrane. In the first stage of hydrolysis, these long-chain complex organics are converted into simpler molecules, which are then transported into the cell and metabolized.

Hydrolysis of complex organics is a rather slow process and is catalyzed by extracellular enzymes such as amylases, proteases, lipases and nucleases (Levenspiel, 1972; Gaudy and Gaudy, 1980; Lettinga, 1984). Carbohydrates and proteins are hydrolyzed to simple sugars and amino acids, respectively, which can easily diffuse through the cell wall into the bacteria. Fats are hydrolyzed to glycerol and long chain fatty acids. While glycerol can move across the cell wall, the fatty acids molecules are too large to be assimilated by the bacteria cell. The end products resulting from hydrolysis are generally used as carbon and energy sources by acid formers which carry out the first stage fermentation.

The rate of hydrolysis is considered to be a function of many factors such as pH, temperature, biomass concentration, type and size of the particulate, and the present concentration of degradable particulates. Eastman and Ferguson (1981)

found that the hydrolysis rate at constant temperature is approximately first order with respect to the remaining concentration of degradable complex COD. According to Eastman and Ferguson (1981), all biochemical extracellular organics conversion steps are assumed to be of first order to reflect the cumulative effect of a multi-step process. Thereafter, many studies described anaerobic hydrolysis based on biodegradable substrate concentrations (Pavlostathis and Giraldo-Gomez, 1991) as described in Equation 2.1.

$$\frac{d[\text{COD}]}{dt} = -k_1[\text{COD}] \text{ ----- Equation 2.1}$$

Where [COD] represents the concentration of complex organics, mg/L; k_1 is the first order hydrolysis constant, d^{-1} .

2.1.2.3 Acidogenesis

In the second stage, these lower molecular weight organic compounds from hydrolysis are used and converted into simple volatile fatty acids by “acid formers”. The oxidized end products from the acidogenesis are primarily short-chain volatile acids such as acetic, propionic acids and to a lesser extent, butyric, valeric, and caproic acids can also be found. These are called fatty acids since compounds of this type are readily available from naturally occurring fats and oils. It has been reported by Jeris and McCarty (1965) that acetic and propionic acids are the precursors of about 85% of the methane produced from the digestion of complex organic wastes. Relative concentrations of the various intermediates are influenced by both the environmental conditions and the specific growth rate imposed upon the substrate (Andrews and Pearson, 1965).

The bacteria responsible for the hydrolysis and acidogenesis are a very complicated mixture of various bacterial genera. Most of these bacteria are obligate anaerobes (Toerien and Hattingh, 1969), but some facultative anaerobes which can metabolize either aerobically or anaerobically may be present. The obligate bacteria are strict anaerobes sensitive to oxygen, and *Clostridium* is the major group of this species which produce spores in order to survive in aerobic

conditions. *Flavobacterium*, *Alcaligenes*, *Achromobacter* and various enteric bacteria are common facultative microorganisms that have been identified in wastewater treatment systems. It was originally thought that acid formation was mainly performed by facultative bacteria. Studies have shown that the obligate anaerobes are the primary organisms involved in this process (Toerien *et al.*, 1967; Thiel *et al.*, 1968).

The acid formers utilize the soluble organics originally present or produced from the hydrolysis phase to carry out the acidogenesis as described in Equation 2.2.

$$\frac{d[sCOD]}{dt} = k_1[COD] - k_2[sCOD] \text{-----Equation 2.2}$$

Where [sCOD] represents the concentration of soluble organics, mg/L; and k_2 is the acidogenesis constant, d^{-1} .

2.1.2.4 Methane formation

The organic acids produced from acidogenesis are converted by a unique group of micro-organisms identified as “methane formers” into gaseous end products consisting of carbon dioxide, methane and cells. The methane-producing bacteria are subdivided into acetoclastic methane bacteria (acetophilic) and hydrogenotrophic methane bacteria (hydrogenophilic). These methanogenic bacteria are strictly anaerobic and thus vulnerable to even small amounts of oxygen. Naturally, they are only found in completely anaerobic environments like the bottom of lakes, rumen of cattle and the wet wood of trees. The methanogenic bacteria are very difficult to isolate in pure culture. Although many studies have been conducted, relatively little is known about their biochemistry. One of the most significant features of the methanogenesis is that very few substrates can act as energy sources for the methanogens. The discovery indicated that methanogenic bacteria are unable to metabolize alcohols other than methanol, or organic acids other than acetate or formate (Bryant *et al.*, 1967).

The bioconversion of organics into methane proceeds through a series of

complex biochemical changes, and little is known about the individual steps involved. One identified source of methane in anaerobic decomposition is acetate cleavage into methane and carbon dioxide through decarboxylation. The reaction proposed by McCarty (1964) is shown below.

Acetic acid is one of the most important volatile acids formed from the decomposition of organics and is the main source of methane in anaerobic digestion. Most of the remaining methane is formed from the reduction of carbon dioxide, using hydrogen as the energy source by the carbon dioxide-reducing methanogens through the following reduction.

Carbon dioxide is reduced by hydrogen, which is removed from the organic matter by enzymes. The carbon dioxide hence functions as a hydrogen or electron acceptor. There is always an excess of carbon dioxide in the system, and thus the availability of carbon dioxide is never a limiting factor for the methanogenesis.

Some methane can also be produced by the conversion of formate, methanol, methylamines and carbon monoxide as presented in Equation 2.5 to 2.8 (Winfrey, 1984).

Early taxonomic studies included methanogens in a family termed as *Methanobacteriaceae*, while is divided into three genera on the basis of cell morphology. They are generally grouped by *Methanobacterium* in rods, *Methanosarcin* in curves, and *Methanococcus* in spheres. More new genera have

been added in the family including *Methanobrevibacter*, *Methanomicrobium*, *Methanogenium*, and *Methanospirillum* (Montgomery, 1984).

Jeris and McCarty (1965) demonstrated that 65-70% of methane production from a complex substrate is through acetate cleavage accomplished by *Methanosarcina* and *Methanothrix*, while reduction of carbon dioxide by hydrogen-oxidizing methanogens is responsible for the rest (Harper and Pohland, 1987). Ehlinger and co-workers (1987) also reported that *Methanosarcina* predominated at high acetate concentration, whereas *Methanothrix* predominated at lower acetate levels.

2.1.2.5 Rate-limiting stage

Anaerobic digestion technique is attractive in terms of lower energy cost since no aeration is required, along with energy yield in the form of biogas. However, a principal drawback of anaerobic digestion is slow microbial conversion resulting in long retention time and large digester volume. Hence, it is critical to study the rate-limiting stage in the process before any improvement method can be considered. The existing literature indicated that there are two tendencies of rate-limiting steps in anaerobic digestion, namely the hydrolysis and methanogenesis.

2.1.2.5.1 Hydrolysis limitation

It is known that hydrolysis of particulate organics into soluble substances requires the mediation of exo-enzymes that are excreted by fermentative bacteria. However, due to the limitation in mass-transfer of sludge particles, hydrolytic consortia often take considerable long time to approach the cell-bound substrate during the hydrolysis phase. As a result, hydrolysis of particulate organics often limits the entire anaerobic degradation process (Eastman and Ferguson 1981; Shimizu *et al.*, 1993). This is especially the case at low temperatures and high concentrations of particulate organics in the system (Veeken and Hamelers, 1999; Ferreira and Soto, 2003).

Even though Eastman and Ferguson (1981) suggested that the soluble hydrolysis products are consumed so rapidly that they do not accumulate in the system if favourable conditions for bacterial growth are provided, it could also be that the hydrolysis products are bound to the cell so they cannot diffuse away.

According to Veeken and Hamelers (1999), in a hydrolysis limitation anaerobic digestion, the accumulative methane production can be described by hydrolysis rate.

$$CH_4 = CH_{4,max} [1 - EXP(k_H \cdot t)] \text{-----Equation 2.9}$$

Where CH_4 is accumulative methane, $CH_{4,max}$ is the maximum methane yield, k_H is hydrolysis rate constant, t is the digestion time. Parameter values for $CH_{4,max}$ and k_H were estimated by using non-linear least squares curve fitting of the net cumulative methane production.

2.1.2.5.2 Methanogenesis limitation

Methanogenic bacteria, on the other hand, are much slower in growing and far fastidious in environmental requirements than the hydrolytic and acidogenic bacteria (Ronald, 1997). Methanobacterium, one of the important species in methane formation, has an estimated doubling time of about 50 hours during exponential growth at 35°C. Comparatively, the acidogenic bacteria are much faster growing and have typical doubling times of approximately 30 minutes at same condition. As a result, major problems encountered with digester are often long start-up, low substrate-methane conversion, and even irreversible acidification (Brummeler and Koster, 1990).

The production of methane and carbon dioxide is the real waste stabilization step. Since the failure of the system is usually diagnosed by decreased gas production and increased volatile acid concentrations, this step could be also considered to be the rate-limiting step. The accumulation of acids, caused by the slowed growth of the methanogenic bacteria which consume volatile fatty acids, is always deemed as an indicator for methanogenesis limitation.

Moreover, methanogenesis limitation is often the most concern for anaerobic digester during start-up or organic shock loading, in which the vital task is to develop adequate methanogenic biomass to accommodate the excessive volatile acids as quickly as possible. As the growth rate of methane formers is extremely low compared with that of acid formers, it appears that the entire anaerobic decomposition process is dependent on the vitality of methane formers. All of these discussions led to the conclusion that the metabolism of methane formers is likely to be the rate-limiting in the anaerobic treatment process.

2.1.3 Environmental Requirements and Control

Anaerobic waste treatment is such a sensitive biological process that a variety of environmental conditions must be maintained for efficient treatment. The environmental requirements include a careful control of optimum system pH, temperature, nutrients, and tolerable toxic substances.

2.1.3.1 pH

Anaerobic treatment proceeds well at a system pH varying from 6.6 to 7.6, with an optimum range of 7.0 to 7.2 (McCarty, 1964). The efficiency drops off rapidly at pH value below 6.2. Acidic conditions occur when the methane formers are overburdened due to rapid increase in volatile fatty acids concentrations. The acidic conditions are usually caused by organic overloading or hydraulic stress by washing out excessive amounts of the slow-growing methane formers (Young, 1980).

Maintaining an optimum system pH is especially crucial during the sensitive start-up period. A pH below 6.5 can increase the length of start-up considerably. The anaerobic systems are able to tolerate higher fluctuation of pH only when steady-state condition is reached, and also able to recover rapidly from short-term departures of pH from optimum (Young, 1980).

2.1.3.2 Temperature

Temperature has a significant effect on the rate of reaction in anaerobic systems. Enzymatic reaction rates follow the classical Arrhenius reaction equation (Grady *et al.*, 1980) where rates increase with increasing temperatures.

$$K = Ae^{\frac{E^*}{RT}} \text{ ----- Equation 2.10}$$

Where K is specific rate constant, s⁻¹; A is constant, s⁻¹; E* is activation energy, kJ/mol; R is gas constant as 8.314 × 10⁻³ kJ/mol-K; and T is reaction temperature, K.

But the rates cannot increase indefinitely. Increasing temperatures denature the proteinaceous enzymes, resulting in the loss of activation and decreasing reaction rate. Therefore, there is a certain temperature range at which the increased enzymatic rates would be counterbalanced by the decreased activities. It was found that the systems perform better at elevated temperatures in the thermophilic range from 45 to 65°C (Harris and Dague, 1993).

Although waste decomposition proceeds more rapidly at thermophilic temperatures, the costs associated with maintaining such temperatures may offset the benefits of higher reaction rates. Therefore, most anaerobic treatment systems are designed to operate in the mesophilic range of 20 to 45°C. It has been shown that most optimum temperatures are around 33 to 40°C (Zehnder and Wuhrmann, 1977). Anaerobic treatment can be performed at lower temperature below 20°C in the psychrophilic range (Iza *et al.*, 1991). However, operation of the system in this low temperature range is disadvantageous, owing to the extremely reduced rates of reaction and the resulting longer solids retention times.

Sudden temperature changes are often detrimental to the anaerobic systems. It has been reported that changes of only a few degrees in temperature can cause an imbalance between the major bacteria populations leading to digester upset (Grady *et al.*, 1980).

2.1.3.3 *Nutrients*

The inability of many anaerobic bacteria to synthesize some essential vitamins or amino acids indicated that these nutrients are required to be supplied in the feeding substrate. Nitrogen and phosphorus are the primary macro nutrients. COD: N ratios between 400:7 and 1000:7 are required for high and low substrate loadings, respectively (Henze and Harremoës, 1983). Speece and McCarty (1964) have shown that the minimum theoretical COD:N:P ratio may be assumed to be 350:7:1 for anaerobic systems.

Necessary trace elements include iron, zinc, sodium, potassium, calcium, chloride, nickel, magnesium, calcium, sodium, barium, tungstate, molybdate, selenium and cobalt. Selenium, tungsten and nickel are used in the enzyme systems of the acetogenic and methanogenic bacteria. For example, selenium and tungsten are used by the enzyme formate dehydrogenase, and nickel is found to be essential in the synthesis of an important coenzyme, F_{420} , in electron transfer in the terminal stages of methanogenesis (Thauer, 1981).

Some B vitamins were reported as stimulants of methane fermentation from acetate. Vitamin B_{12} , a methyl-group carrier, has been found in significant quantities in sewage sludge (Jeris and Kugelman, 1986). Municipal sewage sludge, besides nitrogen and phosphorus, contains all the other trace nutrients required for the metabolism and growth of anaerobic bacteria. Industrial wastewater, however, may require addition of these nutrients.

2.1.3.4 *Toxicity*

There are many substances which may be toxic or inhibitory to the anaerobic treatment. Toxicity in biological treatment is normally considered as a relative phenomenon since the extent of inhibition is in relation to the concentration of the toxic material. At low concentrations, some inhibiting materials have a stimulative effect upon the process. As the concentration is increased above the optimum level, the bacterial activity begins to decrease.

Microorganisms are often able to acclimatize to inhibitory substances. The extent

of adaptation depends on many parameters and in some cases, the biological activity after adaptation may resume back to the original levels as in the absence of the toxicity. Speece (1983) reported that, in general, methanogenic bacteria are more susceptible to toxicity than other groups of bacteria in anaerobic process. The sensitivity to toxicant of the anaerobes can be reduced by acclimation (Parkin *et al.*, 1983), and by maintaining a longer solid retention time (Obayashi and Gorgan, 1985).

Apart from various organic substances which can inhibit anaerobic systems, there are more common toxic materials that cause process failure or upset in anaerobic treatment. These include volatile acids, ammonia, heavy metals, alkali and alkali-earth salts, and sulphide.

2.1.3.5 Volatile fatty acids

Volatile fatty acids (VFA) are perhaps the most common inhibitors of anaerobic system. It is known that VFAs are important intermediate compounds for methane generation and may also cause microbial stress if present in excessive concentrations (Hill *et al.*, 1987). According to Cobb and Hill (1991), a low VFA concentration is an indicator for a healthy and stable anaerobic digester. The mechanisms are somewhat obscure, but it is believed that the unionized volatile acids play a role (Andrews, 1969). Due to varied operating conditions and diverse substrate, however, different thresholds for VFA inhibition were established from 1000 mg/L to 4000 mg/L (Hill *et al.*, 1987; Dogan *et al.*, 2005; Stafford, 1982), and even high concentration of 20,000 mg/L in the case of cheese whey digestion (Backus *et al.*, 1988).

2.1.3.6 Ammonia

Ammonia is a common toxic substance resulting from the degradation of wastes containing proteins or urea. Ammonia may be present either in the form of ammonium ion or as dissolved ammonia gas. It is believed that free undissociated ammonia is most toxic with inhibition reported at 0.1-0.2 kg N/m³ (Henze and Harremoes, 1983). If concentration of free ammonia exceeds 150

mg/L, severe toxicity will occur, whereas concentration of ammonia ion must exceed 3000 mg/L to exert the same effect (McCarty, 1964). Total ammonia and ammonium concentrations as high as 5-8 kg N/m³ can be tolerated if the reactor pH is within the normal operation limits (Henze and Harremoes, 1983). When the ammonia-nitrogen exceeds 3000 mg/L, the ammonium ion itself will become toxic regardless of system pH, and process failure can be expected (McCarty, 1964).

2.1.3.7 Feed characteristics

Sludge anaerobic digestion applies to primary sludge, secondary sludge (waste activated sludge, WAS), or mixture of the two kinds. The primary sludge contains more readily degradable organic materials than secondary sludge, resulting to higher total volatile solids destruction efficiencies (WEF and ASCE, 1992). Literature indicates that as much as 70% of the primary sludge is biodegradable (Parkin and Owen, 1986). However, secondary sludge is generally reported to be half as digestible as primary sludge.

The biodegradability of secondary sludge depends on the active anaerobic biomass present; while the characteristics of the biomass greatly depend on the solids retention time (SRT) of the aerobic activated sludge process (Gossett and Belser, 1982; Pavlostathis and Gossett, 1985). High SRTs results in biomass with greater resistance to lysis and consequently, to decrease anaerobic degradation rates. Gossett and Belser (1982) reported that the ultimate secondary sludge biodegradability ranged between 30-50%. More than 50% of the secondary sludge COD escapes from anaerobic digestion, resulting in digester effluents high in COD and VS, and having the necessity of further biodegradation as well as the potential of more biogas yield.

Typically, municipal wastewater treatment plants combine and thicken primary and secondary sludges (the combined sludge is also named consolidated sludge) before anaerobic digestion. The biodegradation of volatile solids in the consolidated sludge occurs at similar rates and efficiencies when the primary or secondary sludges are digested alone.

2.1.4 Features of Anaerobic Digestion

2.1.4.1 Advantages of anaerobic digestion

The anaerobic treatment process offers several advantages over aerobic systems. One of the main characteristics of aerobic systems is that, the growth rate of the microorganisms is considerably faster as much energy can be secured from the oxidation of organic waste. Consequently, a large portion of the organic matter is used in the synthesis of biomass. The organics converted to biomass have not actually been stabilized, but are simply changed in form. The significant amount of biological solids generated in the aerobic process requires further sludge treatment for ultimate waste stabilization.

On the other hand, in anaerobic treatment the problem of sludge disposal is significantly minimized, because only a small portion of the waste is being converted into biomass. In anaerobic treatment, the anaerobes are capable of converting the organic wastes into methane and carbon dioxide. Biomass yields are typically 10 percent for anaerobic systems, compared with about 50 percent for aerobic systems (Benefield and Randall, 1980).

This results in lower costs for the anaerobic process for sludge treatment and disposal. Since anaerobic treatment does not require oxygen in waste decomposition, the rates of reaction are not limited by oxygen transfer. In addition, there is notable saving in the energy needed for aeration. Moreover, the combustible end product of methane gas represents an additional source of energy for other operations such as heating and generating electricity.

2.1.4.2 Limitations of anaerobic digestion

There are however, some limitations on the anaerobic process. The main reason for the slow digestion degradation rates is that the anaerobic bacteria must degrade the more complex organic substrates found in sludge, particularly the difficult to degrade bacterial cells generated by the aerobic treatment (Gossett and Belser, 1982; Pavlostathis and Gossett, 1985). In contrast, aerobic treatment handles the simple organic contaminants, mainly soluble or colloidal, found in

wastewater. In the treatment of soluble organics, it was found that aerobic and anaerobic processes receiving the same substrate required the same hydraulic retention time to result in comparable COD removal efficiencies. Novak et al. (2003) suggested that digestion by either aerobic or anaerobic process will not destroy all the bioavailable protein and degradation of activated sludge might be best accomplished by combined aerobic and anaerobic processes.

The limitation is also related to the slow growth rate of the methane-production bacteria. Slow growth rates require a relatively long retention time in the reactor for adequate waste decomposition. Even after several decades of optimization, a retention time of more than 20 days and the construction of huge digesters are usually necessary for efficient degradation in an anaerobic process.

The sensitive and delicate nature of the methanogens also limits the rate at which the process can adapt to changing organic loadings, temperatures, or other environmental conditions. It is essential that the bacterial have been allowed to acclimatize to the new conditions, especially in starting up the reactors for subsequent satisfactory operation. Longer start-up period is therefore needed in anaerobic process.

Acceleration and better performance of the anaerobic process could be achieved by finding an alternative to the slow hydrolysis or improving environmental conditions to promote methanogenesis. Recent techniques in pre-treatment of sludge have showed a great deal of promise in modifying sludge characteristics to benefit the following anaerobic digestion. With increasing solubilization of the organic substances, more volatile solids become biodegradable. Thus, the efficiency of anaerobic digestion might be enhanced by using physical and/or chemical pre-treatment processes (Eastman and Ferguson, 1981).

2.2 PRE-TREATMENT OF SLUDGE FOR ANAEROBIC DIGESTION

Various pre-treatments of sludge had been studied to improve anaerobic digestion efficiency. These pre-treatments led to rupture of the cell walls and membranes of bacteria in sludge resulting in release of organic substances to the

outside of the cell. These organic substances can easily be hydrolyzed to their unit molecules by extracellular enzymes of anaerobic microbial origin leading to an improved anaerobic digestion. The main methods of pre-treatment were demonstrated as follows.

2.2.1 Thermal Treatment

Thermal treatment of sludge was first developed to improve the dewaterability of sewage sludge. Thermal treatment is carried out through pasteurization by injecting steam at a temperature of 120-175 °C with approximately 1×10^5 Pa pressure into a holding tank, mixing with the sludge and raising the bulk suspension temperature to 70 °C for 30 min. Thermal treatment at a temperature of 170-175 °C breaks down the cells of microorganisms in the sludge into soluble organic matters, thereby improving the efficiency of anaerobic digestion and methane production (Stuckey and McCarty, 1984).

Heating sludge to above 150 °C for 30 minutes would cause the breakdown of cell walls and the possible conversion of organics into more readily digestible forms. Experiments indicated that a significant fraction of the volatile solids was liquidized following thermal treatment, and an increase in gas production of approximately 34% was noted. However, an acclimatization period was necessary for the digesters, and the quality of the supernatant liquors (in terms of the COD) was affected. Furthermore, this process requires more electrical energy than mechanical processes (Baier, 1997).

2.2.2 Chemical Treatment

2.2.2.1 Ozonation

The degree of biodegradability of the organic matter can be raised with the help of partial oxidation of digested sludge with ozone (Yasui and Shibata, 1994). The idea is to apply additional treatment methods to these refractory sludge components, which could not be disintegrated in either the one-stage or the two-stage anaerobic degradation process. The refractory sludge components will then be partially oxidized either with ozone or with ozone in combination with

hydrogen peroxide, which will lead to more complete degradation (Müller *et al.*, 1998). It is not suitable for aerobic digestion due to nitrification and other problems.

2.2.2.2 Alkali

The alkaline pre-treatment may be used to hydrolyze and decompose lipids, hydrocarbon, and protein into smaller soluble substances such as aliphatic acids, polysaccharides, and amino acids (Chiu *et al.*, 1997). Alkali treatment yields a significant reduction in microbial density and the release of COD from the sludge body, especially at $\text{pH} \geq 10$. Lime and sodium hydroxide could be used for alkaline pre-treatment of sludge to improve the solubilization efficiency of sludge. Lime treatment is the addition of either CaO or Ca(OH)_2 in order to raise the pH to values of 11 or higher to kill off pathogens. However, the addition of chemicals increases the volume of wastes generated by the digester and the high pH of the medium favors the undesirable volatilization of ammonia (Chui *et al.*, 1997).

2.2.2.3 Acids

Acidification leads to decreasing floc size, resulting in thicker filterer cake solids. Non-alkaline chemicals, either bactericides or oxidants, are seldom used because of their high cost.

Jean and co-workers (2000) observed that adjustment of pH value for two hours could disinfect the micro-organisms in the sewage sludge by using total coliform bacteria as microbial indices. Microscopic observation revealed that in acidic conditions, the sludge floc retained its shape and structure, which exhibited a large size.

Although the chemical pre-treatment methods have indicated improvement on solubilization of sludge; the addition of inorganic chemicals, however, increased the volume of sludge, hence increasing the final waste volume. When acid or alkali is used, the salinity of the sludge will also be affected, thus possibly

causing problems in sludge disposal (Woodard and Wukasch, 1994).

2.2.3 Mechanical Treatment

Mechanical disintegration is a well known process to obtain intracellular products such as proteins or enzymes in biotechnological applications (Kopp, *et al.*, 1997). Even for short grinding times, significant reduction of the mean particle size and an increase in surface area of the sludge could be observed, because the floc structure of the sludge had been destroyed (Müller *et al.*, 1998). The mechanical disintegration of sewage sludge destroys the floc structure of sludge and disrupts the cell walls of the micro-organisms. The intracellular components are set free and are immediately available for biological degradation which leads to an acceleration of the process. Facultative anaerobic micro-organisms are disrupted as well and become degradable, thus resulting in a higher degree of degradation. However, mechanical disintegration needs high energy input. The investment for the disintegration aggregates has to be seen in relation to the reduction of digester volume and digestion time needed.

Ultrasound pre-treatment is also classified into mechanical treatment and will be elaborated in much detail in the later section.

2.2.3.1 High-pressure homogenization

High-pressure treatment degrades sludge by utilizing the high shear stress produced when the sludge is released to the atmosphere. High-pressure homogenization is the most widely known method for large-scale operation. Sludge is compressed to approximately 60 MPa and then released from the compressor through a valve at high speed, shooting onto an impaction ring. Cell disintegration of 85% can be achieved (Choi *et al.*, 1997).

2.2.3.2 Stirred ball mills

Ball-mills generate high shear stress by grinding beads to break the cell walls. The best result can be obtained when using the stirred ball mill for long grinding

times, at high agitator speeds and with small particle sizes of the grinding beads (Müller *et al.*, 1998).

2.2.4 Enzyme Treatment

The application of enzymes for the treatment of the primary sludge with a high content of lignocellulosic material seems to be the most appropriate. The use of enzymes can increase degradation; however, it is a highly cost technique while producing a strong odour (Knapp and Howell, 1978).

2.2.5 Irradiation Treatment

Irradiation can be generated by either directly ionizing of particles or indirectly by ionizing radiation of electromagnetic nature obtained from radionuclide sources. Bacterial cells structures are influenced by both the direct and indirect action of ionization products, disrupting the DNA and cell division. Viruses can be damaged by chain capture of the nucleic acid (Yeager, 1983). Irradiation treatment can substantially increase the concentrations of soluble organic matter. A significant improvement was seen in the hourly biogas production study at the thermophilic temperature with 10 days over the first eight hours (Müller, 2001).

However, the results of irradiation have not proven to be reproducible under the variety of conditions encountered in wastewater treatment plants, and the energy costs have made it generally prohibitive.

2.3 FUNDAMENTAL OF ULTRASOUND

2.3.1 Introduction

Although ultrasound technology had been widely applied in industrial world for last century, it was only during the last decade that due consideration was given to this technology on environmental engineering world.

Ultrasound is the term which is used to describe sound energy at frequencies above 20 kHz, i.e. above the range of which is normally audible to human beings

(Figure. 2.3). Ultrasound is usually generated by a transducer, which converts mechanical or electrical energy into high-frequency vibrations. Ultrasound energy can be delivered into a fluid system via a horn or probe.

Figure 2.3 Ultrasound frequency ranges and dominant processes

Sound is composed from longitudinal waves comprising rarefaction (negative pressures) and compressions (positive pressures). It is these alternating cycles of compression and rarefaction which, in high-power ultrasound applications, create the phenomenon known as cavitation. A broad range of frequencies and acoustic intensities can be generated by ultrasound. If high acoustic energy is applied to a liquid system, it is possible to generate physical and chemical reactions which can significantly modify the character of dissolved and particulate substances present in the liquid. These reactions are mainly resulting from the generation and collapse of cavitation bubbles, which are produced under this acoustic condition (Neppiras, 1980).

2.3.2 Cavitation Phenomenon

2.3.2.1 Generation of cavitation

Cavitation is the formation, growth and collapse through implosion of

microbubbles. These bubbles can be either gas or vapour filled and form in a wide variety of liquids under a wide range of conditions. Cavitation occurs in water, organic solvents, biological fluids, liquid helium, and molten metals, as well as many other fluids. Cavitation can be initiated by either setting up a tension in the liquid or by depositing energy into it (Figure 2.4). It should be noted that this review is only relevant to the cavitation generated in sound fields.

Figure 2.4 Classification scheme for the different origins of cavitation

Cavitation is accompanied by a number of effects having their origin in the dynamics of the bubbles generated. Cavitation bubbles tend to collapse exceedingly fast, emitting shock waves and even light (sonoluminescence). They erode solid surfaces and induce chemical reactions (Kuttruff, 1991).

2.3.2.2 Acoustic cavitation

When ultrasound waves with high acoustic intensities are applied, particularly in the low and mid frequency range, gas bubbles are generated which will grow by taking in gas and vapour from the liquid. They change in size in relation to the acoustic wave and can collapse in the compression cycle (implosion), with the final implosion of the bubbles. This is called acoustic cavitation. At implosion of the bubbles, dramatic conditions exist in the gaseous phase: extreme temperatures (5000 K) and high pressures (500 bars) (Neis *et al.*, 2000).

The bubble implosions produce short-lived (lasting micro-seconds) “hot spots” in the liquid, which can release sufficient energy to drive a variety of chemical

reactions (Clark and Nujjoo, 2000). The cavitation effect is influenced by a number of factors, such as liquid temperature, viscosity, surface tension, ultrasonic levels (often referred to as the acoustic energy density or intensity) and frequency of ultrasound vibration.

The minimum amount of energy which is required to initiate cavitation is referred to as the cavitation threshold, and this threshold varies for different fluids. Only the energy applied above the threshold will contribute to the formation of a cavitation bubble. In water, cavitation will generally occur once the ultrasonic energy rises above 1 W/cm^3 levels (Clark and Nujjoo, 2000).

It is difficult to create cavitation at frequency beyond 1 MHz because the acoustic intensity which needs to be applied to create cavitation increases with increasing frequency. In the high frequency range greater than 1 MHz, the acoustic wave impact on the liquid creates microcurrents together with stable, oscillating bubbles. These bubbles do not collapse, and may occasionally rise to the surface of the water body (Neis *et al.*, 2000).

2.3.3 Cavitation Bubble Dynamics

2.3.3.1 Formation of bubbles

When the acoustic pressure at rarefaction cycle is greater than the local cavitation threshold pressure, any minute cavity available will grow in size and collapse at resonant radius (Laborde *et al.*, 1998). Therefore, the process of disintegration is viewed as a competition between the liquid strength P_c^v (Equation 2.11) and acoustic pressure P_A (Equation 2.12). When $P_A > P_c^v$, the cavitation bubble will be formed (Abramov, 1998; Tatake and Pandit, 2002).

$$P_c^v = P_0 - P_v + 1.09(\sigma_L/R_0) \sqrt{\frac{\sigma_L/R_0}{P_0 - P_v + 2\sigma_L/R_0}} \text{ ----- Equation 2.11}$$

$$P_A = 1.41\sqrt{I\rho C} \text{ -----Equation 2.12}$$

Where P_c^v is cavitation threshold pressure (MPa); P_v is the saturation vapour

pressure (MPa); R_0 is the initial bubble/cavity radius (cm), σ_L is the surface tension (N/m); P_A is the acoustic pressure (Pa); I is the ultrasound intensity (W/m^2), ρ is the density of the medium (kg/m^3), C is the velocity of sound in that medium (m/s).

Cavitation bubble collapse occurs when the expanding bubbles have reached their resonant radius. The resonant cavitation bubble radius is a function of the ultrasound frequency. In pure water and low surface tension, it can be calculated by the following equation:

$$\rho \omega_r^2 R_r^2 = 3\gamma P_o \text{ ----- Equation 2.13}$$

Where ρ is the density of water (g/cm^3), ω_r is the resonance angular frequency (kHz), R_r is the resonant bubble radius (cm), P_o is the pressure exerted on the liquid (atm), and γ is the ratio of the specific heats of gases (dimensionless). γ correlates to the heat released upon gas compression (Hua and Hoffmann, 1997) and varies from 1.66 to 1.4 and 1.33 for monoatomic, diatomic and triatomic gases, respectively.

Taking the case of air bubbles in water at atmospheric pressure, the ultrasonic cavitation bubble radius can be approximated as:

$$R_r \approx 3.28 f_r^{-1} \text{ ----- Equation 2.14}$$

Where the resonant bubble radius R_r is expressed in millimeters and f_r is the resonance frequency in kHz (Young, 1989). The bubble radius is inversely proportional to the ultrasound frequency. The application of low frequencies creates larger cavitation bubbles. Upon bubble collapse, hard mechanical jet streams are produced that are responsible for many cavitation effects observed on solid surfaces.

2.3.3.2 Two types of cavitation bubbles

Two distinct types of bubble behaviour are generally identified: stable bubbles

and transient bubbles, which are related to the sonication intensity (Abramov, 1998). If the peak sound pressure in the rarefaction cycle is not high enough to force bubble to expand to its resonant radius, the bubble remains stable and oscillates for a time scale of thousands of acoustic cycles (Laborde *et al.*, 1998). The transient cavitation is referring to a condition that the acoustic pressure is able to exert cavity expansion to its resonant radius enabling collapse of bubbles within half acoustic cycle.

Transient cavitation involves large-scale variations in bubble size (relative to its equilibrium size) over a time scale of a few acoustic cycles, and this rapid growth usually terminates in a collapse of varying degrees of violence. Stable cavitation, on the other hand, usually involves small-amplitude (compared to the bubble radius) oscillations about an equilibrium radius. Stable cavitation in most instances results in little appreciable bubble growth over a time scale of thousands of acoustic cycles. However, this classification of cavitation is not strict. Stable cavitation can lead to transient cavitation, and the collapse of a transient cavity can produce smaller bubbles that undergo stable cavitation.

2.3.4 Effects of Ultrasound

2.3.4.1 Chemical effects

As outlined before, acoustic cavitation generates extreme temperatures and high pressures in the gaseous phase. These dramatic conditions lead to pronounced chemical reactions with the application of ultrasound. These reactions are caused by the creation of highly reactive radicals ($H\cdot$, $OH\cdot$) and thermal breakdown of substances (pyrolysis), which mainly belongs to the field of sonochemical reactions.

The principal products from the ultrasonic irradiation of water are H_2O_2 and H_2 , and various data support the hypothesis of the intermediacy of hydroxyl radicals and hydrogen atoms, which was first reported by Schmitt (Neis, 2000).

The wide range of oxidations and reductions that occurs with aqueous sonochemistry is often a consequence of secondary reactions of these high-energy intermediates.

2.3.4.2 *Biological effects*

With the development of various aspects of acoustic cavitation, of acoustic radiation forces and of acoustic streaming, ultrasound is proven great application in biological and medical technique, such as sterilization, cell disruption, dental descaling, fibrinolysis, sonoporation and treatment of Meniere's disease.

The high-pressure shockwave that emanates from the location of the bubble is capable of causing mechanical damage to surrounding material. In cases where the bubble is adjacent to a solid surface, a high-velocity liquid jet may shoot through the bubble, impacting on, and damaging the cell walls. The high temperatures can cause bond dissociations in molecules, producing free radicals that can react with biomolecular species in much the same way as those produced by ionizing radiations (Hiraoka *et al.*, 1984).

The inhomogeneous cyclic field established around stably oscillating bubbles can cause steady flow of the fluid medium surrounding the bubble in a process known as microstreaming. If the streaming velocities are great enough, shear stresses resulting from the decreasing velocity with distance from the bubble can be sufficient to damage microbial cells (Monnier *et al.*, 1999). It is clear that acoustic cavitation is the primary mechanism for the production of biological effects in most solutions, suspensions, plants, and insects. Some of these effects occur at levels lower than used clinically. Carstensen *et al.* (1979) found that exposure of plant roots to ultrasound caused reduction of growth. The growth reduction was most significant at a frequency of 1 and 2 MHz; subharmonic and noise signals were emitted from the tissue when the intensity was above 3 W/cm²; the growth reduction was much less when the tissue was under 20 atm hydrostatic pressure during exposure to ultrasound.

**2.4 ULTRASOUND APPLICATION IN ENVIRONMENTAL
ENGINEERING**

2.4.1 Introduction

While the use of ultrasound has been routine for many years in fields such as medical diagnosis, cleaning and others, application of ultrasound technology in environmental engineering is still in its earliest phase, with only the first applications operational at a technical scale. Table 2.1 provides an overview of current ultrasound applications in water, wastewater and sludge systems.

While ultrasound shows great potential in environmental engineering, a number of scientific and technical questions exist which include the influence of ultrasonic parameters, dissolved gases and suspended solids on cavitation; optimal digester design; economy, reliability and life expectation of ultrasound equipment.

Table 2.1 Ultrasound applications in environmental engineering

Domain	Objective
Potable water	Inactivate bacteria (disinfection) Improve separation of solids Remove encrustations in pipes and wells
Wastewater	Sonochemical pollutant degradation Improve biological degradation
Sludge	Disintegrate biosolids Decompose bulking activated sludge flocs to allow sedimentation Improve dewatering

2.4.2 Ultrasonication on Wastewater Treatment

Biological treatment of wastewaters is usually the preferred choice because of its low cost compared to chemical or physico-chemical processes, which holds true unless bacteriotoxic or refractory pollutants inhibits biological activity, as happens in many industrial liquid wastes. When this occurs, more expensive

chemical or physical methods have to be used.

Ultrasound treatment shows some similarity to advanced oxidation processes (ozone, H_2O_2 , UV), in which OH radicals are produced by the sonolysis of H_2O . Mechanisms involved in sonochemical transformations are still misidentified. However, acoustic cavitation appeared early as the main phenomenon responsible for chemical transformations (Neis, 2000).

It has been shown that a variety of wastewater pollutant can be degraded using ultrasound. Different types of chemical pollutants, for instance chlorinated solvents and aromatics, hydrocarbons, pesticides, phenols, and polymers have been investigated. Ultrasound cavitation generates pyrolytic reactions and hydromechanical forces. In many cases these processes were deemed as the dominant factors in the ultrasound degradation of pollutants. It had been demonstrated that the reaction mechanisms vary depending on the different physicochemical properties of a particular pollutant:

- Volatile pollutants are degraded preferentially by pyrolytic reactions which occur in the vapour phase of the cavitation bubble (Gonze *et al*, 1999).
- Hydrophobic pollutants accumulate and react in the hydrophobic boundary layer of the cavitation bubble. The concentrations of OH radicals and H_2O_2 in the boundary layer are significantly higher than in the surrounding liquid. Pyrolysis and radical reactions contribute to the degradation (Henglein and Korman, 1985).
- Hydrophilic pollutants in the bulk liquid are degraded by reaction with free radicals or H_2O_2 (Henglein and Korman, 1985).
- Macromolecules and particles are also degraded by hydromechanical forces triggered by the collapse of the cavitation bubbles (Portenlänger, 1999; Tiehm *et al.*, 2001).

Table 2.2 Degradation of solutions with different compounds

Compounds	Conditions of sonication	Intermediate products identified
Phenols	20 and 487 kHz, 30 W, air, 0.5 mM	hydroquinone, catechol, 2,5-dioxohexen-3-dioic acid, muconic, maleic, succinic, formic, propanoic, oxalic and acetic acids
2-chlorophenol	20 and 541 kHz, 30 W, air, 100 mg/l	chlorohydroquinone, catechol, 3-chlorocatechol, chlorides
3-chlorophenol	20 kHz, 50 W, air, 0.05 mM	chlorohydroquinone, 3- and 4- chlorocatechol,
4-chlorophenol	20 kHz, 50 W, air, 0.05 mM	hydroquinone, 4-chlororesorcinol, 4-chlorocatechol, chlorides
Pentachlorophenol	500 kHz, air, 0.1 mM	chlorides
Parathion	20 kHz, 84 Watt, air 0.1mM	p-nitrophenol, sulfates, phosphates, formic, oxalic and acetic acids
Benzenes	20 and 487 kHz, 30 W, air, 0.5 mM	phenol, catechol, hydroquinone, 1,2,3-trihydroxybenzene, maleic and muconic acids, formaldehyde, acetylene
Chlorobenzene	20 and 487 kHz, 30 W, air, Air, O ₂ , 0.5 mM	4-chlorophenol, 4-chlorocatechol, hydroquinone, acetylene
Chloroform	200 kHz, O ₂ , Ar, air 20 kHz, 200 W, air	N/A
Carbon Tetrachloride + phenol	20 and 500 kHz, 30 W, air, phenol: 0.5 mM, CCl ₄ : 3.8 mM	chlorides, 2-chlorophenol, 2,4-dichlorophenol, chlorobenzoquinone

For the practical studies and experiments, the results of different chemical pollutants in wastewater after ultrasound treatment are listed in Table 2.2 (Gonze *et al.*, 1999). Among all the applications of ultrasound, wastewater treatment appears to be an original and expanding field of study. This process is convenient and simple in terms of temperature, pressure (ambient conditions) and reagents

(no reagents). But the energy consumption for total pollutant mineralization is very high. The ultrasonication process is, therefore, considered a preoxidation step (Gonze *et al.*, 1999).

2.4.3 Ultrasonication of Sludge for Anaerobic Digestion

As mentioned in previous sections, anaerobic digestion is the most popular technique for sewage sludge stabilization resulting in the reduction of sludge volatile solids and the production of biogas. Anaerobic digestion is a slow process and the rate limiting step is usually the hydrolysis of particulate organic matter to soluble substances or slow methanogenesis acclimation.

It has been postulated that the cavitation bubbles produced during sonication enhance the subsequent anaerobic digestion of the sludge by causing the cell to disrupt/lyse and release readily biodegradable intracellular organics in solution (Tiehm *et al.*, 1997; Neis *et al.*, 2000; Chu *et al.*, 2002). In addition, the physical action which is produced by the cavitation bubbles can reduce the sludge particle size distribution, which potentially increased the number of sites available for microbial action in the subsequent anaerobic digestion.

2.4.3.1 Case studies

Table 2.3 summaries the technical parameters and main achievements for previous studies on ultrasound pre-treatment for anaerobic sludge digestion. Neis *et al.* (2000) investigated the effect of ultrasound pre-treatment on sludge degradability by testing the increase of COD and size reduction of sludge solids. Semi-continuous fermentation experiments with disintegrated and untreated sludge were done for four months on a half-technical scale. The result indicated that the fermentation of disintegrated sludge remained stable even at the shortest residence time of 8 days with biogas production of 2.2 times that of the control fermenter.

The effects of ultrasound frequency on the disintegration by varying the frequency within a range from 41 to 3217 kHz, and the impact of different

ultrasound intensities and treatment times on anaerobic digestion were also examined (Tiehm *et al.*, 1997). It was reported that low frequency ultrasound could generate larger cavitation bubbles resulting better sludge disintegration.

Table 2.3 Technical specifications of the sonoreactors

Items	Neis <i>et al.</i> (2000)	Tiehm <i>et al.</i> (1997)	Chiu <i>et al.</i> (1997)	Clark & Nujjoo (2000)	Laffitte & Forster (2002)	Jean <i>et al.</i> (2000)
Digester volume	2000 L	1500 L	1 L	10 L	400 ml	-
Sonicator volume	1280 cm ³	-	1000 cm ³	10 L	100 ml	-
Frequency	31 kHz	31 kHz	20 kHz	20-35 kHz	23 kHz	-
Number of transducers	48	-	-	-	-	-
Hydraulic Retention Time in digester	4-16 d	8-22 d	-	12-15 d	8-12 d	-
Sonication time	64 s	64 s	14-24 s/ml	<60 s	90 s	20-120 min
Power consumption	3.6 kW	3.6 kW	120 W	9 kW	47 W	-
Acoustic intensity	5-18 W/cm ²	-	-	-	-	-
Acoustic power density	2.2-7.9 W/cm ³	-	-	-	-	0.11-0.33 W/mL
Digestion Temperature	37 °C	37 °C	30-36 °C	35 °C	-	-
Duration	-	4 months	-	12 months	-	-

Chiu *et al.* (1997) found a critical ultrasound power above which, the floc structure was effectively disintegrated, microbial level acceptably disinfected, and particulate organic compounds sufficiently transformed into soluble state. They also found that both ultrasonic vibration and bulk temperature rise contributed to the treatment efficiency.

Clark and Nujjoo (2000) studied the cell lysis and particle size reduction after ultrasound pre-treatment. A series of laboratory-scale anaerobic digesters had been operated and significant increases in biogas yield have been noted following ultrasonication. Experiments were completed with a variety of ultrasonic devices (of different geometries and construction materials).

Jean *et al.* (2000) investigated the effects of ultrasound and pH values on the microbial density level in sewage sludge by using total coliform and heterotropic-plate-count (HPC) bacterial. High pH breaks up large flocs into smaller aggregates.

2.4.4 Reactions of Ultrasonication in Sludge Treatment

Based on the previous studies, several factors are supposed to be responsible for the disintegration of sludge with ultrasound treated. They can be summarized in three aspects:

- 1) Sonochemical effects
- 2) High mechanical forces
- 3) Thermal breakdown of volatile hydrophobic substances

2.4.4.1 Sonochemical effects

The temperature and pressure inside the collapsing cavitation bubbles could rise up to about 5000 K and several hundred atmospheres, respectively. These extreme conditions can lead to the generation of very reactive hydroxyl radicals ($H\cdot$, $OH\cdot$) (Young, 1989). In this way sonochemical reactions can degrade volatile pollutants by pyrolytic processes inside the cavitation bubbles and non-volatile pollutants by hydroxyl radical reactions in the bulk liquid (Pétrier and Francony, 1997; Tiehm *et al.*, 1999). Although these reactions can theoretically occur at ultrasound frequency within 20 kHz - 1 MHz, they are more commonly observed at frequency higher than 100 kHz (Hua and Hoffmann, 1997; Pétrier and Francony, 1997).

2.4.4.2 Mechanical forces

Many studies show that mechanical forces are the key factor to contribute to the ultrasonic disintegration of sewage sludge. As described by Neis (2000), when the acoustic wave first impacts, sludge flocs are separated and a large number of single cells are unleashed. While sonication continues, single bacteria cells may act as nuclei for the formation of bubbles. This mean they might be captured and ruptured in the cavitation bubbles which, during the rarefaction cycle, can grow

up to 175 μm in diameter before collapsing. The violent collapse produces very powerful hydromechanical shear forces in the bulk liquid surrounding the bubbles.

The mechanical forces are most effective at frequencies below 100 kHz, which is the same frequency range of the best disintegration achieved (Tiehm *et al.*, 1999). It had been shown that macromolecules with a molar mass above 40,000 are disrupted by the hydromechanical shear forces produced by ultrasonic cavitation. On the other hand, sonochemical processes, i.e. production of hydroxyl radicals, were most significant at frequencies between 200 to 1000 kHz (Mark *et al.*, 1998). Therefore, hydromechanical forces produced by ultrasonic cavitation are more important for sewage sludge disintegration than sonochemical processes.

2.4.5 Influencing Parameters

2.4.5.1 Frequency

Sludge disintegration was the most significant at lowest frequencies tested of 41 kHz (Tiehm *et al.*, 2001). The decreasing sludge disintegration efficiency observed at higher frequencies (up to 3217 kHz) was attributed to smaller cavitation bubbles which did not allow the initiation of such strong shear forces (Neis *et al.*, 2000).

Theoretical considerations are useful to understand the decrease in disintegration efficacy with increasing ultrasound frequency. As outlined by Equation 2.14 discussed previously, the resonant cavitation bubble radius is inversely proportional to the ultrasound frequency. Low-frequency ultrasound creates large cavitation bubbles which, when they collapse, generate more powerful shear forces. A valid assumption might be that the energy released by a jet stream is a function of the bubble size at the moment of collapse. Starting at a point where R is about 4 μm , the degree of cell disintegration increases proportionally to the logarithm of the bubble radius (Neis *et al.*, 2000).

Another explanation might be derived from the function of wavelength. In the

medium, ultrasound energy is propagated by the alternating compressions and rarefactions. The wavelength represents the distance between the adjacent compressions and rarefactions. The wavelength is related to the wave number, propagation velocity and frequency as Equation 2.16 shows:

$$\lambda = \frac{c_0}{f} \text{ ----- Equation 2.16}$$

Where λ is the wavelength, (m); c_0 is the propagation velocity, (m/s); f is the sound frequency (Hz).

According to Equation 2.16, the wavelength is inversely proportional to the ultrasound frequency. At lower frequency, ultrasound is propagating at longer wavelength and the ultrasound energy reaches locations remote from its source.

Based on the experimental results and theoretical calculation of Tiehm et al. (2001), the fixed frequency to generate large cavitation bubbles and distribute sound energy in the treated sludge was set to 20 kHz. It is not known, however, if this was the optimum length in our particular study, but this optimization was beyond the scope of this thesis.

2.4.5.2 Sonication time

The amounts of the concentrations of organic substances in the supernatant, such as protein, carbohydrate and COD, increased proportionally with ultrasonic pre-treatment time (Wang *et al.*, 1999). Short sonication times resulted in sludge floc deagglomeration without the destruction of bacteria cells. Longer sonication brought about the break-up of cell walls, the sludge solids were disintegrated and dissolved organic compounds were released to the liquid phase (Neis *et al.*, 2000).

There should exist an optimum pre-treatment time in terms of efficiency and energy cost. Chu *et al.* (2001) proposed that the ultrasonic treatment consists of several stages. At the first stage of sonication (0-20 min) at a power input 0.11 – 0.44 W/mL, the porous floc can be readily deteriorated into compact flocculi, while the dewaterability of sludge was markedly deteriorated. In the second

stage (20-60 min), although the floc size had remained almost unchanged, both heterotrophic bacteria and total coliform were effectively disinfected. The soluble COD value increased accompanied with the reduction in the microbial density levels. In the final stage (60-120 min), if the bulk temperature was controlled, ultrasonic treatment had essentially no effects on the sludge characteristics. However, the raised bulk temperature of sludge could induce continuous transformation of solid-state organic compounds into a soluble form. The pre-treatment for more than 30 min did not lead to continued extensive increases in methane generation (Wang *et al.*, 1999).

2.4.5.3 Energy level (intensity / density)

The degree of disintegration is increased by the increase of the acoustic intensity in applied range. The degree of disintegration was more than doubled by an increase of the sound energy from 6 to 8 W/cm² intensity. This is due to the higher mechanical shear forces produced at higher intensities. Thus more microorganisms are ruptured (Neis, 2000). The tests at 0.11 W/mL had almost no effects on the floc size. Only when the power level had exceeded 0.22 W/mL would the particle size apparently decrease (Chu *et al.*, 2001). The cavitation threshold for water was reported to be about 0.4 W cm⁻² by Lorimer (1990). But Neis *et al.* (2000) observed disintegration phenomena at a rather low intensity of 0.1 W cm⁻². A lower cavitation threshold for sludge seems reasonable due to the presence of a large number of small particles and gas bubbles acting as cavitation nuclei.

2.4.6 Methods to Enhance Ultrasound Efficiency

Ultrasound is a pressure wave that propagates through a medium with a vast amount of energy dissipation. Using the simultaneous ultrasonic and alkaline treatment, the pre-treatment time for municipal waste activated sludge can be greatly shortened resulting in a high amount of SCOD released (Chiu *et al.*, 1997). Since the two methods rely on the two different mechanisms to solubilize particulate organic substances, a combination of these two methods will take

advantages of two mechanisms and achieve better efficiency.

It has been found that the joint activity of polyelectrolytes and ultrasound are particularly favourable for the reduction of sludge volume. The mechanism of this method may be explained by a partial dehydration, i.e. the removal of the water dipoles from some part of the particle surfaces in the solid phase, thus giving rise to disturbances in the stability of the hydration layer, which is replaced by an orientation of polyelectrolyte macroparticles with long chains that “bridge” simultaneously several particles. This leads to the increase in the number of minute particles present in the suspension (Kowalska *et al.*, 1978).

2.5 SUMMARY

Anaerobic digestion is a rather slow process because of the rate-limiting hydrolysis and large digesters are normally designed. Arising from escalating wastewater sludge quantity and disposal cost, extensive research work has been initiated exploring ways to improve sludge digestion through pre-treatment. Comparing with other pre-treatment methods such as the thermal, ozone, and chemical treatments, ultrasound treatment exhibits a greater potential for being environmentally and economically sound. Ultrasonication could lead to sludge disintegration thereby releasing the intracellular substances, and transformation of a portion of the insoluble particulates into a soluble state. It has been presumed that both the hydro-mechanical shear forces and the sono-chemical effects contribute to sludge disintegration.

Application of sonication pre-treatment technique is yet to be accepted mainly due to limited information on several important concerns, including disintegration mechanism of sludge, bioconversion of sonicated sludge, feasibility of sonicated sludge in continuous digester operation and optimal working conditions for cost-effectiveness process. This study was carried out to explore answers for these above-mentioned questions and to derive a better position to master this advanced technique for widely application in the near future.

CHAPTER 3 METHODS AND MATERIALS

3.1 SLUDGE SAMPLES

All tests and experiments were conducted with municipal wastewater sludge obtained from the Ulu Pandan Water Reclamation Plant, Singapore. Figure 3.1 illustrates the wastewater treatment process in the plant. To keep the samples fresh, sludge samples were collected at least once a week. The primary sludge was collected directly after the primary treatment and secondary sludge was collected after the unit of thickener. All samples were stored in a refrigerator at 4°C for laboratory tests.

Three types of sludge were examined in the preliminary studies, namely primary sludge, secondary sludge and mixed primary and secondary sludge at different ratios. Based on the sludge disintegration efficiency, the sludge type with the best disintegration efficiency was selected for further investigation into the effects of ultrasound treatment for anaerobic digestion.

3.2 SONICATION PRE-TREATMENT

3.2.1 Ultrasonic Reactor

Sonication of sludge was carried out in a glass container by batch using Sonics Vibracell 750W Model. Figure 3.2 illustrates the schematic diagram of sonication treatment sludge, which was conducted with an ultrasound reactor equipped with a probe transducer (Autotune Series, Singma Chemical Co. U.S.A). The photograph of sonication treatment of sludge is also presented as Figure 3.3.

Figure 3.1 Schematic flow of wastewater treatment process

Figure 3.2 Schematic drawing of sonication treatment process

Figure 3.3 Photograph of sonics Vibracell VCX 750 ultrasonic processor

3.2.2 Sonication Treatment Procedure

The ultrasound frequency was set at 20 kHz with a maximum power output of 200 W. According to Hua and Hoffmann (1997), sonication density relates to the power supplied per sample volume. The sonication density used in this study ranged between 0 - 0.52 W/mL, which was calculated using energy consumption (read from the ultrasound controller in Figure 3.2) and sample volume. The probe was positioned in the middle of the sludge sample, at about 2 cm from the container bottom. In the process of ultrasonication as shown in Figure 3.2, 50 ml of sludge sample was placed in a beaker with the probe of 1/4 inch placed in at the middle of the batch sample, which was at about 2 cm above the beaker bottom. As larger sample volume was required during the digestion operation, sonication was carried out in a 500 ml cylindrical glass beaker (Iwaki_{TE-32}, Asahi Techno Glass, Japan) by batch using Sonics Vibracell 750W Model with a 1 inch standard probe together with a 1:2 booster horn. The probe positioned in the middle of the sludge sample about 5 cm. from the container bottom.

To establish the optimal working conditions for sludge disintegration in respect of sonication time, sonication density, solids concentration and sludge type, the work schedule was carried out as below:

1. Ultrasonication of primary and secondary sludges at different sonication time ranging from 0.5 min to 15 min while other working conditions remained unchanged.
2. Ultrasonication of primary and secondary sludge at different densities, ranging from 0.18 W/mL to 0.52 W/mL while other conditions remained unchanged.
3. Ultrasonication of primary and secondary sludge at different solids concentrations, ranging from 0.98% to 3.75% of total solids.
4. Ultrasonication of primary and secondary sludge at their different mixed ratios of 25%:75%, 50%:50% and 75%:25%.

3.3 LABORATORY-SCALE ANAEROBIC DIGESTION SYSTEM

3.3.1 Batch Digestion

Batch digestion of sludge was used in this study to observe the bioconversion process in situ and to determine the substrate conversion kinetics at individual step of hydrolysis, acidogenesis and methanogenesis. As Figure 3.4 and Figure 3.5 shown, anaerobic digestion of sludge was performed using four identical glass bottles orbitally shaken at 100 rpm (ORBITAL Shaker, DK-0S010, Daiki Sciences Co. Ltd).

Each fermenter had a total volume of 1.5 L and containing 1 L of sludge. Digester D1, serving as a control unit, was fed with untreated sludge, while the other three digesters D2, D3 and D4 were fed with sludge sonicated at 0.18 W/mL, 0.33 W/mL and 0.52 W/mL for one minute, respectively. The biogas produced was collected in calibrated glass cylinders by the water-replacement method and the biogas composition was measured twice a week. Sludge samples were collected from the sampling port at the bottom of the bottle. Samples from digesters were subject to testing of TCOD, SCOD, VFA, pH, and co-enzyme F₄₂₀. The digesters were housed at a constant mesophilic temperature of 35°C in a walk-in temperature-controlled room.

Figure 3.4 Schematic diagram for batch anaerobic digestion

Figure 3.5 Photograph of batch set-up for anaerobic digestion

3.3.2 Anaerobic Digestion in UASB Systems

3.3.2.1 Digester set-up

The geometry of the digester depends on operational factors, such as mixing. An ideal shape is the sphere, but a sphere leads to problems of the formation of encrustations at the top of the digester (Dohányos and Zábranská, 2001). Therefore, most digesters are in the shape of a combination of cylinder or sphere with a cone at the top and bottom. The sludge column in this experiment was designed using a cylindrical column with conical lower part. Anaerobic digestion experiments were performed in parallel with four UASB digesters at 35°C operating at the same hydraulic retention time (HRT). One of the experimental systems is shown in Figure 3.6 and the photograph is also illustrated in Figure 3.7.

3.3.2.2 Experimental stages and digester start-up

One digester was operated with untreated sludge (the control) and the other three digesters were fed with secondary sludge treated at 0.18W/mL, 0.33W/mL, and 0.52W/mL for 1 minute each. The digesters experiments were operated over a period of 1 to 2 months for each respective HRT. All digesters were operated for five HRTs of 20-day, 14-day, 8-day, 4-day and 2-day. All digesters in each HRT were operated until steady-state conditions reached before entering into next HRT.

The extent of floc disintegration was then determined by the increase in soluble chemical oxygen demand (SCOD). Removal efficiency of TCOD, SCOD, total solids (TS) and volatile solids (VS) were measured in regular. Daily biogas production was recorded from the gas meters and biogas composition was analyzed by gas chromatography.

Figure 3.6 Schematic diagram of UASB digester system

Figure 3.7 Anaerobic digestion sludge in four identical UASB digesters

The start-up procedure consisted of seeding the digesters with actively-digesting municipal sludge obtained from a digester in local wastewater treatment plant (Ulu Pandan Water Reclamation Plant, Toh Tuck Avenue, Singapore). The feed sludge and untreated or sonicated sludge at different sonication densities were then pumped into four identical upflow digesters. Initially, seed sludge was mixed with respective sludge (untreated or sonicated sludge at different sonication densities) at a ratio of 1:1 by volume.

All digesters first were operated in a fill and draw mode with occasional recycling of settled effluent solids at temperature 35 °C. This was to prevent washout of seed biomass as well as to facilitate microbial attachment after the inoculation. This mode of operation was continued for around 10 days, by which time some gas was produced per day. No reseedling was deemed required for all the digesters when the satisfactory gas generation was observed. All digesters then were fed with respective feed sludge with the hydraulic retention time of 20-day to 2-day.

While there is no standard definition of what constitutes a successful start-up, the process was deemed to have been completed when gas production and effluent TCOD became stable.

3.4 ANALYTICAL METHODS

3.4.1 Temperature

The temperature change of sludge after sonication could be obtained directly from the LCD screen of sonicator. Normal range of accuracy was 0.1 °C unit. Temperature is a rather important variable for anaerobic digestion where temperature control is often implemented (for mesophilic or thermophilic operation).

3.4.2 Particle Size and Distribution

The sludge particle was examined using Malvern Master Sizer Model 2600c. The Master Sizer measures particle in the size range of 0.05-550 μm based on the principle of laser diffraction. This instrument operates by passing a laser beam, which is diffracted by the particles in the suspended sample. The background reading given by the distilled water alone was measured first, then the measurement of the sample in suspension. The particles-in-liquid suspension of suitable concentration was prepared by adding small portion of the sample to distilled water achieving an obscuration of 0.1-0.2. The concentration was derived using the Beer-Lambert Law. The Malvern uses an iterative technique to generate the results from the light energy data. Since repeated measurement of the same sludge sample exhibited different results, three replicate determinations were done. Results are given as mean particle size and standard deviation.

3.4.3 pH

pH test was conducted according to procedures stated in BS EN 12176:1998 (BSI, 1998) with a pH meter (Orion PH/ISE Meter Model 710A) equipped with a glass electrode. Normal range of accuracy was 0.01 pH unit. Sample pH was measured immediately to minimize increase caused by escape of dissolved carbon dioxide.

3.4.4 Chemical Oxygen Demand (COD)

Sludge was tested for total chemical oxygen demand (TCOD) and soluble chemical oxygen demand (SCOD) according to the standard methods (APHA, 1998) Section 5220 D. TCOD measures the total quantity of oxygen required for oxidation to carbon dioxide and water and indicates the organic availability in the sludge. Previous studies had indicated the necessity of dividing total COD into “readily biodegradable” COD and “slowly biodegradable” COD due to their different biokinetics (Dold et al., 1980, 1986). The former is readily transported into microbial cells whereas the latter comprises larger and more complex molecules that require extracellular breakdown (hydrolysis) to smaller units before. The readily biodegradable COD is normally referring to soluble COD, which is undertaken on the supernatant fraction of the sludges after filtration through 0.45 µm filter paper. The slowly biodegradable COD or called complex COD (cCOD) in this study was calculated using measured TCOD and SCOD as $cCOD = TCOD - SCOD$ (Lesouef et al., 1992; Mamais et al., 1993; Torrijos et al., 1994). All samples and blanks were tested in triplicates with the average results reported. Samples that required storage were preserved with concentrated H₂SO₄ at a pH below 2 and a temperature of 2 to 3 °C.

3.4.5 Dissolved Organic Carbon (DOC)

Analyses of DOC were made using a DOC analyzer (Shimadzu TOC-5000) based on a combustion-dispersive infrared gas analysis method. The DOC concentrations were not measured directly but through the subtraction of inorganic carbon (IC) from total carbon (TC) measurements. About 5 ml of sample filtered through 0.2 µm filter paper was used for each DOC analysis.

3.4.6 Turbidity

One of the most important variables in digestion processes is the suspended solids concentration (SS). High SS concentrations are desired in the reactor for high bio-catalytic activity in the system. The turbidity of sludge samples was measured with a turbidity meter after centrifugation.

3.4.7 Oxidation and Reduction Potential (ORP)

ORP is useful in the evaluation of magnitude and characteristics of anaerobic sludge. It measures the potential for oxidation or reduction to occur. In the process of reduction and oxidation, electrons are exchanged. The ORP was determined electrometrically with instrument Horiba ORP Meter D-24. The anaerobic bacterial could function best between ORP values of + 50mV and - 400mV (Reddy *et al.*, 1995).

3.4.8 Sludge Volume Index (SVI)

The SVI test was conducted in a 100-ml measuring cylinder based on method employed by Chen (1996). The ratio between the final and initial sediment heights (l_f / l_i) was reported after 24-hour settling.

3.4.9 Total Solids (TS) and Volatile Solids (VS)

Suspended solids concentrations were determined for both total and volatile fractions in accordance to procedures described in standard methods (APHA, 1998) Section 2540 D and 2540 E, respectively.

3.4.10 Biogas Production and Gas Composition

Gas production of each digester was recorded daily from a wet gas meter (Ritter TG 05). The gas composition was analyzed by a Gas Chromatograph (Hewlett Packard HP 5890 A) for methane, carbon dioxide and nitrogen.

3.4.11 Volatile Fatty Acid (VFA)

Volatile fatty acids (VFAs) were determined using a High Performance Liquid Chromatograph System (Series 200 Diode Array Detector with series 200 pump, Auto sampler and column oven).

3.4.12 Co-enzyme F₄₂₀

Methanogens have a specific co-enzyme, F₄₂₀, a 5-deazaflavin analog that acts as

an electron carrier in metabolism. Its oxidized form absorbs light at 420 nm (Cheeseman *et al.*, 1972) and this blue-green fluorescence coenzyme has been proposed for use in quantifying methanogens in mixed cultures (van Beelen *et al.*, 1983).

Measurement of co-enzyme F_{420} was adopted the procedure described by Ivanov *et al.* (2004). The measurement of co-enzyme F_{420} was made using a Fluorescence/Luminescence Spectrometer LS-50B (Perkin-Elmer, Wellesley, MA, USA) and 3ml quartz cuvette using a synchronous scan regime. The difference between excitation and emission wavelengths was 20 nm. The excitation wavelength was changed from 360 to 480 nm and the emission wavelength was synchronously increased from 380 to 500 nm. Fluorescence at 420 nm was used as a measure of the gross methanogenic biomass. All sludge samples for enzyme assay were first reserved in phosphorous buffer saline (PBS) to maintain cell morphology. All enzymatic activity was determined in triplicate for each sample tested.

CHAPTER 4 EFFECTS OF ULTRASOUND ON SLUDGE

4.1 INTRODUCTION

An understanding of the nature of sludge as well as the effects of ultrasound on sludge is essential in the design and operation of ultrasound pre-treatment. In the preliminary studies, the effects of sonication treatment on sludge characteristics were investigated in terms of microscopic investigation, particle size, temperature, soluble chemical oxygen demand (COD), dissolved organic carbon (DOC), volatile fatty acids (VFA), pH, alkalinity, ammonia, oxidation-reduction potential (ORP), sludge volume index (SVI) and turbidity. Possible reasons for the changes of characteristics by sonication are offered. The potential influences of these modified characteristics on the subsequent anaerobic digestion are also discussed where applicable.

Due to the fact that ultrasonication is an energy-consuming process, the cost-effectiveness of this technique might be of a concern to the wastewater treatment industry. However, considerations on process optimization are barely found in the existing literatures perhaps due to a lack of overall investigation of the operating conditions. Hence, in an attempt to establish cost-effective sonication conditions, this chapter also examines the influences of sonication operating conditions in terms of sonication time, sonication density, sludge types and solids concentrations based on the specific energy (kWh/kg DS) evaluation.

Moreover, the interdisciplinary nature of this technique implied that the mechanism of sludge sonication must be derived from a good understanding of the behaviour of ultrasound waves in sludge. Although it is believed that ultrasonic sludge disintegration is mainly attributed to the phenomena of cavitation bubbles

during sonication (Harrison, 1991; Tiehm *et al.*, 1997), studies on correlations among cavitation bubbles, sonication parameters and sludge disintegration are yet to be established. Hence, this chapter dedicates to incorporate cavitation kinetics into the results of sludge modification. The role and significance of the formation, collapse and behaviour of cavitation bubbles in sludge sonication were also discussed.

4.2 CHARACTERISTICS OF ORIGINAL SLUDGE

The original properties of primary and secondary sludge were examined within two hours after collection from wastewater plant in order to prevent subsequent changes. Inherently sludge samples obtained from the wastewater plant exhibited certain fluctuations. The overall properties of the primary sludge and secondary sludge tested are listed in Table 4.1.

The results showed that all original sludge samples were of low SCOD/TCOD, indicating large proportion of TCOD originated from solids phase. Higher VS/TS range of 77%-83% showed a high amount of organic matter present in the secondary sludge. All sludge samples were found to have a low average oxidation-reduction potential of less than -206 mV, which indicates a low ability to sanitize. The sludge had an average pH ranging from 6.1 to 6.6. It should be noted that secondary sludge had a lower soluble COD concentration and a higher VS/TS than the primary sludge. The mean particle size of the primary sludge was slightly larger than the secondary sludge.

Table 4.1 Properties of untreated sludge

Properties	Primary sludge	Secondary sludge
SCOD (mg/L)	1000-1500	500-700
TCOD (mg/L)	14000-17500	12500-18000
SCOD/TCOD	0.05-0.09	0.03-0.06
DOC (mg/L)	90-260	75-220
VFA	150-570	120-490
ORP (mV)	(-264)-(-348)	(-274)-(-297)
pH	6.1-6.5	6.2-6.6
Turbidity (NTU)	22-38	35-45
TS (%)	0.9-3.9	0.8-3.9
VS/TS (%)	76.4-78.6	77.3-82.6
Mean particle size(μm)	47.2-53.4	45.6-50.4

4.3 EFFECTS OF ULTRASOUND ON SLUDGE CHARACTERISTICS

4.3.1 Microscopic Investigation

The most intuitionistic evaluation of the disintegration effects of ultrasound can be obtained by microscopic analysis, which provided a visual appraisal of the pre-treatment. Figure 4.1 and Figure 4.2 depict the morphology of primary and secondary sludge, respectively, before and after ultrasound treatment at various sonication times at a magnification of 1000 times.

As shown in Figure 4.1 (a) and Figure 4.2 (a), the original sludge floc exhibited clear solid-liquid boundaries and large flocs complex. After sonication treatment, significant sludge disintegration was observed based on flocs breakage, boundary disappearance for solid-liquid phase and intracellular materials release to liquid.

Figure 4.1 Microscopic photograph of the primary sludge at different ultrasound duration (a) Untreated; (b) 1min; (c) 5 min; (d) 10 min

Figure 4.2 Microscopic photograph of secondary sludge at different ultrasound duration (a) Untreated; (b) 1min; (c) 5 min; (d) 10 min

These images reveal that the degree of sludge flocs disintegration was a function of the sonication time. With the increase in sonication time, the floc breakage for sonicated sludge became more and more apparent, indicating that longer sonication time could derive greater sludge disruption. After 1 minute, for example, although the floc structure became somewhat looser and floc size became smaller, the architecture of floc was basically the same as the original sludge. The effects were more obvious after 10 minutes of sonication, with floc breakage became more apparent.

The solids or particles in the untreated primary sludge appeared darker in colour and massive. In contrast, the solids or particles observed in untreated secondary sludge looked somewhat transparent and watery. After 10-min of sonication, although the large particle matrix disappeared, many small particles remained intact in the primary sludge. For the secondary sludge, however, distinct particles were barely observed after 10-min of sonication, indicating a more complete disintegration. The comparison of sonication effects between primary sludge and secondary sludge will be discussed in more detail in the following.

4.3.2 Particle Size

4.3.2.1 Particle size distribution

Besides visible observation from the microscopic images, the extent to which the flocs were disintegrated could be quantitatively established by particle size distribution. Figure 4.3 illustrates particle size distribution of untreated and sludge sonicated at different sonication times as well as various sonication densities for both primary and secondary sludges. The results indicated that particle size distribution of primary or secondary sludge was significantly altered after sonication treatment. As shown in Figure 4.3, comparing to the untreated sludge, the peaks of curves representing sonicated sludge shifted toward left, indicating a decrease in the quantity of larger particles and an increase in smaller particles. This corresponded with the microscopic observation discussed earlier which clearly showed the breakage of large particles and flocs after sonication.

Figure 1.3 Effects of sonication treatment on particle distribution at various sonication levels

The sludge particles of untreated sludge were mainly distributed in the range of 10 - 400 μm , while the particle distribution of the sonicated sludge was observed in the range of 0.1 - 400 μm . The results indicated that the amount of particles smaller than 10 μm increased remarkably as sonication levels increased. Moreover, sonicated samples exhibited a second peak at volume occupied by particles of 0.1-5 μm , which range was not observed for untreated sample. As soluble, colloidal and suspended solids are categorized with diameters of $d < 0.45 \mu\text{m}$, $0.45 < d < 4.4 \mu\text{m}$ and $d > 4.4 \mu\text{m}$, respectively (Wang, 1994; Tawfik *et al.*, 2002), the particle size distribution of sonicated sludge implied a substantial release of soluble and colloidal material from the sludge particles as a result of sludge disintegration.

The structure of wastewater sludge is very heterogeneous, comprising a large number of different compounds (Jorand *et al.*, 1995). In order to make a clearer picture for the effects of sonication on sludge particle size distribution, this study suggested five broad distributions of sludge particles in respect of diameter: $d \leq 0.45 \mu\text{m}$ (soluble compounds), $0.45 < d \leq 4.4 \mu\text{m}$ (colloidal, polymers), $4.4 < d \leq 50 \mu\text{m}$ (median-flocs); $50 < d \leq 125 \mu\text{m}$ (flocs); $d \geq 125 \mu\text{m}$ (macro-flocs, large protozoans), which was based on the previous studies on sludge particle classification (Wang, 1994; Tawfik *et al.*, 2002; Jorand *et al.*, 1995). Figure 4.4 shows the effects of sonication treatment on volume contribution from each group of particles. For both primary and secondary sludge after 15 min of sonication treatment, the volume percentage increased for distributions with $d \leq 0.45 \mu\text{m}$ and $0.45 < d \leq 4.4 \mu\text{m}$, while decreased for distributions of $4.4 < d \leq 50 \mu\text{m}$, $50 < d \leq 125 \mu\text{m}$ and $d \geq 125 \mu\text{m}$. Solids with size inferior to 0.45 μm are considered as soluble solid, and are thus often more available for microbial uptake and biodegradation. Hence, the increase in the volume percentage this fraction observed after sonication suggested that sonicated sludge was able to provide more immediate biodegradable organics for subsequent anaerobic digestion.

Figure 4.4 Effects of sonication time on particle size populations

As discussed previously in the Literature Review, the phenomenon of cavitation bubbles is believed to be responsible for the destruction of sludge particles. During the sonication treatment, it could be observed that a large number of bubbles were continuously generated beneath the bottom surface of the probe. These bubbles tended to locomote violently and agitate irregularly, which could bring out powerful hydromechanical shear forces to compounds surrounding the bubbles. As a result, particles or flocs in sludge samples were disrupted after sonication. Besides the compounds surrounding the bubbles, the compounds inside the bubbles could also

be degraded by cavitation bubbles. It was reported that the temperature and pressure inside the collapsing cavitation bubbles could rise up to about 5000 K and several hundred atmospheres (Mason, 1991; Young, 1989). These extreme conditions would therefore lead to the destruction of compounds present within the vicinity of the cavitation bubbles.

4.3.2.2 Mean particle size

Although particle size distribution could present detailed information, it is more convenient and straightforward to use mean particle size to describe sludge properties in practice. In the following discussion, the mean particle size d_{50} represents the particle size at 50% cumulative frequency. As shown in Figure 4.5, sonication treatment was found to effectively reduce the particle size of d_{50} values. The mean particle size of both primary and secondary sludges decreased sharply as soon as the sonication was employed.

Based on the results, mean particle sizes of the sludges were reduced more significantly with longer treatment duration as well as higher sonication power. For example, at a sonication density of 0.18 W/mL, the mean particle size of primary sludge decreased from 51 μm to 36 μm , 28 μm , 21 μm , 18 μm , 17 μm and 15 μm after sonication time of 0.5 min, 1 min, 5 min, 10 min, 15 min and 20 min, respectively. On the other hand, if sonication time was fixed at 1 min, the mean particle size of primary sludge was decreased from 51 μm to 28 μm , 22 μm and 15 μm at sonication densities of 0.18W/mL, 0.33W/mL and 0.52W/mL, respectively as shown in Figure 4.5.

The size of disrupted flocs was much smaller than those normally expected for an activated sludge plant, which can usually be expected to have floc size of between 200 μm and 50 μm . The reduction of particle size reflected that flocs agglomerations were disintegrated and large particle structures were destroyed in

sonicated sludge, which would provide a better mass transfer conditions beneficial for the subsequent anaerobic digestion.

Figure 4.5 Effects of sonication treatment on mean particle size

4.3.3 Temperature

The original temperature of primary or secondary sludge was around 17-20 °C and the experiment was conducted under consistent room temperature of 25 °C. Figure 4.6 shows that the temperature steadily increased with the sonication time and sonication densities. For a given ultrasound density, both primary and secondary sludge exhibited similar rate of temperature increase. Higher temperature was

associated with higher sonication density after the same treatment time. For example, in the case of secondary sludge treatment at 0.18W/mL, the change in temperature after 10 min of treatment was 16 °C, while greater increase in temperature were derived as 33 °C at 0.33W/mL and 43 °C at 0.52W/mL. After 15 min of sonication at 0.52W/mL, the temperature of both primary sludge and secondary sludge increased markedly to around 70 °C.

Figure 4.6 Effects of sonication treatment on sludge temperature

The temperature increase might be attributed to three effects caused by ultrasonication: the loss of ultrasound energy into the sludge by attenuation and adsorption, the wild thermo-locomotion of bubbles agitation, and the thermal implosions of cavitation bubbles. Since more energy was dissipated in the sludge sample as sonication applied, the rising curve was nearly proportional to the sonication time.

Temperature plays a significant role in the bioconversion of anaerobic digestion process. Generally, 35-40 °C is the most common temperature range for anaerobic digestion. Elevated temperature has a significant contribution both on improving the sludge qualities and offering reliable environment for the thermophilic or mesophilic conditions to start-up. Due to the relatively low initial temperature of the untreated sludge (17 - 20 °C), sludge heating is required to meet mesophilic conditions. To heat up the sludge to the optimal temperature range of 35 – 40 °C for anaerobic digestion, 3 - 5 min sonication are necessary at sonication density of 0.33W/mL and 0.52W/mL, respectively.

The sludge temperature can influence bacterial activity during anaerobic digestion and determines the energy required for heating to maintain the digester under mesophilic or thermophilic conditions. Hence, ultrasonication could benefit anaerobic digestion in terms of energy saving in maintaining digester temperature where pre-treatment is conducted on site.

4.3.4 Soluble Chemical Oxygen Demand (SCOD)

Soluble organics measured as SCOD have been used by many researchers as an indication of the organics availability in sludge. Therefore, SCOD as well as SCOD/TCOD ratio was also selected as the marker analysis in this study to evaluate sludge disintegration efficiency.

The results of SCOD shown in Figure 4.7 indicate that sonication treatment managed to convert a portion of complex TCOD into a soluble form (SCOD). Clearly, for both primary and secondary sludge, soluble COD increased with sonication time. As presented in Figure 4.7, the SCOD increased by nearly three times after sonication for 15 min at 0.52W/mL compared with 990 mg/L for original primary sludge. In the case of secondary sludge, SCOD increased from 522 mg/L to 3210 mg/L by 6 times after 15 min of sonication at 0.52 W/mL. The tendency was consistent with the result of particle size reduction, indicating increase in disintegration efficiency with sonication time and sonication density.

As illustrated in Figure 4.8, the ratio of SCOD/TCOD also increased with sonication time or sonication density for both primary and secondary sludge. Compared with initial ratios of 5% to 9% and 3% to 4% respectively, the SCOD/TCOD for primary and secondary sludge increased up to 17% and 25%, respectively. The results showed that a larger increase in soluble organics concentration was obtained from the secondary sludge than from the primary sludge after pre-treatment, indicating sonication was more effective on secondary sludge. This was consistent with the results of particle size discussed in the last section, where secondary sludge was found to be readily disintegrated into smaller particles after sonication compared with primary sludge.

Figure 4.7 Effects of sonication treatment on SCOD

Figure 4.8 Effects of sonication treatment on SCOD/TCOD ratio

Three possible hypotheses can be put forward to explain the significant increase of the soluble COD derived from sonication treatment. The first reason was the breakage of sludge structures releasing the intracellular materials by destroying flocs and particles. This hypothesis had been proved by microscopic appraisal and particle size analysis. Another reason was related to the temperature increase after sonication as discussed previously. The high temperature could induce the transformation of solid organics into the liquid form, which improved the solubility of organics. The third reason could be owing to the sonochemical reactions which will be discussed in the effects of pH (Section 4.3.6).

It had been reported that the rate-limiting step of anaerobic sludge digestion appeared to be the hydrolysis of particulate organic matter to soluble substances. Increasing the solubilization of the complex organics means more volatile solids become readily amendable to further decomposition (Chiu *et al.*, 1997; Lin *et al.*, 1997). Therefore, SCOD results suggested that the ultrasonication could transform the TCOD in the sludge into the soluble form, which could be beneficial to the anaerobic digestion. Anaerobic bacteria in sonicated sludge could be provided with more nutrients, substrate and available reaction sites in the digestion process. Therefore, a better degradability of sonicated sludge might be expected in view of soluble organics availability.

4.3.5 Dissolved Organic Carbon (DOC)

Another evidence for soluble organics enhancement by sonication treatment was the increase in dissolved organic carbon (DOC). As shown in Figure 4.9, DOC in the primary sludge increased from the original 240 mg/L to 317 mg/L, 417 mg/L, 541 mg/L and 602 mg/L after sonication at 0.52 W/mL of 1 min, 5 min, 10 min and 15 min, respectively. In this study, DOC was measured after sample filtration. Hence, the reasons why DOC increased during ultrasonication are the same as for the SCOD (destruction of flocks and released of soluble organics).

Compared with the primary sludge, the secondary sludge was associated with lower original DOC in the untreated samples but indicated greater increase extent in the treated samples after sonication treatment. The DOC of the

secondary sludge increased from 130 mg/L to 420 mg/L, 583 mg/L, 798 mg/L and 915 mg/L at respective sonication times. It is worth noting that sonication had little effect on the inorganic carbon (IC), as the disruption was thought to be effective on organic cellular substances.

The soluble organic carbon resulting from hydrolysis is generally used as energy sources by acid formers which carry out hydrolysis and acidogenesis (Gaudy and Gaudy, 1980). Therefore, it is reasonable to foresee that digesters fed with sonicated sludge could enhance carbon utilization and facilitate an efficient hydrolysis-acidogenesis process by its increased soluble organic carbon.

Figure 4.9 Effects of sonication treatment on DOC

4.3.6 pH

In this study, a notably decrease in the pH of the sonicated sludge was recorded consistently. The effects of sonication treatment on pH value of primary and secondary sludge are shown in Figure 4.10. pH for secondary sludge exhibited more decrease than primary sludge after sonication. The original pH of 6.9 decreased to 6.2 after 15 min of sonication at 0.52W/mL, while the pH of the primary sludge decreased from 6.4 to 6.1.

Erratic peaks in the first few minutes of sonication indicated that complex physical or/and chemical reactions occurred during the exposure of sludge in ultrasound waves. Mechanisms involved in sonochemical transformations are still unidentified. However, acoustic cavitation was believed to be the main phenomenon responsible for chemical transformations. It was reported that energy concentrated in the bubbles is sufficient to break strong chemical bonds and the main pyrolytic reaction is the dissociation of water (Gonze *et al.*, 1999). Therefore such thermal dissociation could lead to the production of reactive radicals ($H\cdot$, $OH\cdot$) inside the bubbles. As a result, various chemical reactions may bring about after the migration of these highly reactive radicals to the bulk solution and contact with dissolved molecules. Besides the sonochemical reactions, the release of intracellular material might also contribute to the change of pH.

This study was probably the first one to point out the pH change after sonication treatment sludge (Mao *et al.*, 2005; Show *et al.*, 2005). This finding is worth noting since pH is such an important parameter, that any ounce of drop in pH could possibly influence the following digestion rate. Normally, anaerobic digestion proceeds well at a system pH varying from 6.6 to 7.6. The efficiency will drop off rapidly when pH is below 6.2. Therefore, the results suggested that there was a need for pH balancing in the subsequent digestion due to the decline of pH after sonication.

Figure 4.10 Effects of sonication treatment on pH

4.3.7 Volatile Fatty Acids (VFA)

Although some studies had pointed out that sonication treatment could release soluble COD, no effects on VFA have been reported. VFAs are important intermediary compounds in the metabolic pathway of methane fermentation. Most researchers limit the attention to C_1 - C_6 VFAs because these short chain fatty acids are considered as readily biodegradable COD and subject to rapid microbial decomposition. (Gerber *et al.*, 1986; Wang *et al.*, 1999; Chen *et al.*, 2004; Yuan *et al.*, 2006). Figure 4.11 presents the categories and concentrations of VFA (C_1 - C_6) in untreated and sonicated samples for both primary and secondary sludge.

Figure 4.11 Effects of sonication treatment on VFA

The total VFAs for primary sludge increased from an original concentration of 298 mg/L to 444 mg/L, 583 mg/L and 749 mg/L after sonication with 0.18 W/mL, 0.33 W/mL and 0.52W/mL, respectively. Greater improvement was observed on the secondary sludge. The VFA increased from an original concentration of 450

mg/L in the untreated sludge to 780 mg/L, 960 mg/L and 1410 mg/L after sonication at the respective sonication densities.

The total VFA concentration increased markedly after sonication, which might explain for pH decline as well as SCOD increase. Considering the VFA distribution, significant increase of individual category acid was associated with formic acid, acetic acid, propionic acid and heptanoic acid.

From the increase extent and category distribution after sonication treatment, one possible reason might be the conversion from higher level organics into organic acids, as evidenced by the significant increase in total VFA amount after sonication. Such conversion might occur in two situations: VFAs released from microorganism cells and VFAs degraded from higher compounds. This could be reinforced by the increase of DOC in filtrate of sludge by sonication, since VFAs are forms of organic carbon.

It is known that VFAs are main products after stages of hydrolysis and acidogenesis in anaerobic digestion. VFA are regarded as important intermediate compounds for methane generation (Hill *et al.*, 1987). Therefore, the significant increase of VFAs after sonication might give a new perspective to understand the effects of sonication treatment for subsequent anaerobic digestion. On one hand, although no waste stabilization was brought about in the conversion process from complex organics into VFA, it is a step normally considered to prepare the readily substrate in a form amendable for the methanogenesis. On the other hand, VFAs may also cause microbial stress if present in excessive concentrations (Hill *et al.*, 1987). Due to the dual-effects of VFAs on anaerobic digestion, a close monitor for VFA evolution should be conducted to assess whether the increased VFA plays positive or negative roles for sludge digestion. Then, the correlation between VFA increase and digester performance might be a factor in the selection of sonication levels as well as digester operating conditions.

4.3.8 Sludge Volume Index (SVI)

Sludge volume index (SVI), which is directly related to settleability, is typically used to monitor settling characteristics of wastewater sludge and other biological suspensions. As Figure 4.12 shown, SVI values of primary sludge expressed by the ratio between final and initial sediment heights decreased sharply from 0.82 to 0.60 - 0.65 after one minute of sonication and then stabilized. In the case of secondary sludge, the SVI values decreased from 0.88 to 0.68-0.76 at the initial one minute and then re-increased to 0.80 – 0.86. The results indicated that the settling properties of wastewater sludge can be enhanced by sonication only within a certain degree of treatment. The improvement was most significant in the initial treatment of one minute.

The phenomenon of SVI influenced by sonication extent was likely correlated to the nature of sludge water as well as the multi-stage process of ultrasonication. The sludge contains a large quantity of water bound to the solids to a greater or lesser extent. It is usually to distinguish (1) free water, 2) interstitial water contained in the interstices and/or inside the flocs and microorganisms, and 3) the water chemically bound to the particles (Metcalf & Eddy, 1991). It was reported that conventional dewatering processes only remove the free water, while the water chemically bound to the particles can only be released through thermal treatment. These treatments lead to a reduction of the volumetric fraction of particles in the suspension.

Ultrasound treatment in this respect seems to lie between the two processes. At short ultrasound application times, the large flocs agglomerates or perhaps the cells were burst down, which enables the free water and some of the interstitial water to be released, resulting in a more compact settled sludge. At longer sonication time, a large amount of generated micro-particles creating more new particle surfaces, which again attracting some water being attached onto these surfaces (Chu *et al.*, 2001). The settlement would reach the equilibrium when the system particles remain consistent.

Figure 4.12 Effects of sonication treatment on SVI

It was noted that the settleability of secondary sludge tended to be deteriorated in further sonication; whereas the SVI of primary sludge remained almost constant after one minute. This might be owing to different compositions of primary and secondary sludge. Considering the sludge generation source, primary sludge consists of more matters that are ready to be precipitated such as plastics, textile and inorganic matters like sand or earth. But secondary sludge contained a large number of biomass. The breakage of microorganism cells would result in more colloidal material and disrupted cells. Compared with the readily precipitated compounds in primary sludge, the fragments of cells were more difficult to be settled down; and more tended to bound water.

4.3.9 Turbidity

The SVI improvement was achieved at the expense of supernatant clarity. This can be indicated by the colour change of the sludge supernatant after centrifugation as shown in Figure 4.13 (using digital camera Keyence VH-8000 Series with VH-Z450). A light colour of residues reflected that the supernatant of untreated sludge was with good visibility and clarity. The supernatant of sonicated sludge turned to be opaque, turbid and brown in colour. After sonication treatment, the residues on the filter media of supernatant increased and the colour of residues became dark-brown.

Figure 4.13 Samples of sludge residues on filter media

(Left to right: untreated, sonicated sludge at 0.5 min, 1 min, 5 min and 10 min)

Turbidity is one of the approaches to monitor the suspended solid concentration (SS). Figure 4.14 shows that the initial turbidity of primary sludge increased from 32 to 78 after 15 min sonication at 0.52W/mL density, and the initial turbidity of secondary sludge which increased from 40 to 115 after 15 min sonication at 0.52W/mL. The results indicated that ultrasound treatment could result in colloidal suspension which is desired for bacteria reactions in the subsequent digestion process. The supernatant after sonication was more concentrated than sludge before pre-treatment; this indicated that the colloids and dissolved solids in raw sludge increased after ultrasonication and they remained in supernatant. High SS concentration is also desired in the reactor for high bio-catalytic activity in the system.

Figure 4.14 Effects of sonication treatment on turbidity

4.3.10 Oxidation-Reduction Potential (ORP)

The original primary and secondary sludge had a low average oxidation-reduction potential (ORP) of nearly -300 mV, which indicated a low ability to be sanitized. ORP of the sludges increased with increasing sonication power and time. Figure 4.15 presents the ORP effects of the primary sludge after sonication treatment. After 15 min of ultrasound treatment at 0.52W/mL, the ORP value was found to increase to -130 mV. It should be noted that the secondary sludge had a greater ORP improvement than the primary sludge (-180 mV) after sonication under the same test conditions.

Figure 4.15 Effects of sonication treatment on ORP

Higgins and Novak (1997) reported that calcium and magnesium cations are incorporated into the biopolymer matrix of the flocs. In this study, sonication treatment could significantly disintegrate sludge flocs/matrix, which would likely cause the release of calcium and magnesium. This might then explain the increased ORP value. Another possible reason might be attributed to the phenomena of sonochemical reactions during sonication, which resulting in generation of reactive radicals with positive charges, such as hydrogen atoms. The formation of H_2O_2 in the aqueous phase during sonication also likely contributed to enhancing the oxidizing conditions. On the viewpoint of oxidation ability, the results indicated that sonication treatment might promote the sludge stabilization in the subsequent anaerobic digestion.

4.4 EVALUATIONS OF SONICATION EFFICIENCIES

Ultrasonication is a high energy consumption process. Hence, cost-effective operation is an important concern for the plant. But the information on the relationship of energy input and pre-treatment efficiency at different working conditions has been barely reported, as a result, the optimal extent of ultrasonic pre-treatment is still not clear. Therefore, there is a need to investigate the optimal working parameters for cost-effective operation and to establish economic justification of benefits arising from ultrasonic pre-treatment.

The diverse sludge characteristics or concentration, the sonication density and duration make this technique a complex compromise to balance the energy cost and effective pre-treatment. Among testing parameters, sludge particle size and soluble COD are regarded as two main indicators to evaluate the efficiency of sludge disintegration. Other parameters were also discussed as appropriate.

4.4.1 Sonication Time

As discussed in sections of 4.3.1 to 4.3.10, sludge modification was investigated in terms of various parameters. The results indicated that sonication time was a critical factor in sonication pre-treatment, and the extent of sludge disintegration increased with the sonication time. Considering the process of sonication of sludge, tremendous cavitation bubbles are continuously being generated from the probe once the power is on. But as soon as the power is switched off, the bubbles generation ceased and the liquid agitation stopped immediately. Therefore, sonication of sludge is apparently related to the exposure time in sonication field. But to what extent sonication time is considered as both effective and efficient requires further consideration.

4.4.1.1 *Optimal sonication time for sludge disintegration*

In the section of particle size distribution, it was worth noting that populations of particle size larger than $4.4\ \mu\text{m}$ (including $4.4 < d \leq 50\ \mu\text{m}$, $50 < d \leq 25\ \mu\text{m}$ and $d \geq 25\ \mu\text{m}$) exhibited the most significant impacts in the initial one minute, after which the change was insignificant by further sonication (Figure 4.4). This

suggested that macro-flocs were less resistant to ultrasound than the micro-flocs made up of strongly bound bacteria. The results of mean particle size shown in Figure 4.5 also confirmed that the most significant effects lied in the initial period. After these initial sonication periods, later sonication had little contribution in destroying the diminished particles further. The sharpest decrease was observed in the initial one minute and the final product of 15 minutes remained almost the same to that of one minute. This also provided the explanation for the significant SVI improvement after the first minute (Figure 4.12), indicating a substantial portion of released water took place in the initial period. On this basis, this study deduced that the optimal sonication time was one minute in terms of particles disruption.

Unlike the pattern of particle size change, SCOD increased with sonication time. Other parameters indicating soluble organics, such as DOC and VFA also climbed generally with sonication time. This suggested that soluble organics increase was not only arising from physical disintegration sludge, but also attributed to the other cavitation-related phenomena, such as thermal reaction, sono-chemistry and etc.

4.4.1.2 Discussion on sonication time

As discussed in Literature Review and previous sections, cavitation-related effects caused by sonication waves are responsible for the sludge disintegration. Cavitation lies in the formation of tiny discontinuities or cavities in liquids followed by their growth, pulsation, and collapse.

If the bubble formation requirements are satisfied, which will be discussed in much detail in later section, the initial cavity/nuclei will grow in size. The time of its growth is represented by Equation 4.1:

$$\tau_g = 0.75T + (i - 1)T \text{ ----- Equation 4.1 (Abramov, 1998)}$$

$$T = \frac{1}{f} \text{ ----- Equation 4.2}$$

where τ_g is the time for bubble growth (s), f is sound frequency (Haze), T is the

period of ultrasound wave (s) and i is the number of acoustic cycles the bubble experienced.

Once the bubble begins to grow, further behaviour of the bubble is diverse: it can pulsate around its equilibrium radius either linearly or nonlinearly. Generally, two distinct types of bubble behaviour are identified: the stable bubbles and transient bubbles. If the peak sound pressure in rarefaction cycle is not enough to force bubble to expand its collapse radius, the bubble remains stable and oscillates for a time scale of thousands of acoustic cycles as indicated in Equation 4.1 (Laborde *et al.*, 1998).

Considerin a range of 1-10000 acoustic cycles and a sound frequency of 20 kHz, the time for one stable bubble existence is around 0.05 - 0.5 second as calculated in the following:

$$\tau_g = 0.75T + (i - 1)T = 0.75T + 999T = 0.0000375 + 0.05 \approx 0.05 \text{ second}$$

$$\tau_g = 0.75T + (i - 1)T = 0.75T + 9999T = 0.0000375 + 0.5 \approx 0.5 \text{ second}$$

On the other hand, the transient cavitation refers to the acoustic pressure required to expand the cavities to its resonant radius in half or several acoustic cycles and then rapidly collapse. Taking the case of 10 acoustic cycles, the time for transient bubble to grow was about 0.0005 seconds.

The formula for the duration of collapse is expressed in Equation 4.3.

$$\tau_c = 0.915 R_{\max} \sqrt{\frac{\rho_L}{P_0}} \text{ ----- Equation 4.3 (Abramov, 1998)}$$

where τ_c is the collapse time (s); $R_{\max}$ is the resonant or maximum radius (cm); ρ_L is the density of liquid (kg/m³); P_0 is the pressure of system (Pa).

The resonant radius $R_{\max}$ is inversely proportional to the ultrasound frequency and can be approximated by Equation 4.4 (the unit of $R_{\max}$ here is mm):

$$R_{\max} \approx 3.28 \frac{1}{f} \text{ ----- Equation 4.4 (Young, 1989)}$$

Hence, the time for transient bubble collapse in this study can be calculated as (take ρ_L as 1000 kg/m³ and P_0 as atmosphere pressure 10⁵ Pa):

$$\tau_c = 0.915 R_{\max} \sqrt{\frac{\rho_L}{P_0}} = 0.915 * 0.0164 * 0.1 \approx 0.0015 \text{ second}$$

Hence, the total period for transient bubble existence is the sum of its growing time and collapse time, which is about 0.002 second. The results indicated that the behaviour of transient bubbles is much faster than that of stable bubbles.

More violent than stable bubbles, transient bubbles are able to bring about non-linear phenomena in liquid. Studies had proved that it is at the moment of bubble implosion, non-linear energy transformation occurs into very small volume triggering localized high temperatures (5000 K). Moreover, the rate of cavity collapse can be so high that it produces a hydraulic shock wave with pressures reaching tens of thousands of MPa (Laborde *et al.*, 1998; Neis *et al.*, 2000). Hence, transient bubbles should be regarded as the major contributor for sludge disintegration. Although stable bubbles could pulsate and locomote around the bulk liquid, which may also contribute to flocs dispersion, the disintegration power is not comparable to transient bubbles.

The theoretical approach gives evidence that sludge particle disruption was most effective in the initial period. Since the powerful transient bubbles were extremely fast, any breakable particles could be disintegrated immediately. The most significant disintegration was derived at the first minute, which was chosen as the cost-effective sonication time in further digestion experiments.

These physical mechanisms relating cavitation bubbles also provided a justification the efficiency of ultrasound pre-treatment compared with other methods. It was noticed that some pre-treatment methods, such as alkali or ozone treatment, the required treatment time was normally several hours, in some cases even more than 24 hours before the effect can be seen (Weemaes *et al.*, 2000).

But for sonication treatment in this study, 30 seconds could make a difference. This might be mainly due to its non-linear effects caused by transient bubbles occurring in microseconds.

4.4.2 Sonication Density

Ultrasound can be applied in a range of densities. Hence, it is easy to expect that the higher the density, the more complete degradation would be. But at the same time, applying high ultrasound level is at a cost of greater energy supply. The most beneficial parameters of sludge sonication were determined by observations of reduction in particle size and soluble COD.

4.4.2.1 Specific energy

When dealing with the ultrasonication efficiency, the employment of net energy expenditure relating to the degradation was found to be useful for evaluation of energy consumption. In order to express the relationship of disintegration degree and the net energy cost, specific energy (kWh/kg DS) as expressed in Equation 4.5 was employed to compare the efficiency at different sonication densities.

$$E = P \cdot t / DS \cdot V_s \text{ ----- Equation 4.5}$$

Where E is the specific energy (kWh/kg DS); P is the applied sonication power (kW); t is the sonication time (s), DS is the solids concentration of sludge (g/mL); Vs is the sludge volume for sonication (mL).

Specific energy was therefore considered as the energy input considering the sonication time, density and dry solids content of sludge. It would be fairer and more reasonable to compare the pre-treatment efficiency with this definition and give a better picture on the relationship between energy consumed and benefits obtained.

4.4.2.2 Optimal sonication density for sludge disintegration

The effects of specific energy on particle size at different ultrasound density are shown in Figure 4.16.

Figure 4.16 Effects of specific energy on mean particle size

Interestingly, energy input at higher density was found more effective on sludge disintegration. For example, when specific energy of 20 kWh/kg was applied, the treatment can reduce the particle size of the primary sludge from 49 μm to 13μm at 0.52W/mL, but reduced to a larger particle size of 19 μm at 0.18 W/mL. This indicated that higher sonication density could exert more powerful cavitation-related effects to disintegrate sludge particles at a cost of the same amount of energy.

In Figure 4.17, the result of the SCOD followed the same pattern of the result of particle size reduction which reveals that higher sonication density was associated with soluble COD increase upon the equal amount of specific energy.

Figure 4.17 Effects of specific energy on SCOD increase

Take secondary sludge as an example, an expenditure of specific energy of 40 kWh/kg DS could increase the SCOD in sludge by 1.2 times at sonication density of 0.18W/mL; but a higher improvement of 1.4 times and 1.9 times at 0.33W/mL and 0.52W/mL, respectively can be achieved. Therefore, higher sonication density required less energy to disintegrate sludge in terms of SCOD release.

From the results presented, it appears that ultrasound pre-treatment was more effective, economical and complete at higher sonication densities. This suggested

that sonication density is a vital parameter to be evaluated in the course of design and selection in order to achieve cost-effectiveness sonication treatment. This is an essential consideration for plant to compromise energy cost and treatment efficiency.

4.4.2.3 Discussion on sonication density

It is believed that ultrasonic sludge disintegration is mainly attributed to the occurrence of cavitation bubbles. Hence, basic theoretical considerations on the formation and behaviour of cavitation bubbles would underline the mechanism of sludge disintegration. Sonication density plays a critical role in both areas of bubble formation and bubble behaviour.

The discussion should be started from the formation conditions of cavitation bubble. Ultrasound is composed from longitudinal waves comprising rarefactions (negative pressures) and compressions (positive pressures). When the acoustic pressure at rarefaction cycle is greater than the local cavitation threshold pressure, any minute cavity available will grow in size and becoming stable or transient bubbles (Laborde *et al.*, 1998). As mentioned in Literature Review, the process of bubble formation could be regarded as a competition between the liquid strength P_c^v (Equation 2.11) and acoustic pressure P_A (Equation 2.12).

$$P_c^v = P_0 - P_v + \frac{2}{3\sqrt{3}} \sqrt{\frac{(2\sigma_L/R_0)^3}{P_0 - P_v + 2\sigma_L/R_0}} \quad \text{-----Equation 2.11}$$

$$P_A = \sqrt{2I \cdot \rho \cdot C} \quad \text{-----Equation 2.12}$$

Where P_c^v is cavitation threshold pressure (MPa); P_v is the saturation vapour pressure (MPa); R_0 is the initial bubble/cavity radius (cm), σ_L is the surface tension (N/m); P_A is the acoustic pressure (Pa); I is the ultrasound intensity (W/m^2), ρ is the density of the medium (kg/m^3), C is the velocity of sound in that medium (m/s).

From Equations 2.11 and 2.12, P_c^v is dependent on the nature of the medium, and P_A depends on both properties of medium and ultrasound. Hence, given the same sample, where P_c^v , ρ and C are constant, the occurrence of bubble formation will be solely determined by sonication intensity.

It should be noted that the parameter of sonication intensity can be used in lieu of sonication density in this study. Table 4.2 demonstrates the working conditions in terms of applied electrical power, sonication intensity and sonication density.

Table 4.2 Sonication treatment conditions

Sample	Sonication intensity (W/cm ²)	Sonication density (W/mL)	Energy input (W)
1	0	0	0
2	32	0.18	90
3	56	0.33	166
4	92	0.52	260

When applying this principle to sonication pre-treated sludge, the disintegration efficiency might be regarded as a competition between the sonication density and the strength of sludge complex (including cells, particles, flocs and etc.). Hence, there is likely a critical sonication density level, under which these complex interior binding strength started to be broken up. Only if the mechanical forces induced by ultrasound exceed this critical level, the ultrasound disintegration of sludge can take place. Based on Equation 2.12, the acoustic pressure P_A is proportional to the square root of sonication intensity. Hence, the higher the sonication intensity, the more readily the cavitation bubbles to be effective.

From Equations 2.11 and 2.12, both P_c^v and P_A depend on the nature of the medium. Therefore, unlike the homogeneous system, the cavitation threshold for different kinds of sludge might not be a fixed value since different solids concentration, content, and dissolved gases could affect the P_c^v . This might provide a possible reason for the inconsistent sludge thresholds reported in different studies: 0.1W/cm² by Tiehm (2001), 0.22W/mL by Chu *et al.* (2001), 20 kJ/L by Bougrier *et al.* (2005) and 30 kJ/L by Gonze *et al.* (2003). The

minimum ultrasound level of 0.18W/mL (32 W/cm²) used in this study appeared to have exceeded the threshold evidenced by particle size decrease as much as 35% after 1 minute under this ultrasonic level.

Due to the fact that sludge is of very heterogeneous nature and comprising of various compounds (Gonze *et al.*, 2003), there exists a range of liquid strength levels, therefore resulting in different levels of thresholds for sonication sludge. As shown in Figure 4.18, the acoustic pressure generated by ultrasound increased with sonication intensity applied. Therefore, the higher the sonication intensity, the more powerful acoustic pressure is exerted to overcome stronger liquid strength P_c^v , which leads to a more complete disintegration. This gives the theoretical basis that higher sonication density results in better sludge disintegration.

Figure 4.18 Acoustic pressure as a function of sonication intensity
In the distilled water: $C = 1482 \text{ m/s}$ (Cutnell and Johnson, 1997); $\rho = 1000 \text{ kg/m}^3$

Besides the bubble formation, the behaviour of cavitation bubbles in the form of stable or transient is also related to sonication density. As discussed in the last section, there is a maximum/resonant radius, upon which cavitation bubble cannot grow further, but collapse rapidly. For the stable bubble, although the sound pressure could overcome the threshold and initiate cavitation bubbles, but it was not high enough to force bubble to expand to reach its maximum radius. As a result, bubble remained as stable and oscillated for a time scale of thousands of acoustic cycles. On the other hand, the transient cavitation refers to

the acoustic pressure could exert the bubble in expanding further to the maximum radius and collapsed within microseconds. Hence, acoustic pressure, which is dependent on sonication intensity, is a paramount factor to determine the number of transient bubbles.

As discussed earlier, transient bubbles are more powerful than stable bubbles in the process of sludge disintegration due to its extremely high temperature and high pressure accompanying with the collapse of bubbles. Considering the process of formation and collapse for the transient bubble is extremely fast (within a few microseconds), the effects of transient bubbles in a shorter time may be more efficient than the effects of stable bubbles in a longer time. Hence, sufficient sonication intensity/density may function as a more important parameter than sonication time on the view of bubble behaviour.

This hypothesis is in agreement with the reports that under the same energy input, higher ultrasonic intensity with short sonication time provided better disintegration than lower intensity with longer sonication time (Mao *et al.*, 2004; Grönroos *et al.*, 2005). This suggests that the process optimization would be more cost-effective by enhancing the ultrasonic intensity but reducing sonication time to produce more powerful transient bubbles, which leads to lower energy cost of treatment process.

4.4.3 Solids Concentrations

Besides the ultrasonic parameters, the efficiency of the sonication of sludge could also be influenced by the sludge conditions in terms of solids concentration and sludge type in this study. To examine the effects of solids concentration, a series of experiments were conducted to establish pre-treatment efficiency at different solids concentrations for both primary and secondary sludge. Solids concentration was indicated by total solids (TS).

4.4.3.1 Optimal sludge concentration

Figure 4.19 shows the change of mean particle size with specific energy at different solids concentrations of the primary sludge. From the results, the ultrasound disintegration of the primary sludge performed well at solids concentration of 0.98% TS, 1.7% TS and 2.6% TS. But when the solids contents increased to 3.6% TS, ultrasound treatment appeared to be less effective. Figure 4.19 also shows the mean particle size distribution at 0.52 W/mL of different solids concentration of the secondary sludge. Similar with the trends of the primary sludge, sonication disintegration of the secondary sludge was significant at solids concentrations of 1.0% and 1.7% TS, a little decline but still well at 2.9% TS, and obviously inferiorly at 3.8% TS. The results suggest that ultrasonication sludge could exert effective performance within a certain range of solids concentration.

The influence of solids concentration on sludge disintegration could be more clearly reflected from the results of SCOD. As illustrated in Figure 4.20, ultrasonication requires less specific energy input to degrade the primary sludge when its solids contents increased to 2.6%. At the same specific energy of 20 kWh/kg DS, for example, the original SCOD can be increased by about 1.6, 2.4 and 4.0 times if the sample was in the concentration of 0.98% TS, 1.7% TS and 2.6% TS, respectively. However, when the solids concentration increased further to 3.6% TS, the SCOD increase trends to decline. It can be seen from Figure 4.20 that the SCOD increase scope at 3.6% TS was lower as compared with that of 1.7% TS and 2.6% TS. In the case of the secondary sludge, the sonication could obtain more SCOD increase at the same specific energy at higher solids concentration within the range of 1.0-2.9% TS. Similar to the primary sludge, when solids concentration of the secondary sludge increased to 3.8% TS, at which the sludge contained the most amount of organics in the testing range of this study, the trend of increase in the SCOD did not exceed those of 2.9% TS.

Figure 4.19 Effects of solids concentration on particle size decrease

This occurrence is likely due to the fact that impacts of cavitation bubbles are influenced by the properties of both the sludge and ultrasound. Firstly, since the increased soluble organics were converted from the complex organics present in the sludge, as long as sonication bubbles were sufficient, a greater improvement of SCOD from thicker sludge makes sense due to its more complex organics available to be disintegrated..

On the other hand, if the solid concentration is too high, the loss of ultrasound energy, which would be discussed in later section, could hamper further improvement. In this study, when solids concentration further increased to 3.6% TS in the case of the primary sludge or 3.8% TS for the secondary sludge,

sonication treatment was found ineffective compared with the lower solids concentrations. This indicated that the negative effects of energy attenuation and adsorption caused by increasing solids had overshadowed the benefits of offering more organics at this high concentration level.

Figure 4.20 Effects of solids concentration on SCOD

Neis (2000) also found that the efficiency of sludge disintegration increased with solids concentration. That study, however, did not indicate the possible negative effects of thickened sludge when the solids concentration was too high. The results obtained in this study suggested there is a limit for the positive relationship between solids concentration and disintegration efficiency. In other words, there exists an optimal solids concentration range for cost-effective pre-treatment.

The performance of ultrasonication depends on multi-parameters, and their interactions could cause the analysis a complicated process. In order to minimize the complexity and to investigate the optimal range of sludge solids concentration, this study proposes a definition of ultrasonication disintegration index D, which reflects a relationship between the disintegration efficiency and sludge solids concentration as shown in the following Equation 4.8:

$$D = \gamma * (S / E) \text{ ----- Equation 4.6}$$

Where S (mg/L) is the SCOD in sludge after ultrasonication, E (kWh/kg DS) is the specific energy consumption to treat 1 kg dry solids of sludge. S/E is the slope of the trendline for SCOD vs specific energy obtained from Figure 4.20. γ is a correlation constant relative to the ultrasound density (in series experiments of concentration effects, the density remained 0.52W/mL, so γ is regarded as 1).

Based on Equation 4.8, index D represents the extent of SCOD improvement upon each unit of specific energy consumption. Figure 4.21 indicates the relationship between solids concentration and index D for sonication treatment of both primary and secondary sludge. Higher index D indicating more efficient sonication treatment, which was associated with solids concentration. From Figure 4.21, it can be established that the optimal thickness range of both primary and secondary sludge for sonication was around 2.3% - 3.2% TS to derive a cost-effectiveness operation. In other words, the highest SCOD increase can be derived per unit specific energy if sonication was applied for sludge within the optimal TS range.

The experiments revealed that there exists an optimal solids concentration range for sludge treatment, in which ultrasonication can achieve a satisfactory treatment at the lowest energy cost. It should be noted that index D might be influenced by different types of sludge. The relationship between solids concentration and disintegration degree should be experimentally established under various conditions.

Figure 4.21 Optimal solids concentration range for sonication treatment

4.4.3.2 Discussion on solids concentration

Propagation of ultrasound waves in real media (i.e. sludge in this study) is accompanied with unavoidable energy loss, such as attenuation, adsorption, and energy dissipation (Abramov, 1998). The occurrence of cavitation bubbles is accompanied with their additional attenuation related to the energy loss for the heating of gas in oscillating bubbles and the subsequent transfer of this heat to liquid, to the scattering of part of acoustic energy from the bubbles, and to the energy loss caused by acoustic streaming. The sound energy attenuation therefore can be attributed to diverse approaches.

The character of sound dissipation depends on the nature and the extent of medium inhomogeneity. Generally, equal portions of acoustic energy are

adsorbed over a given path interval as shown in Equation 4.9.

$$I_x = I_0 e^{-2\alpha \cdot x} \text{ ----- Equation 4.7 (Abramov, 1998)}$$

Where I_0 is the sound intensity at the source; I_x is intensity at the distance x from the source, α is the coefficient of absorption; x is the distance covered by the water.

It had been proved that the absorption coefficient increased with the liquid viscosity (Abramov, 1998). Hence, a thickened sludge posed a greater energy adsorption based on a study that the viscosity of sludge increased with solids concentration (Mikkelsen and Kudo, 2001). It was likely that sludge with too high solids concentration could largely hamper and reduce the ultrasound intensity in the areas remote to the sonicator probe. As a result, low ultrasound intensity in those remote areas fails to initiate active cavitation bubbles (especially transient bubbles), leading to inadequate sludge disintegration.

Another drawback for sludge with too high solids concentration is that a proper concentration range of particles was necessary for ultrasonication to work well in a liquid-solid system. If the solids concentration is too high, liquid which required to be vaporised to form microbubbles are insufficient during cavitation resulting in incomplete cavitation reactions. More seriously, if the solids concentration is too high, the generated cavitation bubbles cannot disperse away due to lack of liquid channels and intensively collapse around the probe, resulting in localized high temperature and high pressure. This could cause operation failure, probe erosion, and reduce the equipment use-life.

This study pointed out an inherent limitation of solids concentration in the process of sonication pre-treatment. Based on the results and discussion, it might be deduced that there exists an optimal concentration range for cost-effective operation. This suggests that solids concentration plays an important role in maximizing the benefits from ultrasonication of sludge.

Due to the fact that wastewater sludge properties are very diverse, depending on

many factors such as wastewater treatment design and scheme, weather change, water source and etc., it may not be possible to control solids concentration of sludge for sonication. But it is still highly desirable to establish a limiting solids concentration for monitoring of sonication system. In this manner, interruption due to overloading can be avoided; highly expensive sonicator can also be protected. Last but not least, the solids concentration is also a critical factor in determining the installation location of sonicator, such as before or after thickening process, by incorporating real working conditions in a wastewater plant.

4.4.4 Sludge Type

4.4.4.1 Optimal sludge type

Primary and secondary sludge are two kinds of sludge produced in the process of wastewater treatment. As discussed in the early section, secondary sludge exhibited greater improvement in critical parameters of particle size reduction as well as SCOD increase, indicating ultrasonication was more effective on secondary sludge than primary sludge. Besides particle size and SCOD, sludge type was found to also affect the results of DOC, pH, and SVI as illustrated in Figure 4.9, Figure 4.10 and Figure 4.12, respectively. These results revealed that sludge content influenced sonication pre-treatment and sludge modification was more significant for secondary sludge under the same parameters.

Furthermore, this study also conducted the investigation of sonication disintegration on mixed primary and secondary sludge at different mixing ratio. It was necessary since it is a common practice for wastewater treatment plant to mix primary and secondary sludge together before anaerobic digestion.

Figure 4.22 and Figure 4.23 illustrate the effect of sonication treatment on primary sludge, secondary sludge, and mixed primary and secondary sludge with mixing ratios of 75:25, 50:50 and 25:75, respectively. Obviously, the results indicated secondary sludge exhibited the most significant sludge disintegration in terms of its smallest mean particle size and highest increase folds in SCOD after

pre-treatment. Therefore, it might be concluded that ultrasonication indicated the best performance on the secondary sludge than both the primary sludge and mixed sludge at any ratio tested in this study. For this reason, the secondary sludge was selected as the test sludge for further investigation on anaerobic digestion.

Figure 4.22 Effects of sludge type on particle size decrease

Figure 4.23 Effects of sludge type on SCOD increase

The effects of sludge type on the sludge disintegration efficiency might be explained on the viewpoint of different composition contained in these two kinds of sludges. The cavitation strength of a liquid is determined by its

physicochemical properties and primarily by weak spots it contains (Abramov, 1998). Primary sludge consists mainly of materials that are hard to be disintegrated such as plastics, textile and inorganic matters like sand. On the other hand, secondary sludge (or called wasted activated sludge) mainly contained biomass, which is more readily to be disintegrated upon ultrasonic treatment. As shown in Figure 4.23, the sonication of the secondary sludge caused a more significant increase in SCOD than that of the primary sludge. This was likely due to the fact that the cells, present in the biomass-rich secondary sludge, were destroyed (cell lysis) and released a great portion of soluble organics.

Sonication treatment of sludge is a high energy-consuming technique; the results might suggest that only secondary sludge should be submitted for sonication, since the primary sludge and the mixed sludge obtained less benefit from pre-treatment. This would be especially the case when energy consumption is a crux for a wastewater plant.

4.5 SUMMARY

Findings derived from the study presented in this chapter can be summarised as follows:

1. The effects of ultrasound treatment on sludge characteristics were investigated in terms of particle size, soluble chemical oxygen demand (SCOD), dissolved organic carbon (DOC), temperature, pH, volatile fatty acid (VFA), oxidation-reduction potential (ORP), settleability and turbidity.
2. The results indicated that the sonication resulted in a reduction of sludge particle size from 47-51 μm to 7-15 μm , and an increase in the soluble chemical oxygen demand (SCOD) to total COD (TCOD) ratio from 3-9% to 17-25%. Experimental results illustrated that ultrasound treatment appears to be an efficient disintegration method to modify the characteristics of sludge by disrupting flocs/particles/cells and increasing the soluble/degradable organics.

3. Ultrasound treatment could be influenced by sonication time, sonication density, sludge type and solids concentration.
4. The extent of sludge disintegration increased with the sonication time applied, while the most significant reduction in particle size was within the first one minute.
5. A higher ultrasound density required less specific energy (kWh/kg DS) to derive a better sludge disintegration. The transient bubbles generated by ultrasonic waves were the dominant reason for sludge disintegration. Sonication density plays a very important role in determining the threshold, the number and the behaviour of cavitation bubbles in the treatment process.
6. Optimal solids concentration range was established for a cost-effective sonication treatment. Within the optimal solids concentration, efficient sonication can be effected and sludge can be disintegrated efficiently. The ultrasound would be attenuated by scattering and absorption if the solids concentration exceeds the optimal range.
7. Ultrasonication had a better performance on the secondary sludge than the primary sludge and mixed sludge at different mixing ratios, as more significant disintegration could be derived through treating secondary sludge, which essentially consisted of organic biomass.
8. The most significant benefits of sonication were achieved with the secondary sludge at high sonication density (0.52W/mL), an optimum total solids content of 2.3 - 3.2% TS, and a sonication time of 1 minute.

CHAPTER 5 BATCH DIGESTION OF SECONDARY SLUDGE

5.1 INTRODUCTION

The direct effects of ultrasound pre-treatment on sludge characteristics were presented in Chapter 4. Optimal sonication conditions for cost-effective sludge disintegration were established based on the experimental results and theoretical considerations. But how these modified sludge characteristics can really benefit the subsequent anaerobic digestion should be justified by further investigation. In this respect, Chapter 5 examines the effects of sonication on anaerobic digestion using batch digesters.

It had been reported that sonication treatment could improve the subsequent anaerobic digestion in batch in terms of organics degradation and biogas production (Tiehm *et al.*, 2001; Wang *et al.*, 1997; Onyeche *et al.*, 2002). These studies concluded that the improvement was owing to the accelerated hydrolysis after sonication treatment based on a presumption that hydrolysis was solely the rate-limiting stage. These studies however did not give any quantitative indication nor produce any fundamental explanation for the hydrolysis acceleration by ultrasonication.

Moreover, there is scarce information on correlations between sonication treatment of sludge and the behaviour of each dynamic step in the anaerobic degradation. Due to the fact that anaerobic digestion is completed through the interactive actions of hydrolysis, acidogenesis and methanogenesis, any of which may play as a crux if the balance between the biomass consortium and substrate is altered (Valentini *et al.*, 1997). Hence, it is essential to establish sufficient knowledge of how and to what extent ultrasound treatment is able to affect each step thereby influencing the process as a whole.

Hence, the objective of this chapter is to investigate the batch digester performance fed with sonicated sludge in situ, by which the effects of ultrasonication on respective steps of hydrolysis, acidogenesis and methanogenesis in anaerobic digestion process were examined. The role and significance of sludge disintegration for each dynamic step are discussed. The impacts of altered individual dynamic step on the overall anaerobic digestion are also discussed with respect to digestion efficiency and digester stability. The mechanism for improved digester performance by sonication treatment is hypothesised based on the results.

5.2 BATCH DIGESTER PERFORMANCE

5.2.1 Characteristics of Untreated and Sonicated Sludge

Since the sludge samples in this study were collected from wastewater plant once a week, sludge quality exhibited certain fluctuations throughout the experiment. Although the effects of sonication treatment on sludge characteristics had been discussed in detail in Chapter 4, major characteristics of sludge tested in the anaerobic digestion stage are also presented to evaluate the corresponding anaerobic digestion performance.

Figure 5.1 summaries the average characteristics of untreated and sonicated sludge at different sonication densities before feeding in batch digesters. Significant sludge disintegration by sonication treatment was evidenced by remarkable reduction of biosolids particle size and increase of soluble organics. The results indicated that sonication could disintegrate sludge particles from original range of 44.96-55.92 μm , to 29.02-38.03 μm , 19.23-28.66 μm and 14.98-20.53 μm at sonication densities of 0.18W/mL, 0.33W/mL and 0.52W/mL, respectively. Compared with 523-922 mg/L in the untreated sludge, SCOD increased to 723-1136 mg/L, 890-1380 mg/L and 1202-1767 mg/L after

Figure 5.1 Feeding sludge characteristics in terms of:
(a) TCOD and SCOD; (b) DOC and IC; (c) Mean particle size; (d) Ammonia and alkalinity; (e) VFA amount and distribution. The sonication time was fixed at one minute.

treatment at respective sonication densities (Figure 5.1). Correspondingly, the ratio of SCOD/TCOD also increased from an initial 2.9-4.1% to 3.8-4.6%, 4.4-6.1% and 5.1-6.9%, respectively. Total VFA increased from an original concentration of 331-376 mg/L to 394-465 mg/L, 563-614 mg/L and 690-766 mg/L after sonication at 0.18 W/mL, 0.33 W/mL and 0.52W/mL, respectively.

5.2.2 TCOD and SCOD Removal

Digester D1, serving as a control unit, was fed with untreated sludge, while the other three digesters D2, D3 and D4 were fed with sludge sonicated at 0.18 W/mL, 0.33 W/mL and 0.52 W/mL, respectively. Organics degradation efficiency was determined by TCOD removal after 16 days of anaerobic digestion. As illustrated in Figure 5.2, the TCOD removal efficiency was 44% for D1, and increased to 54%, 61% and 67% for D2, D3 and D4, respectively. The results demonstrated that digesters fed with sonicated sludge (D2, D3 and D4) could accelerate the complex organics degradation and achieve better organics degradation over the control digester (D1) fed with untreated sludge. TCOD removal is an indicator for the overall performance of anaerobic digestion. Improved TCOD removal from digesters fed with sonicated sludge actually reflected the accumulative benefits from sonication pre-treatment on each stage of hydrolyzation, acidification and gasification. A significant TCOD removal increase by 10-23% indicated that anaerobic community was much more comfortable and efficient in sonicated sludge than untreated sludge.

The significance of sonication treatment on TCOD removal is further demonstrated in comparing treatment performance among digesters fed with sonicated sludge. Digester D4, treating sludge sonicated at the highest sonication density of 0.52W/mL, exhibited about 13% and 6% higher removal efficiency than digesters D2 (0.18W/mL) and D3 (0.33W/mL), respectively. The superiority of D4 over D2 and D3 suggests that TCOD removal in the batch mode increased with the sonication densities applied in this study range. This revealed that the efficiency of anaerobic digestion is highly related to the sludge disintegration.

Figure 5.2 TCOD and SCOD removal efficiency after 16 days digestion

Compared with an 85% for the control digester D1, SCOD removal efficiencies increased to 90-91% for digesters fed with sonicated sludge (D2, D3 and D4). An increased SCOD removal implies that there was a more efficient utilization of soluble organics by anaerobes in digesters fed with sonicated sludge. This is likely due to either promoted biomass activity or improved mass-transfer conditions provided by the sonicated sludge.

5.2.3 Biogas Production

As shown in Figure 5.3, all digesters started to generate biogas from the first day without any delay. Compared with long period start-up of normal continuous digester system, a quick start-up of small batch digester in this study and other studies (Wang *et al.*, 1999; Bougrier *et al.*, 2005) might be due to better mixing, small amount sample assayed, and robust seed sludge selected. Moreover, small batch digestion in these studies used solution displacement to record biogas promptly. In contrast, continuous or/ and large scale system usually applied wet gas meter, which requires certain biogas accumulated to move the index.

All digesters exhibited a considerable increase in biogas yield in the initial 8 days (192 hours), after which the biogas generation gradually decreased and levelled off after 16 days digestion. From the initial hours, digesters D2, D3 and D4 began generating biogas at higher rate than the control unit D1. This finding

was attributable to the fact that sonication treatment provided more readily degradable solids (Figure 4.4), which accelerating the biogas response.

Figure 5.3 Accumulated biogas production after 16 days digestion

Digesters fed with sonicated sludge exhibited superiority in gas yield over the control digester throughout the digestion period. Compared with 1530 ml from the control unit D1, the final accumulative biogas production increased to 1840 mL, 2140 mL, and 2390 mL for digesters D2, D3 and D4, respectively. Therefore, sonication pre-treatment could greatly increase both the production rate and ultimate gas yield. The increased biogas yield from sonicated system was corresponded with the result of TCOD removal efficiency, indicating that conversion efficiency of complex organics into biogas could be improved by sonication pre-treatment.

In addition to the increase of biogas yield, a change in biogas composition in digesters fed with sonicated sludge was noted. The methane content in the control digester D1 remained at 57%, while higher percentages of 61%, 64% and 66% were measured in digesters D2, D3 and D4, respectively. Similar increase in the methane content from 62% to 69% through sonication pre-treatment was also reported by Tiehm *et al.* (2001), but the mechanism remained unclear. The discussion on altered biogas composition will be provided in section 5.3.4.3.

The results of this section indicated that ultrasound pre-treatment of sludge was able to improve the organics removal efficiency, enhance the biogas production and increase the methane content in the biogas for a batch digester. A better anaerobic digestion efficiency derived from digesters fed with sonicated sludge was likely attributed to either to a more readily biodegradable TCOD in the sonicated sludge or to improved mass transfer conditions due to disrupted sludge flocs. It should also be noticed that although the pH of the sludge decreased after sonification, it remained within the suitable range for anaerobic processes. Likewise, the effect of the ORP on the subsequent anaerobic digestion was not conclusive.

The results obtained from this study corresponded with gas enhancement through sonication treatment by an extent of 16-122% in 22 days of digestion reported by Tiehm *et al.* (1999); 12-69% in 11 days reported by Wang *et al.* (1999) and 25-140% in 15 days reported by Bougrier *et al.* (2005). In general, the higher SCOD after the treatment, the more methane and higher organics degradation were achieved from batch anaerobic digestion. However, previous studies had not addressed the role and significance of sonicated sludge characteristics on each dynamic step of hydrolysis, acidogenesis and methanogenesis. The next section in this chapter attempts to answer these questions.

Figure 5.4 Average biogas composition for different digesters

5.3 BIOCONVERSION KINETICS

5.3.1 Theoretical Background

Discussions on anaerobic digestion kinetics in this study are based on the reaction scheme described by Zehnder *et al.* (1982). A simplified treatment of Zehnder model was outlined in Figure 2.1. The complex particulate organics are first converted by hydrolytic bacteria into dissolved simple organics at a hydrolysis rate constant k_1 . Subsequently acidogenesis bacteria converted soluble organics into organic acids at a rate constant k_2 . Finally, the methanogenic biomass degraded the organic acids into methane and carbon dioxide at a rate constant of k . It is deemed that hydrolytic bacteria and acidogenesis bacteria are the same kind of microorganisms called fermentative biomass, which is differentiated from methanogenic biomass (Zehnder *et al.*, 1982; Hill *et al.*, 1984).

Since methanogenesis is the ultimate reaction to complete anaerobic digestion, hence the rate-limiting step of the overall process could be identified by the availability between methanogenic biomass and their degradable organic acids substrate. If the specific production rate of organic acids in hydrolysis-acidogenesis is faster than the specific degradation rate in methanogenesis process resulting in an accumulation of excessive organic acids, the rate-limiting step is methanogenesis and the overall digestion rate depends on the growth rate μ of methanogenic biomass. Otherwise, if methanogenesis biomass is adequate, supplying degradable organic acids from hydrolysis-acidogenesis is the rate-limiting step.

5.3.2 Hydrolysis

5.3.2.1 Pre-hydrolysis

Under normal conditions, hydrolysis of complex organics such as sludge is a rather slow process and is catalyzed by extracellular enzymes such as amylases, proteinases, lipases and nucleases (Gaudy and Gaudy, 1980). One of the most significant modifications from sonication pre-treatment was its pre-hydrolysis effect evidenced by an instant increase in soluble substances. As shown in Figure

5.1 from the total TCOD and SCOD results, although sonication treatment exerted little impact on the total solids concentration, it did manage to convert a fraction of the particulate matter into soluble form. Compared with an average SCOD of 724 mg/L for the untreated sludge, the SCOD increased to 1070 mg/L, 1290 mg/L and 1690 mg/L after sonication at 0.18, 0.33 and 0.52 W/mL, respectively, with increases ranging between 48 and 161%. Another evidence of soluble organics released from cells disruption by sonication treatment was the marked increases in dissolved organic carbon (DOC), which increased from the original 95 mg/L to 132 mg/L, 187 mg/L and 245 mg/L after sonication at respective sonication densities.

Comparing to the untreated sludge, it can be deduced that a portion of complex organics in the sonicated sludge had already been hydrolyzed into readily degradable substrate even before anaerobic digestion. With increasing solubilization of the organics by pre-treatment, more volatile solids would become readily amendable to further decomposition (Chiu *et al.*, 1999; Lin *et al.*, 1997). The soluble organics resulting from sonication are generally used as carbon and energy sources by hydrolytic bacteria and acid formers which carry out hydrolysis and acidogenesis (Gaudy and Gaudy, 1980). Therefore, the increased soluble organics in pre-hydrolysis could provide more readily substrate for microorganisms growth. It is reasonable to predict that digesters fed with sonicated sludge pose favourable conditions for an efficient hydrolysis-acidogenesis process arising from more soluble substances released after ultrasound.

5.3.2.2 First order rate of hydrolysis

Many studies described anaerobic hydrolysis with empirical first order kinetics based on biodegradable substrate concentrations as described in Equation 5.1.

$$\frac{d[cCOD]}{dt} = -k_1[cCOD] \text{ -----Equation 5.1}$$

Where $[cCOD]$ represents the concentration of complex COD, which was derived from the balance between TCOD and SCOD, mg/L; k_1 is the first order

hydrolysis constant, d^{-1} . This kinetics model assumes the removal of insoluble COD (called complex COD) represented the hydrolysis of complex organic matter. The insoluble COD might represent both complex and ready digestible organics. It is therefore very difficult, in practice, to isolate hydrolysis from some of the other phenomena occurring during anaerobic digestion. The method used in this thesis is an approximation that is common in the field (Pavlostathis and Giraldo-Gomez, 1991).

Figure 5.5 shows complex COD degradation along with the first order fitting curves, from which hydrolysis constants were derived with confidence $R^2 > 0.97$.

Figure 5.5 (a) cCOD degradation and (b) hydrolysis constant rate k_1 derived from linear regression

The first order hydrolysis constants obtained in digester D2, D3 and D4 were 0.046, 0.056, and 0.067 d⁻¹, respectively, compared 0.038 d⁻¹ in control digester D1. The adequate fitting with first-order kinetics implied that hydrolyzation of complex organics in all four digesters took place without any delay. This suggests that the hydrolytic enzymes had occupied available degradable adsorption sites at the beginning due to the initial presence of hydrolytic enzymes on the substrates or the fast growth of hydrolyzing bacteria (South *et al.*, 1995; Veeken and Hamelers, 1999). Hydrolysis constant is a useful tool to prove that ultrasonication has accelerated the hydrolysis rate of particulate organics, and to quantify the improvement extent, which was in positive relationship with the sonication density for batch digestion in this study.

5.3.2.3 Surface-based hydrolysis rate

Various factors including temperature, solids concentration, retention time, and substrate category could influence the hydrolysis rate (Pavlostathis and Giraldo-Gomez, 1991). A significant increase of hydrolysis constants for digesters fed with sonicated sludge in this study would be attributed to the modification of sludge characteristics after pre-treatment since all digesters were operated under identical working conditions.

Based on the fact that hydrolysis is carried out by the enzymes synthesised by the biomass, it is likely that better conditions for bacterial growth were associated with digesters fed with sonicated sludge. Some authors reported that anaerobic hydrolysis constants can be increased by decreasing the particle size of substrate in the case of anaerobic hydrolysis of tomato biowaste (Hill and Nakano, 1984) and cellulose (Chyi and Dague, 1994). This concept might be also suitable to describe the hydrolysis of sludge since the sludge particle size was significantly changed after pre-treatment.

To assess the correlation of surface areas of sludge and the hydrolysis rate, the particle size distribution of untreated and sonicated sludge were measured and specific surface areas referred to the mass have been calculated according to Palmowski and Muller (2000).

For calculation most authors assume the particles of a substrate are spherical in shape (Sanders et al., 2000). Due to the heterogeneous nature of wastewater sludge, particles contained in sludge demonstrate a large range of size distribution (around 0.058 - 400 μm). A significant error would therefore be introduced when using only one average particle size to derive the surface area. The Master Sizer machine used in this study could report the particle size distribution in about sixty different size groups. Hence, the particle size distribution of each size group was considered and the specific surface area A_m referred to the mass was calculated as shown in Equation 5.2.

$$A_m = \frac{\sum_{i=1}^{i=n} 4\pi \times r_i^2 \times p_i}{\left[\sum_{i=1}^{i=n} \frac{4}{3} \pi \times r_i^3 \times p_i \right] \times \rho} \text{ ----- Equation 5.2}$$

Where A_m is the specific area (m^2/kg), r_i is the radius for particle size in each group (μm), p_i is the volume percentage for each size group (%), ρ is the density of dry solids (kg/m^3), which was assumed as the empirical value of $80 \text{ kg}/10^3 \text{ m}^3$ (Metcalf & Eddy, 2003).

As Table 5.1 shown, the specific surface areas calculated were 0.4663, 0.5171, 0.5716 and $0.6362 \text{ m}^2/\text{kg}$ for untreated sludge and sludge sonicated at 0.18W/mL, 0.33W/mL and 0.52W/mL, respectively. Greater specific surfaces were observed in sludge sonicated at higher sonication densities. The results suggest that sonication is able to disintegrate sludge particles leading to higher particle specific surfaces, which in turn create more enzyme-adsorption sites for a quicker hydrolysis reaction.

This surface-based hydrolysis constant provided a description of the anaerobic digestion with kinetic parameters which were intrinsically independent of particle size. The surface-based hydrolysis constants for D2, D3 and D4 were 0.0882, 0.1008 and $0.1056 \text{ d}^{-1}/\text{m}^2/\text{kg}$ respectively, which represents an increase by 7-28% compared the c of $0.0823 \text{ d}^{-1}/\text{m}^2/\text{kg}$ in the control digester. Therefore, when compared the improvement of 7%-28% by pre-treatment using

surface-based constants to 19%-75% using first order hydrolysis constants, the difference of surface-based hydrolysis constants from the four digesters became much closer. It might suggest that decreasing particle size which in turn increasing the surface area was an essential contributor for hydrolysis acceleration.

Table 5.1 Correlations of surface area and hydrolysis constants

Digester	D1	D2	D3	D4
Sonication treatment	control	0.18W/mL	0.33W/mL	0.52W/mL
Specific surface, A_m , (m^2/kg)	0.4663	0.5171	0.5716	0.6362
First order hydrolysis Constant, k_1 , (d^{-1})	0.0384	0.0456	0.0576	0.0672
Surface based hydrolysis constants, k_1/A_m , ($d^{-1}/m^2/kg$)	0.0823	0.0882	0.1008	0.1056

Another studies by Veeken *et al.* (1999) and Tong *et al.* (1990) reported that the higher hydrolysis rate of particulate organics was always associated with higher degradability. This suggested that ultrasonication was able to destroy the bounded structures of biosolids, flocs or cells to release more easily degradable components, as a result of the increase in the effective amounts of enzyme-adsorption sites per specific area.

Moreover, a rapid hydrolysis from digester fed with sonicated sludge was also likely due to its better access to the degradable substrate. The reduction of particle size revealed that flocs agglomerations were disintegrated and solids/substrate was dispersed after sonication treatment. With the mass-transfer conditions improving as well as soluble organics increasing (Figure 5.1), sonicated sludge would exhibit an enhanced diffusion of substrate among the bulk solution, the particle surface and bacteria communities.

5.3.3 Acidogenesis

5.3.3.1 Pre-acidogenesis

In addition to the effect of pre-hydrolysis by sonication treatment as discussed earlier, response of acidogenesis was also noted in sonicated sludge as evidenced by a notable increase in volatile fatty acids (VFAs). As shown in Figure 5.1 (e), the average VFA increased from an original concentration of 358 mg/L to 454 mg/L, 583 mg/L and 749 mg/L after sonication at 0.18 W/mL, 0.33 W/mL and 0.52W/mL, respectively.

Acidegenesis contributes to transform sludge into a more amendable form for subsequent methanogenesis. While VFAs are important intermediate compounds for methane generation, they may also cause microbial stress if present in excessive concentrations (Hill *et al.*, 1987). VFA inhibition was not observed under the batch digestion conducted in this study. But a pre-acidogenesis phenomenon after sonication treatment should be a factor to consider in avoiding system upset and maintaining optimum digester operation and performance.

5.3.3.2 First order rate of acidogenesis

The acidogenesis bacteria utilizing the soluble organics in sludge carry out the acidogenesis step as expressed in Equation 5.3.

$$\frac{d[sCOD]}{dt} = k_1[cCOD] - k_2[sCOD] \text{ ----- Equation 5.3}$$

Where [sCOD] represents the concentration of soluble organics, mg/L; k_2 is the acidogenesis constant, d^{-1} . As shown in Figure 5.6, the derived acidogenesis constant k_2 were 0.109 0.113, 0.113 and 0.111 d^{-1} for digesters D1, D2, D3 and D4, respectively.

Figure 5.6 (a) SCOD degradation and (b) acidogenic constant rate k_2 derived from linear regression

The results indicated that acidogenesis constants were not significantly impacted by sludge sonification. All digesters exhibited a faster acidogenesis rate than their corresponding hydrolysis rate. The hydrolysis constants were in a range of 0.0384–0.0672 d^{-1} for D1 to D4; while acidogenesis constants were almost similar ranging above 0.1 d^{-1} attributed to easier hydrolysis of the soluble organics than in the particulate organics.

However, overly “efficient” acidogenesis is often considered as a dangerous indicator to bring about digester depression characterized by sharp pH drop and

volatile acids accumulation. The main disadvantage of batch system is therefore deemed as the irreversible acidification at the start-up of the batch process (Veeken and Bamelers, 1999).

5.3.3.3 *pH and VFA*

To assess the self-buffering capacity of untreated sludge and sonicated sludge during system acidogenesis, no pH buffering was provided in anaerobic sludge digestion. Figure 5.7 illustrates that all digesters experienced a pH decrease in the initial period (<120 hours), implying an initially prevailing acidification process evidenced by a marked accumulation of VFAs as shown in Figure 5.8. The maximum total VFAs concentrations reached 702, 1070, 1220 and 1515 mg/L from digesters D1 to D4 respectively. All digesters exhibited a sharp increase in VFAs, indicating that the activity of the slow-growing methanogens was lagging behind the fast-growing acid formers in the initial digestion period, which resulting in an accumulation of the intermediate product i.e. VFA.

It is interesting to note that, although experiencing a greater VFA accumulation, digesters fed with sonicated sludge (D2, D3 and D4) exhibited much smaller pH reduction than the control digester D1. In the first 120 hours of digestion, the pH in D1 decreased from 7.4 to 6.2, with a substantial reduction in the pH value of 1.1, while the system pH for D2, D3 and D4 was maintained in a smaller range of 6.9-6.5 with a less reduction of 0.4 (Figure 5.7).

It is well known that sharp pH decrease is a very dangerous sign for proper digester operation. A main disadvantage of batch system is deemed as an irreversible acidification at the start-up (Veeken and Bamelers, 1999). The comparatively stable pH environment observed in digesters D2-D4 suggests that digesters fed with sonicated sludge contained adequate treating capacity to accommodate a greater production of volatile acids in the acidification process.

Figure 5.7 pH evolution over the digestion time

Figure 5.8 VFA development over the digestion time

5.3.4 Methanogenesis

5.3.4.1 Methane production rate

A significant benefit of digesters fed with sonicated sludge is the ability to enhance methane production as well as methane content (Figure 5.3 and Figure 5.4). After operated for 16 days, D4 demonstrated the highest accumulated biogas production of 2350 mL, followed by D3 with 2150 mL, and D2 with 1840 mL. The control digester D1 produced the lowest biogas production at 1540 mL. Compared with the control digester D1, biogas production increased by 19%,

40% and 53% for digesters D2, D3 and D4, respectively.

As shown in Figure 5.9, methane production rate for all digesters drastically increased in the initial period reaching respective maximum rate, after which the rate decreased steadily with time. The maximum methane production in ascending order was 4.5, 7.1, 8.8 and 10.4 mL/L.hour for digesters D1 to D4 and the time required to reach the maximum point was 72 hours for D1 but a shorter of 48 hours for D2, D3 and D4.

These results associated with the methanogenesis activity measured by co-enzyme F₄₂₀ (Figure 5.10) demonstrated that the methane production rate depended on the development of methanogenesis biomass in their initial acclimation period, in which methanogenesis was the rate-limiting step and the consumption rate of VFA was slower than the production rate as evidenced by the accumulation of VFA at the corresponding period (Figure 5.8).

Figure 5.9 Conversion kinetics over digestion time (D1-Control, D2-0.18W/mL, D3-0.33W/mL and D4-0.52W/mL; markers: experimental data; lines: fitted with equation $\frac{d(\text{CH}_4)}{dt} = \text{CH}_{\text{max}} \cdot k_{\text{H}} \cdot \exp(-k_{\text{H}} \cdot t)$)

Figure 5.10 Coenzyme F_{420} activities over digestion time

The time needed for methanogenesis acclimation in digesters D2 to D4 was reduced by 50% compared with D1, indicating digesters fed with sonicated sludge exhibited a faster development of necessary methanogenesis biomass to remove the excessive VFA compared with digester fed with untreated sludge. This could enhance the digester stability since long-term methanogenesis limitation is always involving the risk of digester inefficiency, expensive maintenance and even irreversible acidification.

5.3.4.2 Co-enzyme F_{420} development

A further measurement of co-enzyme F_{420} , a specific co-enzyme secreted by methanogens for conversion of substrate to gaseous products, verified that digesters fed with sonicated sludge contained more active methanogens throughout the digestion. Significant increase of co-enzyme F_{420} was observed from sonicated sludge over untreated sludge throughout the digestion process. Figure 5.9 shows the average concentrations of co-enzyme F_{420} determined for D2, D3 and D4, which were increased by 45%, 94% and 140% comparing with the control D1. The highest methane production rate of digester D4 was likely associated with the greatest secretion of co-enzyme F_{420} .

The enhancement is attributed to the fact that the disrupted cells in the sonicated sludge are able to overcome inhibition of substrate diffusion across the bound biosolids, which allowed more contact between biomass and the substrate. This could improve the digester performance since the sensitive, delicate and slow growing methanogens are always deemed as the limiting factor in anaerobic process. On the other hand, a slow and inadequate methanogenesis in the control digester D1 could be due to the unfavourable pH dropping to as low as 6.2 (Figure 5.7).

It can be hypothesized from the results obtained that, in addition to accelerating the conversion of complex organics into degradable substrate, the digesters fed with sonicated sludge would also stimulate and promote the growth of methane-producing bacteria resulting in shortening of the acclimation period and enhancement of methane yield.

5.3.4.3 *Altered biogas composition*

It is worth noting that sonication pre-treatment could also influence the biogas composition. As mentioned in previous section, methane content of the control digester D1 remained at 57%, while higher percentages of 61%, 64% and 66% were measured in digesters D2, D3 and D4, respectively.

As discussed in Chapter 2, the bioconversion of organics into methane and carbon dioxide could proceed through a series of complex biochemical pathways. Different conversion pathways conducted in anaerobic digestion may result in different biogas composition. Therefore, if an increase in biogas amount indicated that sonicated sludge could accelerate biogas formation; an altered biogas composition, however, implied that the pathways of methane formation process were also modified by sonication treatment in one way or another.

Two hypotheses were proposed to explain the altered gas composition in this study. Firstly, it might be related to the different growth rate of two kinds of methanogenesis biomass: acetotrophic and hydrogenotrophic bacteria. Henzen and Harremones (1983) found that the bacteria producing methane from

hydrogen and carbon dioxide (hydrogenotrophic) grow faster than those utilizing acetate to produce both methane and carbon dioxide (acetotrophic). There was possibly a greater enhancement for hydrogenotrophic bacteria than acetotrophic bacteria in a sonicated sludge digestion system, resulting in a shift to hydrogenotrophic methanogenesis. Further study is needed to explore further this possibility through microbial study using advanced techniques such as DNA identification.

Another reason was likely due to the fact that the nature of substrate could influence the biogas composition. It was reported that a higher methane content of 71% was derived from protein substrate and a lower of 50% from carbohydrates (Malina and Pohland, 1992). Hence, it is likely that a higher methane content was derived from sonicated sludge if sonication pre-treatment could bring out greater increase extent for protein degradation than that of carbohydrates. This hypothesis is in agreement with the finding reported by Wang *et al.* (1999) that a greater increase extent of protein than that of carbohydrate was observed in the supernatant after sonication treatment of sludge. Higgins and Novak (1997) had reported that shear will release a mixture of protein and polysaccharides into solution. Hence the increased release protein in the solution might be attributable to the shear forces generated by cavitation bubbles during sonication pretreatment.

5.4 EFFECTS OF SONICATION TREATMENT ON RATE-LIMITING STAGE

5.4.1 Identification of Rate-limiting Stage

A sound anaerobic digestion of complex organics requires a balance between the acidogenic and methanogenic bacteria. The methanogens and acidogens form a syntrophic relationship in which each bacteria group constitutes a significant link in a complex chain of bioconversion (Zehnder *et al.*, 1982). After respective maximum methane production rate, all digesters exhibited a decrease in methane production rate, reduction of VFA and gradually increase pH indicating the rate-limiting step thereby had been switched to the hydrolysis.

To study the effects of ultrasound treatment on the limiting step in anaerobic sludge digestion, the modified differential first order kinetics (Equation 5.3) based on Veeken and Hamelers (1999) was adopted in this study.

$$\frac{d(CH_4)}{dt} = CH_{\max} \cdot k_H \cdot \exp(-k_H t) \text{ -----Equation 5.4}$$

Where $\frac{d(CH_4)}{dt}$ is the methane production rate (mL/L.hour); $CH_{\max}$ is theoretical maximum methane production; k_H is the hydrolysis constant based on methane production. According to Veeken and Hamelers (1999), methane production can only represent the hydrolysis rate of particulate organics when hydrolysis is the rate-limiting stage. To verify the fact that rate-limiting stage had been switched, the experimental and the theoretical data were compared in Figure 5.9.

Figure 5.10 shows a comparison of actual experimental data with calculated methane production from Equation 5.3. The results indicated that Equation 5.3 was not applicable to the methane production rates in all digesters before their respective maximum rate. Nevertheless, the model fitted well after the peak in methane production (correlation coefficients $R^2 > 0.97$). The hydrolysis constants derived from Equation 5.3 were 0.048, 0.060, 0.065, and 0.070 d^{-1} for digesters D1 to D4, respectively. When these values were compared with their respective first order hydrolysis constants of 0.0384, 0.0456, 0.0576, and 0.0672 d^{-1} derived from complex organics degradation (section of 5.3.2.2, page 123), it could be concluded that the two groups of hydrolysis constants were in fact similar. The results verified that hydrolysis of complex organics was the rate limiting phase in the digestion after the maximum methane production in all digesters.

Equation 5.3 suggests hydrolysis is not the rate limiting step during the initial anaerobic digestion. As discussed earlier on the VFAs evolution, all digesters initially exhibited an increase and accumulation of VFAs, indicating that the activity of the slow-growing methanogens was lagging behind that of the fast-growing acid formers (Figure 5.8). Hence, methanogenesis was initially the rate-limiting step of the anaerobic degradation of the sonicated sludge.

Digesters fed with sonicated sludge could not only accelerate the conversion of particulate organics into degradable substrate but also stimulate and promote the growth of methanogenesis biomass to shorten the acclimation period and enhance the methane conversion efficiency.

5.4.2 Contribution from Each Limitation Stage

After identification of restricted steps, further analysis was conducted to assess the specific contribution from each stage in digesters fed with sonicated sludge. Table 5.2 illustrates the evaluation procedure on the basis of methane improvement.

In the first period of 0-36 hours, all digesters were suffering the methanogenesis limitation; methane increase at this stage was attributed to the improved growth and activity of methanogenic biomass. In the second period of 36-72 hours, digester D1 was still restricted by methanogenesis process while digesters D2, D3 and D4 had gone through this stage and switched to hydrolysis limitation. The increased methane in this period might be regarded as the competition of methanogenesis efficiency in D1 and hydrolysis efficiencies in D2 to D4. In the final period of 72-386 hours, anaerobic digestion in all digesters was in the hydrolysis limitation; therefore, any improved methane yield was owing to the increased hydrolysis rate.

Table 5.2 Analysis of improvement contribution from limitation stages

	D1-Control (1)	D2-0.18W/mL (2)	D3-0.33W/mL (3)	D4-0.52W/mL (4)
The entire period				
Total methane yield, mL(A)	872.1	1125.4	1369.6	1577.4
Increase amount, mL (B) $[A_{2-4}-A_1]$	-	250.3	497.5	705.3
Total increase per, % (C) $[B_{2-4}*100/A_1]$	-	29.0	57.0	80.9
Initial 0-36 hours				
Limitation stage	Methanogenesis	Methanogenesis	Methanogenesis	Methanogenesis
Methane yield, mL (D)	126.7	231	325.1	369.6
Increase amount, mL (E) $[D_{2-4}-D_1]$	-	105.0	199.1	243.6
Increase per at stage, % (F) $[E_{2-4}*100/A_1]$	-	12.0	22.8	27.9
Contribution at stage, % $[E_n*100/B_n, n=2, 3, 4]$	-	41.9	40.0	34.5
Middle 36-72 hours				
Limitation stage	Methanogenesis	Hydrolysis	Hydrolysis	Hydrolysis
Methane yield, mL (G)	223.4	251.9	291.8	314.8
Increase amount, mL (H) $[G_{2-4}-G_1]$	-	28.5	68.4	91.4
Increase per at stage, % (I) $[H_{2-4}*100/A_1]$	-	3.3	7.8	10.5
Contribution at stage, % $[H_n*100/B_n, n=2, 3, 4]$	-	11.4	13.7	13.0
Final 72-384 hours				
Limitation stage	Hydrolysis	Hydrolysis	Hydrolysis	Hydrolysis
Methane yield, mL (J)	522.1	643.0	754.6	892.3
Increase amount, mL (K) $[J_{2-4}-J_1]$	-	120.9	232.4	370.2
Increase per at stage, % (L) $[K_{2-4}*100/A_1]$	-	13.9	26.7	42.4
Contribution at stage, % $[K_n*100/B_n, n=2, 3, 4]$	-	48.3	46.7	52.5

As shown in Table 5.2, digesters fed with different sonicated sludge exhibited various extents of increase in methane at different periods. Compared with the control digester D1, the methane production from digester D2 increased by 29%, where 12% came from 0-36 hours, 3.3% from 36-72 hours and 13.7% from the last 72-386 hours. For digester D3, the total increase of 57% was the sum of 22.8% from the first period, 7.8% from the second period and 26.7% from the final period. Similarly, the increased 80.9% methane from digester D4 was consisted of 27.9%, 10.5%, and 42.4% from respective periods.

The results indicated that about 35-42% of the increased methane yield from digesters fed with sonicated sludge was attributed to their promoted methanogenic activity; about 11-14% was related to their faster methanogenesis acclimation; and 47-53% was owing to their increased hydrolysis rate.

This analysis quantitatively demonstrated that the improved batch anaerobic digestion was actually the combined effects of the improved methanogenesis and hydrolysis by sonication pre-treatment. Although the increased methane from the limitation stage of methanogenesis was less than that of hydrolysis, considering the very short domination period of methanogenesis limitation stage, such improvement was impressive indeed.

Previous studies on this area mainly reported on which aspect (gas production and organics removal efficiency) and to what extent pre-treatment could improve the performance of batch digester fed with sonicated sludge (Tiehm *et al.*, 2001; Wang *et al.*, 1997; Onyeche *et al.*, 2002). This study, however, was elaborating on how such improvement take place in the angle of the improvement on each step, especially the rate-limiting step (hydrolysis or methanogenesis). The role and significance of sludge disintegration for each dynamic step as well as the effects of altered behaviour of each step for the overall anaerobic digestion were discussed with respect to digestion efficiency and digester stability. These results might shed a new light on understanding of the mechanism involved in sonication of sludge.

However, batch test could provide only limited information about pre-treatment of sludge on static conditions. Chapter 6 will further examine the feasibility and reliability of pre-treatment of sludge in a continuous anaerobic digester system, which is more commonly applied in practice.

5.5 SUMMARY

The influence of ultrasonication on hydrolysis, acidogenesis and methanogenesis in anaerobic decomposition of the secondary sludge was examined in the batch digestion of the secondary sludge. Findings derived from the study presented in this chapter can be summarised as follows:

1. The results of overall performance suggested that ultrasonication could enhance batch anaerobic digestion of the secondary sludge resulting in an accelerated bioconversion, improved organics degradation, improved biogas production and methane yield.
2. First order hydrolysis rates increased from 0.0384 d^{-1} in the control digester, to 0.0456 , 0.0576 , and 0.0672 d^{-1} in the digesters fed with the secondary sludge sonicated at densities of 0.18W/mL , 0.33W/mL and 0.52W/mL , respectively.
3. The sonication appeared to be ineffective in relation to acidogenesis reaction rates, but the fact that digester fed with pre-sonicated the secondary sludge showed consistent pH evolution might be attributed to their better buffering-capacity to diminish adverse impact of acidification.
4. Determination by co-enzyme F_{420} verified that sonication is able to promote the growth of methanogenic biomass and to facilitate a positive methanogenic microbial development in suppressing the initial methanogenesis limitation. The notable fact that sonication pre-treatment of the secondary sludge also increased the methane content from 57% to 66% implied the possibility that greater enhancement of hydrogenotrophic bacteria than acetotrophic bacteria in a sonicated the secondary sludge digester.

5. All digesters were experiencing a methanogenesis limitation initially and then followed hydrolysis limitation. The improved hydrolysis and promoted methanogenesis by sonication treatment together contributed to the entire improvement of digestion rate and efficiency.

CHAPTER 6 ANAEROBIC DIGESTION OF SECONDARY SLUDGE IN UASB DIGESTERS

6.1 INTRODUCTION

As discussed in Chapter 1, it is noted that most studies of sonication pre-treatment were carried out in batch fermentation (Wang *et al.*, 1999; Tiehm *et al.*, 2001; Chu *et al.*, 2002; Onyeche *et al.*, 2002). Information pertaining system performance and stability of digester treating sonicated sludge under continuous operation is barely reported, which is indeed applicable to large-scale wastewater treatment plants. It is imperative to know to what extent the anaerobic microbial community can optimally adapt to the sonicated sludge under continuous feeding. Successful implementation of pre-treatment technique is possible only when sufficient knowledge on reliability of subsequent anaerobic digestion has been established.

Therefore, further experiment is necessary to examine the feasibility and reliability of anaerobic digestion of sonicated sludge using upflow anaerobic sludge blanket (UASB) digester system. The main objectives of this chapter are to verify the feasibility of sonication in a continuous digester operation mode. The role and significance of sonication pretreatment of sludge on organics removal and biogas production were examined. The effects of operating conditions on digester performance were also investigated.

6.2 UASB DIGESTER PERFORMANCE

This study is targeted to examine the feasibility and reliability of sonication pre-treatment of sludge for anaerobic digester under a range of HRTs. Four identical laboratory-scale digesters were operated at five HRT stages of 20-day,

14-day, 8-day, 4-day and 2-day, corresponding to the respective average organic loading rates (OLR) of 1.1, 1.8, 3.6, 7.2 and 14.5 g COD/L.day. Digester D1, serving as a control unit, was fed with untreated secondary sludge, while the other three digesters designated D2, D3 and D4 were fed with sludge sonicated at sonication densities of 0.18W/mL, 0.33W/mL and 0.52W/ml for 1 minute, respectively.

Although it is hard to secure real steady-state operation in practice, performance was evaluated at a pseudo-steady state condition indicated as gas production and TCOD removal fluctuated within 5% for one week (Show, 1996).

6.2.1 Results of Organics and Solids Removal at Different HRTs

Many studies indicated that the performance of upflow anaerobic digester could be more comprehensive if described not only in terms of removal efficiency but also in terms of influent and effluent characteristics (Wang, 1994; Zeeman and Lettinga, 1999; Elmitwalli *et al.*, 2000). The organics removal efficiency of an anaerobic digester can be examined in terms of TCOD and SCOD removal; and the efficiency of solids reduction can be examined through the analysis of TS and VS removal. Figures 6.1 to 6.5 demonstrate the performance of UASB digesters in terms of influent and effluent TCOD, SCOD, total solids (TS) and volatile solids (VS) during steady-state at each HRT stage; and Figures 6.6 to 6.9 summarize the removal efficiencies of organics and solids matters.

Figure 6.1 Performance of UASB digesters: (a) influent and effluent TCOD, (b) SCOD, (c) TS and (d) VS at 20-day HRT

Figure 6.2 Performance of UASB digesters: (a) influent and effluent TCOD, (b) SCOD, (c) TS and (d) VS at 14-day HRT

Figure 6.3 Performance of UASB digesters: (a) influent and effluent TCOD, (b) SCOD, (c) TS and (d) VS at 8-day HRT

Figure 6.4 Performance of UASB digesters: (a) influent and effluent TCOD, (b) SCOD, (c) TS and (d) VS at 4-day HRT

Figure 6.5 Performance of UASB digesters: (a) influent and effluent TCOD, (b) SCOD, (c) TS and (d) VS at 2-day HRT

At 20-day HRT, all digesters exhibited good performances with TCOD removal above 95% and SCOD removal higher than 80% (Figure 6.1). The results suggested that with respect to the treatment capability, operating conditions of 20-day HRT with a loading rate of 1.1 g COD/L.day were well within the functional range of the digesters employed in this study. The effluent TS and VS were slightly higher in the control digester D1 over the other digesters fed with sonicated sludge (Figure 6.1). TS removal was 91%, 92%, 94% and 96% in the control digester and digesters fed with sludge sonicated at 0.18W/mL, 0.33W/mL and 0.52W/mL, respectively. The average VS removal was 90%, 93%, 95% and 96% for the respective digesters.

The efficiency of organics degradation obtained at stage of 14-day HRT began to reveal a clearer difference among the digesters (Figure 6.2). The effluent TCOD and TS from the control digester D1 were apparently much higher than those measured from digesters D2, D3 and D4. The average TCOD removal efficiencies were 91%, 95%, 96% and 97% for digesters D1, D2, D3 and D4. Comparing with an 84% from the control unit, the TS removal efficiency improved to 87%, 92% and 94% for D2, D3, and D4, respectively. VS removal efficiency was 85% from the control unit D1, while higher removal of 89%, 94% and 95% was derived from the respective digesters.

At HRT 8-day, the organics and solids removal efficiencies obtained showed a greater superiority of digesters fed with sonicated sludge over the control unit. As shown in Figure 6.3, the TCOD removal efficiency reached 94% in D4, averaged at 91% in D3, and was 89% in D2. The control digester D1 was associated with the lowest efficiency of 85%. The SCOD removal efficiency increased from the 75% in the control digester to 82%-84% in digesters fed with sonicated sludge (D2, D3 and D4). The results of TS and VS removal further demonstrated the difference of digester performance arising from sonication pre-treatment of sludge. Compared with the VS removal of 74% in the control digester, higher removal of 85%, 91% and 93% were achieved by D2, D3 and D4, respectively.

More improvement was noted when the HRT was further reduced to 4-day as demonstrated in Figure 6.4. The TCOD removal efficiencies were 69%, 82%, 89% and 90% for digesters D1, D2, D3 and D4, respectively. The SCOD removal

efficiency was 64% for the control D1, and 78%, 81% and 80% for D2, D3, and D4, respectively. In terms of the solids removal efficiency, lower TS removal of 55% and VS removal of 57% were observed in the control digester D1 at 4-day HRT. Higher TS removal of 71%, 81% and 83% and VS removal of 76%, 85% and 86% were observed in D2, D3 and D4, respectively.

When the HRT was further shortened to 2-day, digester performance of D1 was severely impaired evidenced by deterioration in TCOD and SCOD removal to as low as 54% and 55%, respectively. Digesters fed with sonicated sludge, however, remained keeping up with the superiority on organics degradation at this phase. Digesters D3 and D4 demonstrated a TCOD removal of 78% and 80%, respectively, followed by a lower removal of 70% for D2. The control digester D1 could only achieve 35% for TS removal and 42% for VS removal. The TS removal was improved to 54%, 71% and 74% for D2, D3 and D4, respectively, while the VS removal increased to 61%, 73% and 76% in the respective digesters. The results indicated that a retention time of 2 days proved to be too short for sludge degradation and the organic loading rate had likely exceeded the capacity of the control digester D1. However, the digesters fed with sonicated sludge could achieve improved organics and solids removal at all shortened HRTs.

As summarized in Figure 6.6 to Figure 6.9, digesters D2, D3 and D4 exhibited improved removal efficiencies of TCOD, SCOD, TS and VS over those of the control digester D1 across all tested HRTs. Comparing with other reported studies, VS removal efficiency from sonicated sludge improved by 6-56% higher than the control in batch mode (Tiehm *et al.*, 2001), and by 10% in a semi-continuous operation at 22-day HRT (Tiehm *et al.*, 1997). An increase in VS removal by up to 34% and TCOD removal by up to 32% from this study demonstrated that improvement on organics degradation can be derived from sonication pretreatment of sludge for digester to be operated under a continuous operation mode.

Figure 6.6 Effects of HRT on TCOD removal during steady-state

Figure 6.7 Effects of HRT on SCOD removal during steady-state

Figure 6.8 Effects of HRT on TS removal during steady-state

Figure 6.9 Effects of HRT on VS removal during steady-state

6.2.2 Results of Biogas Production at Different HRTs

Figures 6.10-6.14 show the biogas production and biogas content at each HRT state. Accumulative biogas production from four digesters at 20-day HRT is illustrated in Figure 6.10 (a). The results indicated that higher amounts of biogas were derived from digesters fed with sonicated sludge than that of untreated sludge. Digester D4, fed with sludge sonicated at 0.52W/mL, demonstrated the highest biogas yield achieving a total of 6.9 L in 33 days of digestion, followed by D3 with 6.0 L, and 3.2 L for D2. Digester D1, fed with untreated sludge, recorded the lowest biogas yield as 2.8 L. Besides the enhanced biogas production, the percentage of methane in the biogas from digesters fed with sonicated sludge was also increased compared with that of the control digester. As shown in Figure 6.10 (b), the methane content remained around 50% in the control unit, while higher percentages of 52%, 53% and 56% were measured in digesters D2, D3 and D4, respectively. Methane was the major contents in the product gas stream and the balance of the total gas consist of carbon dioxide (36-41%), and a small fraction of nitrogen (8%-11%).

In the 14-day HRT operation, digesters fed with sonicated sludge continued to render higher biogas production. As shown in Figure 6.11 (a), the accumulative gas yield in ascending order was 3.9 L, 4.5 L 9.4 L and 10.2 L for digesters D1, D2, D3 and D4, respectively. Compared with the control digester D1, the biogas yield increased by 1.2, 2.4 and 2.6 times in digesters D2, D3 and D4, respectively. Similar to the previous phase at 20-day HRT, higher methane content was observed in the digesters fed with sonicated sludge. The average methane content was 53% in the control unit D1, while higher percentages of 54%, 57% and 63% were measured in digesters D2, D3 and D4, respectively.

Figure 6.10 Biogas production (a) and methane content (b) at 20-day HRT

Figure 6.11 Biogas production (a) and methane content (b) at 14-day HRT

Figure 6.12 Biogas production (a) and methane content (b) at 8-day HRT

Figure 6.13 Biogas production (a) and methane content (b) at 4-day HRT

Figure 6.14 Biogas production (a) and methane content (b) at 2-day HRT

As shown in Figure 6.12 (a), D4 demonstrated the highest total biogas production achieving 29.4 L after 50 days digestion in 8-day HRT, followed by D3 with 27.5 L, 13.8 L for D2 and the control unit D1 with the lowest record of 9.6 L. Compared with the control digester D1, the biogas production increased by 1.4, 2.9 and 3.1 times in digesters D2, D3 and D4, respectively. Methane contents in the product gas during the steady-state conditions remained at around 55% in the control digester, while higher percentages of 66%, 71% and 72% were measured in digesters D2, D3 and D4, respectively (Figure 6.12, b). Correspondingly, the contents of carbon dioxide were 37%, 26%, 22% and 20% for digesters D1 to D4, respectively. The composition of nitrogen, which ranged from 6% to 9%, was found to be unaffected with changing

HRT.

Compared with 55.6 L from the control digester D1, the biogas production increased to 138.1 L, 170.1 L and 112.6 L for digesters D2, D3 and D4, respectively, in the 4-day HRT as shown in Figure 6.13 (a). Digester D3, fed with sludge sonicated at 0.33W/mL, exhibited the highest biogas production at this loading rate. It should be noted that digester D4 which was fed with sludge sonicated at the highest sonication density of 0.52W/mL, did not produce the highest biogas production. The biogas of 112.6 L yield from D4 was almost 19% lower than that of D2 and 34% lower than that of D3. The results indicated that a significant decline biogas production took place in D4, which implied that methanogenesis process in digester D4 was depressed due to loading rate increased at 4-day HRT. The methane content during the steady-state conditions was around 64% in the control unit D1, while higher percentages of 73%, 76% and 77% were measured for digesters D2, D3 and D4, respectively.

When HRT was further shortened to 2-day, digester D2 demonstrated the highest biogas yield achieving 153.2 L after 55 days of digestion, followed by D3 with 147.6 L, and 124.3 L for D4 as shown in Figure 6.14. The control unit D1 recorded the lowest biogas yield of 78.5 L. The lowest methane content of 67% was recorded in the control digester, while higher methane contents of 74% - 76% were measured in digesters D2, D3 and D4.

Average biogas production during the steady-state conditions in all the HRT test phases is shown in Figure 6.15. Compared with the control digester D1, the average gas production in the digesters fed with sonicated sludge increased by 45-202% for D2, 184-220% for D3, and 115-205% for D4 throughout all the five operating HRT stages.

The results obtained indicated that sonication pretreatment of sludge could consistently improve the biogas production as well as methane content in the subsequent anaerobic digestion in a continuously operated UASB system. The improved methane content by sonication pretreatment under the UASB system operation corresponded with the results obtained in the batch mode digestion.

The consistent improvement in biogas production indicated the fact that sonication

pre-treatment could accelerate the organics degradation and convert more biosolids into biogas. The biogas improvement achieved from sonication pre-treatment in batch mode can range from 16 to 104% (Tiehm *et al.*, 2000; Chu *et al.*, 2002; Bougrier *et al.*, 2005). The increased biogas production up to 45-220% from this study demonstrated that the enhancement of biogas from sonication pre-treatment was more significant in the continuously operated digester than those in batch culture.

Figure 6.15 Steady-state biogas production rates

6.3 EVALUATION OF SONICATION PRETREATMENT OF SLUDGE APPLYING IN CONTINUOUS SYSTEM OPERATION

Proper functioning of upflow anaerobic sludge blanket (UASB) systems depends on both physical and biological parameters, which determine the final removal efficiency and conversion of organic compounds. Mahmoud *et al.* (2003) summarised that the major parameters, which have effect on digester performance, are (1) digester operational conditions (i.e. temperature, organic loading rate, hydraulic retention time and liquid upflow velocity), (2) influent characteristics (i.e. concentration, particle size distribution, and charges) and (3) sludge bed characteristics (i.e. charges, sludge hold up and exopolymeric).

In this study, four identical UASB digesters fed with sludge subject to different sonication conditions (untreated sludge, sludge sonicated at 0.18W/mL, 0.33W/mL and 0.52W/mL) were operated in-parallel at five HRTs of 20, 14, 8, 4 and 2-day. By

subjecting to consistent operating loading conditions, any difference in the performance among the digesters can be attributed to the factor of sonication pre-treatment. For a given digester, on the other hand, variation in the digester performance when subject to different HRTs can be regarded as the effects of the hydraulic retention times and the organic loading rate. The knowledge of interactions of sonication pretreatment and loading and operating conditions would provide a better understanding of the influence of sonication pretreatment of sludge on UASB system.

6.3.1 Discussion on Sonication Pretreatment and Removal of Organics and Solids

The results discussed so far have demonstrated that digesters fed with sonicated sludge would significantly improve organics degradation in both batch digester and continuous UASB system. The higher the sonication density, the better would be the organics removal, as demonstrated by digester D4 exhibiting the best organics degradation throughout of all HRTs tested. This suggested that organics removal in UASB digester is in positive relationship with the extent of sonication of sludge.

Improvement in the organics removal could be attributed to the interrelations between changed sludge characteristics and anaerobic biodegradation. Firstly, sonication was able to increase the sludge soluble organics, disrupt particles into smaller sizes, and increase particle surfaces, which result in higher hydrolysis rate in the initial process of anaerobic digestion as reported in Chapter 5. Hence, an enhanced hydrolysis of sludge particles could be experienced in the UASB digester fed with sonicated sludge.

Secondly, the disrupted sludge particle and disintegrated flocs matrix provided a better condition for mass transfer and substance contact. As reported in Chapter 4 (Figures 4.1-4.2), the flocs/particles in the untreated sludge were large in size, irregular in shape and of fluffy edges; while sonicated sludge contained smaller and dense particles. One major problem associated with large and fluffy sludge flocs was the transfer limitation for substrate and biogas between the core and the surface of the particles. Beneficial effects of flocs deagglomeration on the digestion process can be derived from a better exposure and contact of bacteria cells to hydrolysing

extracellular enzymes as compared to cells which are embedded and protected in sludge flocs agglomerates (Morgan and Forster, 1992; Veeken and Hamelers, 1999). With smaller particle size and higher particle surface, diffusion of hydrolytic enzymes and intermediate products or nutrients among the bulk solution, particle and bacteria cells can be enhanced. As a result, digester associated with sonication pretreatment is able to deliver better organics degradation efficiency.

Moreover, improved sludge settleability after sonication pretreatment could be another reason for the increased removal efficiency in the digesters. This is due to the reason that better sludge settleability is the key to maintain valuable biomass and to ensure digester stability in an upflow digester operated continuously (Mahmound *et al.*, 2003). As reported in Chapter 4, the sludge volume index (SVI) of the sonicated sludge reduced from 0.88 to 0.68-0.76 (Section 4.3.8), indicating that the sonicated sludge became denser and settled more readily. Hence, digesters fed with sonicated sludge were able to maintain more solids and to reduce the undesirable occurrence of suspended substances, which improved the quality of the effluent.

To evaluate further the effect of sonication treatment on removal of substances, an analysis of carbon, nitrogen and sulfur removal in the effluent at 4-day HRT was carried out and the results are tabulated in Table 6.1. The results indicated that under steady-state conditions digesters fed with sonicated sludge achieved better removal of all the substances tested. Comparing to the control digester D1, the efficiency for digesters fed with sonicated sludge (D2-D4) increased by 17-30% for carbon removal, 17-33% for nitrogen removal, and 21-37% for sulfur removal.

The improvement in carbon removal was probably due to the reason that digesters fed with sonicated sludge were able to enhance conversion of carbon substances in biosolids to methane. The increased nitrogen and sulfur removal could be attributed to the promoted anaerobic biomass in digesters fed with sonicated sludge. According to Speece and McCarty (1964), there is an obligate requirement for nitrogen and sulfur for active biomass activity. It is likely that sonicated sludge system stimulated the anaerobic biomass growth leading to a greater utilization of nitrogen and sulfur to synthesize new cells. As a result, the effluent nitrogen and sulfur from digesters D2 to D4 were lower than the control unit D1.

Table 6.1 Analysis of carbon, nitrogen and sulfur removal

Digesters	D1-control	D2-0.18W/mL	D3-0.33W/mL	D4-0.52W/mL
Influent				
Influent total solids %	2.47	2.49	2.46	2.45
Compound	38.18	39.13	38.17	38.49
in dry solids	6.26	6.18	6.17	6.29
by weight	1.12	1.03	1.10	1.16
Sulfur %				
Effluent				
Effluent total Solids %	1.09	0.67	0.48	0.33
Compound	36.31	36.07	35.67	33.54
in dry solids	5.96	5.78	5.24	4.34
by weight	1.40	1.32	1.54	1.56
Sulfur %				
Carbon, Nitrogen and Sulfur removal %				
Carbon removal %	58.04	75.20	81.78	88.26
Nitrogen removal %	57.99	74.83	83.43	90.71
Sulfur removal %	44.84	65.52	72.68	81.89
*Improvement extent on removal of D2-D4 over control D1 %				
Carbon removal %	-	17.16	23.73	30.23
Nitrogen removal %	-	16.85	25.44	32.72
Sulfur removal %	-	20.68	27.84	37.05

* The balance of removal efficiencies between D1 and D2-D4 (Removal % D1 – Removal %D2-D4), respectively.

6.3.2 Discussion on HRT and Removal of Organics and Solids

Organics and solids removal efficiency decreased as the HRT was shortened, which is a natural response of the UASB system to higher loading rate. Significant decline in organics removal for the control digester D1 at 4-day and 2-day HRTs indicated that the retention times were too short for sludge degradation and the organic loading rates had probably exceeded the digester capacity. On the other hand, digesters fed with sonicated sludge continued to display better solids removal efficiency at all HRT phases. This confirmed the hypothesis that the released soluble organics and disintegrated flocs structures in the sonicated sludge could relieve the restriction of bioconversion process.

The loading rate can be varied either by changing the influent concentration or by changing the HRT. The interrelations among flow rate, loading rate and retention time are described in Equation 6.1.

$$HRT = \frac{V}{Q} = \frac{COD}{OLR} \text{ ----- Equation 6.1}$$

Where HRT denotes hydraulic retention time, day; Q is the flow rate, L/day; V is the digester volume, L; TCOD is the influent concentration, mg/L; and OLR is the organic loading rate, mg/L.day.

In this study, the HRT was the only adjustable parameter to switch from one phase to another. Therefore, changing the HRT could affect directly the loading rate, upflow velocity and also the solids contact time in the UASB digesters.

In UASB systems, the relationship between the retention time and organics removal can be expressed as an empirical expression as shown in Equation 6.2 (van Haandel and Lettinga, 1994).

$$E = 1 - c_1(HRT)^{c_2} \text{ ----- Equation 6.2}$$

where E is the removal efficiency, constants c_1 and c_2 are characteristics of the anaerobic treatment performance.

In this study, the values of c_1 and c_2 were calculated through non-regression approach

by a data analysis software, namely Statistical Program for Social Science (SPSS). Tables 6.2 and 6.3 illustrate the constant values deriving from TCOD and VS removal among all the digesters. The coefficients for the digesters ranged between 0.94 and 0.99, indicating that the relationships between HRT and removal efficiency of UASB digester in this study can be adequately expressed by Equation 6.2.

The value of c_2 (Tables 6.2 and 6.3) fluctuated but the variation were marginal. On the other hand, c_1 values decreased notably from digester D1 to D4 from 0.84 in D1 to 0.35 in D4 for TCOD removal, and from 1.02 in D1 to 0.31 in D4 for VS removal. Based on Equation 6.2, the removal efficiency from a digester with smaller c_1 is less affected by variation in HRT. The analysis indicated that digesters fed with sonicated sludge were associated with smaller c_1 , which explains their resilience in organics removal against shortening in HRT.

To describe HRT with respect to removal efficiency, Equation 6.2 can be expressed as Equation 6.3 (van Haandel and Lettinga, 1994):

$$HRT = [(1 - E) / c_1]^{1/c_2} \text{ ----- Equation 6.3}$$

The HRT required to achieve a given removal efficiency (90% and 80%) can be calculated and are shown in Table 6.2 and 6.3 in terms of TCOD and VS removal. The results indicated that to achieve the same removal efficiency, the required HRT for the control digester D1 should be much higher than that of digesters fed with sonicated sludge (D2, D3 and D4) by two to three times for TCOD removal, and two to four times for VS removal.

Table 6.2 Empirical values of c_1 and c_2 ; HRT for 80% and 90% TCOD removal

Digesters	c_1	c_2	$E_{\text{COD removal}}$	R^2	HRT for $E_{\text{COD removal}}=0.90$	HRT for $E_{\text{COD removal}}=0.80$
D1 – control	0.84	-0.83	$1-0.84(\text{HRT})^{-0.83}$	0.97	13.0	5.6
D2 – 0.18W/mL	0.54	-0.82	$1-0.54(\text{HRT})^{-0.82}$	0.98	7.8	3.4
D3 – 0.33W/mL	0.38	-0.73	$1-0.38(\text{HRT})^{-0.73}$	0.95	6.2	2.4
D4 – 0.52W/mL	0.35	-0.83	$1-0.35(\text{HRT})^{-0.83}$	0.99	4.6	2.0

Table 6.3 Empirical values of c_1 and c_2 ; HRT for 80% and 90% VS removal

Digesters	c_1	c_2	$E_{\text{VS removal}}$	R^2	HRT for $E_{\text{VS removal}}=0.90$	HRT for $E_{\text{VS removal}}=0.80$
D1 – control	1.02	-0.75	$1-1.02(\text{HRT})^{-0.73}$	0.94	20.8	9.3
D2 – 0.18W/mL	0.60	-0.76	$1-0.60(\text{HRT})^{-0.76}$	0.99	10.6	4.2
D3 – 0.33W/mL	0.33	-0.60	$1-0.33(\text{HRT})^{-0.60}$	0.98	7.3	2.3
D4 – 0.52W/mL	0.31	-0.70	$1-0.31(\text{HRT})^{-0.70}$	0.97	5.0	1.9

As shown in Figure 6.6 (Section 6.2.1), all digesters began to indicate declining organics degradation as the HRT was shortened. However, the extent of decline was lower in the digesters fed with sonicated sludge than in the control unit. It could therefore be postulated that when operating at low HRTs for untreated sludge, the rate-limiting step of hydrolysis dominated the process and restricted the complex organic degradation into soluble form, thereby deteriorating the entire biochemical conversion process. As a result, the TCOD removal of the control digester decreased markedly from 97% at HRT of 20-day to 54% at 2-day HRT with a significant reduction of 43%. On the other hand, higher soluble organics and weakened floc structures present in the sonicated sludge could possibly overcome the restriction of hydrolysis (Chiu *et al.*, 1997; Lin *et al.*, 1997), which in turn resulting in the superior TCOD removal in D4 when operated at 20-day HRT (98%) and 2-day HRT (82%), respectively, with a much smaller decline of 16%.

It is apparent that ultrasound pre-treatment poses to be an effective method to achieve sound organics and solids removal even at reduced HRTs. Since HRT is directly relating to the digester volume and flow rate ($HRT = V / Q$), the reduced HRT allows treatment plant to design for smaller digester volumes, resulting in considerable cost savings. However, it might be too early to conclude that the best operation combination is associated with a higher sonication level and a shorter HRT, since the undesirable biogas depression and VFA accumulation were also noted under these conditions (to be discussed in the next section). Nevertheless, the result has adequately verified the effectiveness of ultrasound pre-treatment of sludge for anaerobic digesters.

6.3.3 Discussion on Sonication Level, HRT and Methane Yield

Marked enhancement in biogas production was noted in all three digesters fed with sonicated sludge in all HRT stages as reported earlier in this Chapter. The results indicated that the biogas production from each digester was significantly affected by the operating HRT as shown in Figure 6.15. All digesters exhibited an increased biogas production rate with reduced HRT. This was in agreement with the results observed by Zhao *et al.* (2004), in which the gas production rate was found to increase

with the solids loading rate.

To compare methane conversion efficiency at different HRT phases, methane yield expressed in liter per kg TCOD degraded is depicted in Figure 6.16. All digesters demonstrated an increasing methane generation as the HRT was shortened to 4-day, after which the methane yield began to decline as the HRT was further decreased. It seems that the corresponding HRT for the peak methane production was the point after which biological stress began to appear. Beyond this point, further shortening of the HRT corresponding to increase in loading rates, the methane yield began to decrease as the loading increased.

The peak methane yield was associated with a HRT of 8-day for digester D4, and with a HRT of 4-day for digesters D1, D2 and D3. This could be explained from the fact that as the organic rate increased with the shortening in HRT, more organics were provided as food to the microorganisms. Several authors reported that up to a certain limit, the treatment efficiency of complex organics in high rate anaerobic digesters increases with increasing loading rate. A further increase in OLR would lead to operational problems such as sludge bed flotation and excessive foaming at the gas-liquid interface, as well as accumulation of undigested ingredients. As a result, the conversion efficiency would deteriorate (Sayed, 1987; Ruiz *et al.*, 1997). Another possible explanation could be due to the effects of liquid upflow velocity which will be discussed in the next section.

As shown in Figure 6.16, all digesters demonstrated different methane yield curve. The control digester D1 exhibited the lowest peak methane yield at its optimal operating HRT, while the digesters fed with sonicated sludge (D2, D3 and D4) could achieve greater peaks of methane yield at their respective optimal HRT. This indicates that sonication pre-treatment of sludge could facilitate the digestion by adequately utilizing the feeding organics to improve the efficiency of methane conversion.

Figure 6.16 Effects of HRT on methane productivity

An interesting finding from this study is that sonication pre-treatment of sludge could alter the compositions of biogas. The percentages of methane were consistently higher in digesters fed with sonicated sludge than that of the control in both the batch culture and the UASB digesters. The methane content of the biogas stream of the control digester D1 was in the range of 50-64%, while higher methane contents of 52-74%, 53-77% and 56-77% were measured in digesters D2, D3 and D4, respectively. The results consistently indicated that sonication pre-treatment could increase the methane purity and correspondingly decrease carbon dioxide in biogas.

The increase of methane content of 2% - 13% achieved under continuous digestion corroborated the increase of 4% - 9% reported in the batch digesters (Figure 5.4). The reasons for the increase in methane content after pre-treatment have been discussed in Chapter 5. Since biogas purification is complex and expensive, biogas with high content of methane by means of sonication pre-treatment could result in cost saving in gas purification for practical applications.

6.3.4 Discussion on Upflow Velocity

Upflow velocity is one of the main factors affecting the efficiency of upflow digesters (Metcalf and Eddy, 1991; Wiegand, 2001). Increasing the flow rate by reducing the HRT can cause the upflow velocity to increase as expressed in Equation 6.4 (Metcalf

and Eddy, 1991).

$$G = \sqrt{\frac{P}{\mu V}} \text{-----Equation 6.4}$$

where G is the velocity gradient (s^{-1}), P is the power input (W), V is the volume of liquid in the digester (m^3), and μ is the dynamic viscosity (Pa s). This equation was developed based on the idea that more power input creates more turbulence and better mixing, which leads to higher velocity.

Low HRT is accompanied by high upflow velocity, which will lead to wash out of influent solids and viable biomass (Hang and Byeong, 1990; Mahmoud *et al.*, 2003). Therefore, severe deteriorated solids removal observed in the control digester at lower HRTs (high OLR) was likely due to high upflow velocities favouring more floatable flocs and lesser settleable solids contained in the digester. On the other hand, sonication pre-treatment of sludge improved solids settleability. Digesters fed with sonicated sludge, therefore, would allow more settleable solids to remain in the digesters, resulting in a better treatment and effluent quality.

On the other hand, high HRT associated with low upflow velocity would cause gas pockets to form and less likely to create adequate hydraulic turbulence in the sludge bed, resulting in poor mixing. Decreasing the HRT will not only enhance mixing by increasing hydraulic turbulence, but also more biogas will be produced at reduced HRTs. According to Hang and Byeong (1990), the upflow velocity should be high enough to provide good contact between substrate and biomass, as well as to facilitate the separation of gas bubbles from the surface of biomass. Hence, decreasing HRT within an allowable range could bring about higher upflow velocity which could offer better mixing and eventually leading to higher biogas production.

6.3.5 Discussion on Volatile Fatty Acids and Biogas Yield

While all digesters fed with sonicated sludge consistently exhibited increased biogas yield compared with the control digester, the highest biogas yield was observed in different digesters, depending on the operating HRT. Digester D4, associated with the

highest sonication density of 0.52 W/mL, exhibited the best biogas production at HRT phases of 20-day, 14-day and 8-day. While D3 with 0.33 W/mL, displayed the highest biogas yield at 4-day, and D2 with 0.18 W/mL showed superiority over D3 and D4 at HRT 2-day. It is likely that shortening HRT caused some kind of inhibition effect in biogas production in digesters fed with sludge sonicated with higher density.

6.3.5.1 VFA inhibition threshold

VFAs are important intermediary compounds in the metabolic pathway of methane fermentation, because complex organics must first be hydrolyzed into volatile fatty acids (VFAs) before further degradation. The establishment and maintenance of this balance is usually indicated by the measurement of VFA concentration (Show, 1996; Veeken *et al.*, 1999).

An examination of correlation of VFA and biogas was shown in Figure 6.17. At 2-day HRT, digester D4 exhibited higher VFA of 7565 mg/L and 1680 mg/L in the digester and in the effluent, respectively, than that of D2 (4594 mg/L and 566 mg/L) and D3 (5633 mg/L and 823 mg/L). According to Cobb and Hill (1991), a low VFA concentration is an indicator for a healthy and stable anaerobic digester.

Many studies had reported that excessive VFA could inhibit the methanogenesis process (Husain, 1998). Due to varied operating conditions and substrate, however, different thresholds for VFA inhibition had been established, ranging from 1000 mg/L to 4000 mg/L (Hill *et al.*, 1987; Dogan *et al.*, 2005; Stafford; 1982), and even at a very high concentration of 20,000 mg/L in the case of cheese whey digestion (Backus *et al.*, 1988). The results indicated that the VFA inhibition in this study had emerged at around 5880 mg/L in digester D4 at HRT of 4-day evidenced by its apparently biogas depression compared with D2 and D3 (Figure 6.15). When the HRT was further reduced to 2-day, the VFA increased to 5950 mg/L in D3 and 7500 mg/L in D4. As a result, the biogas production from these two digesters was markedly depressed.

Figure 6.17 VFA at different HRTs (a) influent; (b) in digester; (c) effluent

6.3.5.2 VFA evolution, sonication pre-treatment and HRT

As reported in Chapter 4, sonication pre-treatment could remarkably increase the soluble organics in the feed sludge. The hydrolysis rates in digesters fed with sonicated sludge were enhanced leading to a faster VFA production process. In the batch testing as reported in Chapter 5, VFA accumulation had been observed in digesters fed with sonicated sludge in the initial period of anaerobic digestion. Since no biogas depression was observed, the accumulated VFA in the batch culture was deemed within the acceptable range of the digesters. On the other hand, increased VFA plays a positive role in improving the conversion efficiency by providing more degradable substrate in the batch test.

According to Young (1980), acidic conditions are usually caused by organic overloading or hydraulic stress in an upflow anaerobic system. In the continuous UASB system operation, the digesters fed with sonicated sludge would continuously be loaded with more VFA and other soluble organics when the HRT was shortened. Due to the fact that the acidogenic bacteria growth is much faster than that of the methanogenic bacteria (Ronald, 1997); it was likely that the population of acidogenic bacteria increased promptly in responding to the increasing loading. Hence, acidogenesis was promoted and generated a substantial amount of VFA shortly after the sludge was fed into the digester. In contrast, slow-growing methanogenic biomass may not be able to catch up with the conversion rate of acidogenic bacteria, and were unable to accommodate excessive VFA. When the VFA is generated faster than it can be consumed, VFA accumulation would build-up in the digesters. VFA inhibition may occur when the VFA accumulated exceeds the digester capacity, like the case for D4 at HRT of 4-day and shorter. At this stage, the negative effects of sludge disintegration derived from sonication may surpass the beneficial effects.

Operational parameter of HRT along with influent characteristics can profoundly affect VFA production (Banerjee, 1997). Since sonicated sludge contained more VFA, digester fed with sonicated sludge would receive greater VFA loading upon HRT shortening. The implication was that digester fed with sonicated sludge would experience more impact from VFA increase upon HRT change, either in a positive or a negative way.

Figure 6.17 indicates that all digesters could adequately accommodate VFA and produce low effluent VFA at HRTs of 20 and 14-day. This indicated that the increased VFA by sonication pre-treatment had been adequately degraded in the anaerobic digestion at HRT 14-day and longer. As a result, the methane yield increased with the sonication density.

VFA inside the digester and in the effluent sharply increased for the D4 when HRT decreased to 4-day and 2-day. VFA accumulation together with depressed biogas production of digester D4 could be deemed as a justification that digesters fed with sludge sonicated at higher sonication density tended to suffer the over-acidogenesis at shorter HRT. Hence, VFA inhibition prevailed as HRT decreased to such an extent that, the negative effects of excessive VFA overshadowed the positive effects of enhancement by sonication.

6.3.5.3 *Biological balance of VFA producer and consumer*

It was from the experiment of continuous system operation, the possible side-effect of sonication pre-treatment in terms of VFA inhibition was observed. The occurrence of VFA inhibition in the subsequent anaerobic digestion was depended on sonication density and the HRT. Within the inhibition threshold (5880 mg/L), the more VFA offered to methanogenic bacteria, the better biogas production. Therefore, at higher HRT, the increased VFA played a positive role in overcoming hydrolysis limitation, which in turn improved the organics degradation and enhanced biogas production. When HRT decreased to an extent in which the methanogenic bacteria was unable to adequately degrade the VFA in the hydrolysis-favourable sonicated sludge, an overly acidogenesis and VFA accumulation would be experienced.

According to Valentini *et al.* (1997), there exists a subtle balance between the biomass consortium and degradable substrate in methanogenesis stage. The conversion of organic material to methane therefore involves a close relationship among different types of bacterial populations with the dynamic balance between production and utilization of VFA. In the UASB digester adopted in this study, three stages of hydrolysis, acidogenesis and methanogenesis all take place in one digester. When operating a digester in a continuous feeding mode, to maintain a favourable

environment for the mixed culture of microorganisms in a single digester, VFA production rate and utilization rate must be balanced.

6.3.6 Selection of Sonication Level and HRT for Continuous Digester Operation

Table 6.4 summarizes that the extent of digester improvement through sonication pre-treatment was largely influenced by sonication density and operating HRT. Greater superiority of the digesters fed with sonicated sludge was demonstrated at lower HRTs as compared with the control digester. The TCOD removal efficiency indicated that all digesters seemed to exhibit somewhat equally sound performance at HRT of 20 and 14-day. This implied that the distinction of organics removal efficiencies among digesters fed with untreated and sludge sonicated was marginal at 14-day HRT and longer.

The HRT of 2-day is deemed as a suboptimal condition for using ultrasound pre-treatment either. Digesters D3 (0.33W/mL) and D4 (0.52W/mL) encountered biogas depression due to VFA accumulation at this HRT. Although no biogas depression occurred, digester D2 (0.18W/mL) demonstrated poor TCOD removal (71%), which was much lower than the TCOD removal (97%) of the control digester D1 at 20-day HRT.

Therefore, the most optimum digester performance appeared to be associated with the digester D4 (0.52W/mL) operating at 8-day HRT. Compared with the control digester D1 at 20-day HRT, digester D4 (0.52W/mL) could achieve comparable TCOD (94%) and TS (92%) removal at 8-day HRT. Meanwhile, the biogas production and methane content were increased significantly in D4 at 8-day HRT.

Table 6.4 Improvement extent of digester performance

HRT	D1-Control	D2-0.18W/m L	Percent increase of D2*	D3-0.33W/m L	Percent increase of D3*	D4-0.52W/m L	Percent increase of D4*
TCOD removal efficiency (%)							
20	97	98	1	98	1	98	1
14	91	95	4	96	5	97	6
8	85	89	5	91	7	94	11
4	69	86	25	92	33	94	36
2	54	71	32	85	57	86	59
TS removal efficiency (%)							
20	91	92	1	94	3	96	5
14	84	87	3	92	8	94	10
8	72	84	12	89	17	92	20
4	55	71	16	81	26	85	30
2	35	54	19	66	31	72	37
Biogas production (mL/day)							
20	35	57	62	90	157	106	202
14	55	84	53	137	149	188	241
8	209	363	74	781	274	835	308
4	563	1638	191	2143	281	1455	158
2	723	2505	249	2474	242	1887	161

* Improvement, expressed as percentage over digester D1

6.4 SUMMARY

Feasibility and reliability of sonication pretreatment of the secondary sludge under continuous feeding mode were investigated using four identical UASB digesters operating at 20 to 2-day HRTs. Findings derived from the study presented in this chapter can be summarised as follows:

1. Feasibility of sonication pretreatment in a continuous digester operation conditions was demonstrated by enhancement on organics degradation efficiency, biogas production and methane content in digesters treating pre-sonicated secondary sludge. The best performance was achieved in Digester D4 at 8-d HRT.
2. The organics and solids removal efficiency increased with the sonication density, indicating that disintegrated secondary sludge was able to overcome the hydrolysis limitation by releasing soluble substances from disrupted flocs.
3. Greater superiority of the digesters fed with sonicated sludge was demonstrated at lower HRTs as compared with the control digester, in which the digestion of untreated secondary sludge seemed to be restrained by the hydrolysis. However, suppression of biogas production was noted at lower HRTs in digester fed with secondary sludge sonicated at higher intensities due to VFA inhibition.
4. It is presumed that the VFA inhibition prevails as the HRT is shortened to such an extent that, the negative effects of excessive VFA may overshadow the positive effects of enhancement by sonication. These findings suggest that in order to achieve the optimal performance of both organics removal efficiency and methane generation under continuous digester operation, VFA accumulation should be a factor to consider for optimization of sonication level and digester organic loading.

CHAPTER 7 COST-BENEFIT APPRAISAL

Experimental results obtained in this study indicated that ultrasound pre-treatment of sludge is a suitable method to improve sludge characteristics for anaerobic digestion. Significant digester improvement in terms of organics degradation, solids removal and methane production had proved the technical feasibility of ultrasound pre-treatment. These benefits, however, were derived from additional equipment cost (sonicator system) and energy consumption for sonication. To assess the economic viability of ultrasound pretreatment technique, a cost-benefit evaluation was conducted and presented in this chapter.

Since existing literature has limited information on economic justification of ultrasound pre-treatment of sludge, this chapter focuses on an analysis work of process optimization and control on the viewpoint of economic feasibility. An objective of the analysis is for the purpose of practical applications. An energy-balance method was used to demonstrate the net energy arising from sonication pre-treatment of sludge. Potential benefits including net energy gain, savings in construction cost, operating cost and disposal cost are summarized in comparison with the performance of practical digester from a local wastewater plant. Besides the economic benefits, beneficial effects on social and environmental areas are also discussed in the end of this chapter.

7.1 ECONOMIC BENEFITS

7.1.1 Comparison of Cost among Different Pretreatment Methods

Table 7.1 summaries the costs of various pre-treatment methods including ultrasonication. Comparing with other pre-treatment methods such as thermal, ozone, and chemical treatments, ultrasound treatment exhibits competitive cost. Based on the analysis from this study and Nickel (2002), ultrasound technique derives the lowest operating cost, indicating a potential of the technique on long-term application.

7.1.2 Net Energy

One of the main potential advantages expected from sonication pre-treatment is energy revenue in the form of enhanced methane production. As sonication requires energy input, the energy revenue derived from enhanced biogas production must surpass the energy cost plus methane obtained without pretreatment to make economic sense.

To find out the net energy gain or loss after sonication pretreatment, Equation 7.1 was used to justify the energy recovery for digester fed with sonicated sludge.

$$\Delta E = E_i - E_{\text{cost}} - E_{\text{control}} \text{ ----- Equation 7.1}$$

While E_i is the equivalent energy of methane produced from digester fed with sonicated sludge, E_{cost} is the corresponding energy cost for sonication or called pre-treatment cost, E_{control} or called opportunity cost is the equivalent energy of methane produced from the control digester at the same HRT, ΔE is the net energy gain or loss by using ultrasound pretreatment. The unit for all parameters in Equation 7.1 is described as kWh/kg COD to facilitate a comparison of digesters under different HRTs.

Table 7.1 Cost for various pre-treatment methods

Items	Ultrasonication		Mechanical disintegration (Müller <i>et al.</i> , 2004)	Chemical treatment with ozone (Verstraet and Ghyoot, 1994; Weemaes <i>et al.</i> , 2000)	Thermal treatment (Zheng <i>et al.</i> , 1998; Rienks, 1998)
	(This study)	(Nickel, 2002)			
Equipment cost, € (assumed 10-year life-scale for equipment)	10,000 (1.5 kW) 300,000 (30 kW)- 600,000 (60 kW)		400,000-900,000	No special equipment required	1,871,000- 5,680,000
Operating cost, €/m ³ sludge	0.12-0.34 ¹	0.45-0.90 ²	1.13 ³	11.25-17.25 ⁴	2.91 ⁵

Based on currency conversion rate: 1 € = 3.1 S \$; 1 € = 2.2 Dutch guilders; 1 € = 1.2 US \$

¹ €12 per kWh (PUB, Singapore); $[0.18\text{W}/\text{mL} \times 10^6 \text{ mL}/\text{m}^3 \times 1\text{min} \times \phi 12] \times [10^3 \text{ W}/\text{kW} \times 60 \text{ min}/\text{h}] = 0.36 \text{ SS}/\text{m}^3$, then $0.36 \times 3.1 = 0.12 \text{ €/m}^3$

²Original info.: 30 kW-system for 120 m³/d sludge at 0.075 €/kWh (Nickel, 2002).

³Original info.: 15 kWh/m³ sludge; based on 0.075 €/kWh (Müller *et al.*, 2004).

⁴Original info.: 0.575 €/kg TS (Verstraet and Ghyoot, 1994) and 0.375 €/kg TS (Weemaes *et al.*, 2000). Assumed sludge with 3% TS, then $0.375 \text{ €/kg TS} \times 30 \text{ kg TS}/\text{m}^3 = 11.25 \text{ €/m}^3$; $0.575 \text{ €/kg TS} \times 30 \text{ kg TS}/\text{m}^3 = 17.25 \text{ €/m}^3$

⁵Original info.: 213 Dutch guilders/ton TS. Based on currency conversion: 1 € = 2.2 Dutch guilders, then $213 \times 2.2 = 97 \text{ €/ton TS}$ (Zheng *et al.*, 1998; Rienks, 1998). Assumed sludge with 3% TS, then $97 \text{ €/ton TS} \times 0.03 \text{ ton TS}/\text{m}^3 = 2.9 \text{ €/m}^3$.

Table 7.2 presents the net energy for the digesters in all HRT phases calculated based on Equation 7.1. It should be pointed out that evaluation according to Equation 7.1 only takes account of energy gain or loss out of the increased methane arising from sonication. Other factors such as savings in construction cost and operating cost will be discussed in the next section.

As sonication was applied at HRT of 20-day, the net energy for digester D2 (0.18W/mL) is negative, which means the sum of pretreatment cost (E_{cost}) and the opportunity cost (E_{control}) is larger than the energy gain from methane in this case. Significant net energy gain would be derived from digester D3 (0.33W/mL) and D4 (0.52W/mL) at 8-day HRT; and digester D2 (0.18W/mL) and D3 at 4-day HRT. This implied that sonication pretreatment could lead to net energy revenue after deducting the pretreatment cost (E_{cost}) and opportunity cost (E_{control}). The energy gain derived from digester D4 was less than that of D2 and D3 as HRT reduced to 4-day and shorter. This could be due to the fact that digester D4 (0.52W/mL) incurred the highest pretreatment cost (E_{cost}) from the highest sonication density applied, which requires a greater enhancement in methane to cover the cost. Moreover, when the HRT reduced to 4-day and 2-day, the suppression of biogas production in D4 further depreciate the net energy gain.

Based on the energy analysis, it is interesting to note that the net energy gain or loss arising from using ultrasound pretreatment is determined by both HRT and the sonication density. Digester D4 operated at 8-day HRT was recommended as the optimal operating conditions due to its significant net energy gain and sound digester performance. Although the highest net energy gain of 2.01 kWh/kg COD was associated with digester D3 at 4-day HRT, the TCOD and VS removal efficiencies in this case were 5% and 8%, respectively, lower than those of the digester D4 at 8-day HRT.

Table 7.2 Net benefit analysis

	20-day HRT	14-day HRT	8-day HRT	4-day HRT	2-day HRT
Methane yield (L/kg COD)					
D1-Control	40.82	26.50	58.06	78.22	52.21
D2-0.18W/mL	52.00	48.00	128.61	207.85	157.93
D3-0.33W/mL	86.73	76.00	214.97	297.67	157.77
D4-0.52W/mL	101.82	104.72	232.00	179.67	128.41
¹ Equivalent energy, E_i (kWh/kg COD)					
D1-Control (E_{control})	0.41	0.27	0.58	0.78	0.52
D2-0.18W/mL	0.52	0.48	1.29	2.08	1.58
D3-0.33W/mL	0.82	0.76	2.15	2.98	1.58
D4-0.52W/mL	0.96	1.05	2.32	1.80	1.28
² Pretreatment energy cost, E_{cost} (kWh/kg COD)					
D2-0.18W/mL	0.14	0.12	0.10	0.10	0.10
D3-0.33W/mL	0.25	0.22	0.19	0.19	0.19
D4-0.52W/mL	0.39	0.34	0.30	0.30	0.30
³ Net energy, ΔE (kWh/kg COD)					
D2-0.18W/mL	-0.03	0.09	0.61	1.20	0.96
D3-0.33W/mL	0.16	0.27	1.38	2.01	0.87
D4-0.52W/mL	0.16	0.44	1.44	0.72	0.46

¹) According to the empirical estimation of 10 kWh/m³ CH₄ (Nickel, 2002)

²) Sonication energy consumption cost: Sonication density $\times$ sonication time $\div$ average COD concentration (i.e. E_{cost} of D2 at 20-day HRT: 0.18W/mL $\times$ 1min $\times$ 10⁻³ kW/W $\times$ 60⁻¹ hour/min $\times$ 1 L/mL $\div$ 0.022 kg COD/L = 0.14 kWh/kg COD)

³) Net benefit $\Delta E = E_i - E_{\text{cost}} - E_{\text{control}}$ (i.e. ΔE of D2 at 20-day HRT: 0.52-0.14-0.41= -0.03)

Figure 7.1 Net energy gain or loss from ultrasound pre-treatment

7.1.3 Other Savings for Treatment Plant

Besides the energy benefits in terms of net energy of the increased methane, other benefits for employing ultrasound pre-treatment are also worth mentioning. For example, the digester fed with sludge sonicated at 0.52W/mL can be operated at 8-day HRT to maintain the same performance with the control digester operated at 20-day HRT. This would bring benefits to the treatment plant in terms of capital saving from construction of smaller digester, operating savings due to reduced HRT and smaller digester, and cost saving in sludge disposal from reduction of digested sludge solids.

Potential savings arising from digester fed with sludge sonicated at 0.52W/mL operated at 8-day HRT are compared with a practical digester (20-day HRT) performance of a local wastewater plant as shown in Table 7.3.

Table 7.3 Summary of relating benefits

	Amount	Remarks
A) Estimated potential savings (comparison of untreated sludge at conventional HRT 20d and sonicated sludge at shortened HRT 8 d)	<p>A capital saving of S\$1,059,800 per digester</p> <p><i>The capital saving derived by S\$1,766,340 $\square$ 60%</i></p>	Capital savings on construction of smaller volume digester due to reducing HRT from 20 to 8 days, through which the digester size could reduce by 60%.
B) Increased energy revenue of methane	<p>Methane revenue increased by S\$760 per day per digester</p> <p><i>Based on a net energy gain of 1.44 kWh/kg COD derived from D4 at 8-day HRT (Figure 7.1) then the increased revenue calculated as:</i></p> <p><i>175 m³/day $\square$ 25kg COD/m³ $\square$ 1.44kWh/kg COD $\square$ 0.12 S\$/kWh = 756 S\$/day</i></p>	Revenue on net energy gain arising from increased methane.
C) Saving in operating cost	<p>An operating cost saving of S\$256 per day per digester</p> <p><i>Based on operating cost is proportional to digester volume, then the cost saving derived by 3552kWh $\square$ 60% $\square$ 0.12</i></p>	Savings on operating cost due to the reduced digester and shortened HRT.

Relevant information provided by a local wastewater plant:

- 1) Size of existing egg-shape anaerobic digester and the land area used: Each 5,000 m³, Radius 21 m, Area 588.78 m².
- 2) Total cost of the egg-shape anaerobic digesters and the existing operational cost: eight numbers. Each cost S\$1,766,340.00; 3,552 kWh/day. Electricity tariffs is S\$0.12/kWh.
- 3) The treatment capacity of the current egg-shape anaerobic digesters: each average is 175 m³/day; the COD average concentration is 25,000 mg/L (25 kg/m³).

The reduced HRT leads to a smaller digester volume designed, which will bring about substantial capital saving from construction of smaller digester. On the assumption that construction cost is proportional to the digester volume, as much as S\$1 million would be saved if HRT were reduced from 20-day to 8-day. The decreased digester volume could also likely reduce the operating cost based on an assumption that the operating and maintaining cost are proportional to digester volume. The increased energy revenue (Table 7.3, B) is a further calculation based on Figure 7.1. An additional energy gain of 1.44 kWh/kg COD arising from sonication pre-treatment would increase the energy revenue by S\$760 per digester per day.

As shown in the Table 7.3, sonication pre-treatment of sludge is a promising technique with profitable potentials. It should be noted that the evaluation in Table 7.3 was conducted by using results obtained from laboratory-scale experiment, it is likely that results from pilot-scale or full-scale experiment would help increase the accuracy of the values in the evaluation. Nevertheless, it could be envisaged that it is possible to derive economic benefits out of sonication pre-treatment.

7.2 ENVIRONMENTAL AND SOCIAL BENEFITS

Besides the economic benefits discussed earlier, there are some other important benefits of ultrasound pre-treatment of sludge, which are not easily quantified. The following sections attempt to discuss these environmental and social benefits qualitatively.

7.2.1 Renewable Energy

Irreversible shortage of fossil fuels is expected before the middle of the 21st century and the supply disruption is expected to start first with natural gas (Donald, 2004). Natural gas is formed from the fossilized remains of plants and animals over a process of millions of years. Biogas, the end produce of anaerobic digestion, has been considered to be a source of renewable energy and poses a great potential to be as substitute for natural gas. Therefore, the markets for

biogas from biomass in local or worldwide are large, widespread, and long-term as long as the biogas production is technologically and economically competitive.

Normally, the biogas from anaerobic digestion is poor competitive with natural gas mainly due to limited production and low value content. With enhanced production via sonication pre-treatment, the purity of methane in the biogas can be improved and the post-treatment cost can be decreased, thereby increasing the commercial competition of biogas. The social acceptance of new biomass technology may also be promoted by its consistent quality.

The results of sludge ultrasound pre-treatment might suggest a possible approach to improve the production of renewable energy from waste, and at the same time to improve anaerobic digestion efficiency. This is doubly advantages in terms of resource conservation and environmental benefits.

7.2.2 Greenhouse Gas

There is an escalating concern of increasing concentrations of atmospheric CO₂, which is believed to be the greenhouse gas responsible for much of the climatic changes and temperature increases. Energy plants must be designed and operated to reduce net CO₂ emissions to the atmosphere under legislations in many countries. Methane and carbon dioxide are two main components in biogas from anaerobic digestion process; however, sonication pre-treatment of sludge could alter the composition of biogas. In a three-year study, a notable decrease of carbon dioxide in biogas was recorded consistently from digesters fed with sonicated sludge. Compared with 30-35% contained in biogas from the control digester, the carbon dioxide reduced to 15-25% in digester fed with sonicated sludge (Show, *et al.*, 2005).

7.2.3 Local Interest

It is well known that the optimal mesophilic temperature range is 33-40°C. Hence, anaerobic digestion technique is especially suitable for local weather since tropic region pose unique advantages of favourable temperature for

anaerobic digestion. Compared with non-tropic regions, where more energy is required to maintain the temperature of the sludge digesters, local industry may obtain more benefits from anaerobic digestion.

With the development of sonication pre-treatment as a new approach to improve the efficiency of energy recovery from waste, biogas will display more important role in the further. Labelling as an environment-friendly, renewable and sustainable green image, biogas production might enhance the value of current waste industry or even cultivate new industry.

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

Based on the experimental results obtained, the following conclusions can be derived.

8.1 ULTRASONICATION ON SLUDGE CHARACTERISTICS

The effects of ultrasound treatment on sludge characteristics were investigated in terms of particle size, total and soluble chemical oxygen demand (COD), dissolved organic carbon (DOC), temperature, pH, volatile fatty acid (VFA), oxidation-reduction potential (ORP), settleability and turbidity. The results indicated that the sonication resulted in a reduction of sludge particle size from 47-51 μm to 7-15 μm , and an increase in the soluble chemical oxygen demand (SCOD) to total COD (TCOD) ratio from 3-9% to 17-25%, indicating effective disruption of sludge solids and transformation of organic substances into soluble form.

Ultrasound treatment can be influenced by sonication time, sonication density, sludge type and solids concentration. The most superior effects of sonication was associated with the secondary sludge, with an optimum total solids (TS) content ranging between 2.3% and 3.2% and a sonication time of 1 minute. The extent of sludge disintegration increased with sonication time and sonication density. But a higher ultrasound density required less specific energy (kWh/kg DS) to derive a better sludge disintegration. Ultrasonication had a better effect on the secondary sludge than the primary sludge and mixed sludge at different mixing ratios. The ultrasound would be attenuated by scattering and absorption if the solids concentration exceeds the optimal solids concentration range.

Generation of cavitation bubbles caused by ultrasonic waves poses to be the

dominant reason for sludge disintegration. The laboratory results suggest that sonication density is more important criteria than sonication time in the selection of sonication parameters. Sonication density played a very important role in determining the number and the behaviour of cavitation bubbles in the treatment process.

8.2 ULTRASOUND PRE-TREATMENT ON ANAEROBIC BATCH CULTURE OF SLUDGE

The influence of ultrasonication on hydrolysis, acidogenesis and methanogenesis in anaerobic decomposition of sludge was examined in the batch digestion of sludge. The experimental results indicated that sonicated sludge exhibited pre-hydrolysis and pre-acidogenesis effects in the anaerobic decomposition process. First order hydrolysis rates increased from 0.0384 d^{-1} in the control digester, to 0.0456 , 0.0576 , and 0.0672 d^{-1} in the digesters fed with sludge sonicated at densities of 0.18 W/mL , 0.33 W/mL and 0.52 W/mL , respectively. It was deduced that the increased first-order hydrolysis rate was mainly due to the increased sludge surface areas and the improved mass-transfer conditions. The sonication appeared to be ineffective in relation to acidogenesis reaction rates, but it provided a better buffering-capacity to diminish adverse impact of acidification. Batch culture fed with sonicated sludge demonstrated enhanced methanogenesis over the control unit, with improvement in biogas production of up to 53%, and increase in methane content in the biogas from 57% to 66%. Determination of co-enzyme F_{420} verified that sonication is able to promote the growth of methanogenic biomass and to facilitate a positive methanogenic microbial development in suppressing the initial methanogenesis limitation.

With a verification of Veeken-Hamelers equation, it was revealed that batch culture fed with sonicated sludge had not only accelerated the conversion of particulate organics into degradable substrate, but also stimulated and promoted the growth of methanogenesis biomass. The acclimation period was shortened and the methane conversion was enhanced. The results suggested that sludge disintegration by ultrasonication could boost anaerobic bioconversion process

resulting in accelerated and enhanced organics degradation, biogas production and methane composition.

8.3 ULTRASOUND PRE-TREATMENT ON UASB DIGESTION OF SLUDGE

The UASB system was used to examine the feasibility and reliability of sonicated sludge in a continuous digester operation at different hydraulic retention times (HRTs) of 20, 14, 8, 4, and 2-day. Comparing to the control digester fed with untreated sludge, the TCOD removal improved by 1-17%, 1-31% and 1-32% in the digesters fed with sludge sonicated at densities of 0.18W/mL, 0.33W/mL, and 0.52W/mL, respectively. The improved total solids (TS) removal was also improved by 1-21%, 3-42% and 5-45% in the respective digesters. The increased TCOD and TS removal efficiency corresponded with the increase in biogas production by 45-175%, 140-220% and 86-220% in the respective digesters, as well as an increase in methane composition by 2-19%.

Greater superiority of the digester fed with sonicated sludge was demonstrated at lower HRTs operation. Biochemical conversion of untreated sludge seemed to be restrained by the limiting step of hydrolysis, while the sonicated sludge was able to relieve the restriction of hydrolysis through disruption of floc structures. The extents of sludge disintegration and organics degradation were in positive relationships with sonication densities within the range tested. Another contribution from this part study was to point out the potential drawback of using ultrasound pretreatment. Suppression of biogas production was noted at lower HRTs in digester fed with sludge sonicated at higher densities, suggesting that VFA inhibition could be a factor to consider for optimization of sonication level and digester organic loading.

8.4 CONCLUDING REMARKS

The results derived from this study demonstrated that ultrasonic pre-treatment is a promising method to improve anaerobic digestion of the secondary sludge. The mechanism of ultrasonication on sludge was proposed in terms of cavitation

bubble formation and collapse, behaviour of transient and stable bubbles, as well as acoustic energy adsorption phenomena. The limiting stage analysis from the batch culture study unveiled that accelerated bioconversion of the secondary sludge is predominantly attributed from the increased rate of first-order hydrolysis and the promoted growth of methanogenic biomass. Determination by co-enzyme F_{420} verified that sonicated sludge culture could enhance the methanogenic microbial development. The work is a new attempt to provide further fundamental understanding on ultrasonication of sludge, leading to a better understanding and control of sludge digestion and biogas yield.

The operating conditions and reactor performance of UASB digesters treating sonicated secondary sludge under continuous operation were established. The digesters fed with sonicated sludge demonstrated more efficient and stable operation even at reduced HRTs, which is expected to bring benefits to treatment plants in terms of capital saving, increase of biogas revenue and cost saving in sludge disposal. Based on the cost-benefit evaluation, optimal digester operating conditions were derived from the point of view of technical performance and economic viability. The information derived could serve as a useful reference for future pilot- or full-scale ultrasound applications for anaerobic digestion.

8.5 RECOMMENDATION FOR FURTHER STUDIES

- The results obtained from this study showed sonication of sludge impacted biogas composition and influenced microbial hydrolysis, acidogenesis and methanogenesis. A microbial study, using advanced techniques such as DNA identification, should therefore be conducted to quantitatively examine the activity of hydrogenotrophic and acetotrophic bacteria during anaerobic digestion of sonicated sludge. Previous studies reported the promoted methanogenic bacteria evidenced by the increased concentration of co-enzyme F_{420} . A future study should investigate further the microbial consortia involved in each anaerobic step by assessing their respective enzyme activity.

- Many organic compounds generate problems during wastewater treatment due to their resistance to biodegradation and potential toxicity to microorganisms. A future study should therefore be conducted to explore the effect of sonication treatment on such compounds.
- An increased nitrogen and sulfur removal from sonicated sludge was noted in this study, which may reflect an increased protein degradation. Future studies should therefore investigate the effects of ultrasound treatment on protein degradation, in order to prevent odor problems for instance.

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Appendix A: Properties of Sonicated Sludge

Secondary Sludge		0	0.5	1	5	10	15
Sonication Time min							
Probe Power 0.18 W/mL							
Specific Energy	kWh/m ³	0.00	1.50	3.00	15.00	30.00	45.00
	Temperature °C	17.40	19.40	20.40	25.90	32.90	38.40
	Size µm	46.8	37.0	31.2	14.6	11.1	10.2
	SCOD mg/L	898	928	1047	1550	1913	2460
	SCOD/TCOD %	3.5	5	7	8.5	10	12
	pH	7.1	7.0	7.0	6.8	6.7	6.5
	ORP mV	-295	-294	-288	-255	-242	-219
Probe Power 0.33 W/mL							
Specific Energy	kWh/m ³	0.00	2.75	5.50	27.50	55.00	82.50
	Temperature °C	19.00	21.50	23.00	37.00	50.00	60.00
	Size µm	46.8	21.3	13.9	9.6	8.6	8.5
	SCOD mg/L	897	900	1500	2260	3140	4000
	SCOD/TCOD %	3.5	7	8	12	16	21
	pH	6.9	7.0	7.0	6.8	6.5	6.4
	ORP mV	-295	-288	-280.0	-245	-215	-160
Probe Power 0.52 W/mL							
Specific Energy	kWh/m ³	0.00	4.33	8.67	43.33	86.67	130.00
	Temperature °C	16.50	20.50	23.50	42.00	58.50	70.00
	Size µm	46.8	14.8	9.8	8.2	7.9	7.7
	SCOD mg/L	898	1184	1920	3080	4100	5342
	SCOD/TCOD %	3.5	5	7.5	15	17	27
	pH	7.1	7.0	7.0	6.7	6.4	6.3
	ORP mV	-295	-285	-260	-220	-150	-130

Appendix A: Properties of Sonicated Sludge (Con't)

Primary Sludge

Sonication Time min	0	0.5	1	5	10	15
Probe Power 0.18 W/mL						
Specific Energy kWh/m ³	0.00	1.50	3.00	15.00	30.00	45.00
Temperature °C	19.00	19.00	21.00	29.00	35.00	39.00
Size µm	49.0	38.0	29.0	21.0	19.0	17.5
SCOD mg/L	1526	1628	1771	2039	2774	2864
SCOD/TCOD %	9	10	11	12	17	17
pH	6.5	6.3	6.2	6.3	6.2	6.2
ORP mV	-292	-291	-288	-277	-292	-278
Probe Power 0.33 W/mL						
Specific Energy kWh/m ³	0.00	2.75	5.50	27.50	55.00	82.50
Temperature °C	17.20	20.20	22.20	36.20	51.20	62.20
Size µm	49.0	23.0	18.0	16.0	15.8	15.5
SCOD mg/L	1102	1236	1080	1526	1860	2150
SCOD/TCOD %	7	8	7	9	11	13
pH	6.5	6.4	6.3	6.2	6.2	6.1
ORP mV	-295	-288	-280.0	-275.0	-279.0	-190.0
Probe Power 0.52 W/mL						
Specific Energy kWh/m ³	0.00	4.33	8.67	43.33	86.67	130.00
Temperature °C	17.60	20.60	23.60	44.60	58.60	69.60
Size µm	49.0	16.0	14.5	14.0	13.0	12.0
SCOD mg/L	835	1080	1036	1392	1481	1615
SCOD/TCOD %	5	6	6	8	9	10
pH	6.5	6.3	6.2	6.3	6.1	6.1
ORP mV	-292.0	-280.0	-263.0	-279.0	-200.0	-185.0

Appendix B: Gas Production Record

1.1 g COD/L.day: Biogas production (ml/d)

Duration (days)	1	2	3	4	5	7	9	11	13	15
control	90	150	280	490	400	240	220	250	110	80
0.18W/mL-1min	20	70	120	250	620	430	430	360	190	160
0.33W/mL-1min	60	180	380	680	380	824	680	520	510	340
0.52W/mL-1min	440	750	947	660	610	540	410	320	300	280

Duration (days)	18	20	22	24	27	31	33
control	100	70	90	80	70	60	70
0.18W/mL-1min	150	120	110	100	90	110	110
0.33W/mL-1min	295	270	210	180	170	180	170
0.52W/mL-1min	240	270	260	230	210	200	190

1.8 g COD/L.day: Biogas production (ml/d)

Duration (days)	1	2	3	4	5	7	9	11	13	15
control	130	200	300	550	440	420	350	320	230	190
0.18W/mL-1min	85	120	205	350	543	551	470	390	280	240
0.33W/mL-1min	100	210	450	720	660	1280	1000	890	815	770
0.52W/mL-1min	640	1150	1440	1000	700	760	560	510	430	390

Duration (days)	18	20	22	24	26	28	33	35
control	160	120	90	100	90	100	80	90
0.18W/mL-1min	235	180	124	184	161	155	140	150
0.33W/mL-1min	557	370	310	280	250	260	250	240
0.52W/mL-1min	350	370	340	310	320	300	290	290

3.6 g COD/L.day: Biogas production (ml/d)

Duration (days)	1	2	3	4	5	6	7	8	9	10	11	12
control	5	15	19	22	25	28	28	31	39	58	78	112
0.18W/mL-1min											0	35
0.33W/mL-1min	15	25	30	35	38	35	40	80	125	180	270	355
0.52W/mL-1min									0	86	148	322
Duration (days)	13	14	15	16	17	18	20	21	22	23	24	25
control	187	221	254	310	365	440	324	325	315	213	280	193
0.18W/mL-1min	79	155	235	395	447	480	510	492	760	766	650	456
0.33W/mL-1min	480	610	780	1040	1022	1245	1327	1356	1750	2100	1610	949
0.52W/mL-1min	445	675	680	860	1124	1281	1455	1583	1820	2240	1580	1020
Duration (days)	26	27	28	29	31	33	34	36	37	39	40	42
control	189	208	211	200	229	266	330	310	464	490	550	590
0.18W/mL-1min	377	320	455	354	306	311	332	322	526	690	820	910
0.33W/mL-1min	778	750	710	579	634	624	645	502	632	610	700	840
0.52W/mL-1min	800	620	760	890	728	723	878	743	863	740	980	1100
Duration (days)	44	46	48	50								
control	450	420	340	378								
0.18W/mL-1min	860	610	580	550								
0.33W/mL-1min	1020	980	990	1090								
0.52W/mL-1min	880	1240	1050	1160								

7.2 g COD/L.day: Biogas production (ml/d)

Duration (days)	1	2	3	4	5	6	7	8	9	10	11	12
control	400	700	600	600	890	1000	1100	1400	1400	1500	1510	1000
0.18W/mL-1min	900	1200	1300	1000	1270	1400	1700	2500	1300	1900	2100	2400
0.33W/mL-1min	800	1400	1100	800	1400	1800	2100	3400	3620	3800	3450	3510
0.52W/mL-1min	600	1000	1200	1300	1400	1200	1700	2700	1900	2000	2400	1900
Duration (days)	13	14	15	16	17	18	19	20	21	22	23	25
control	900	1700	1300	900	1700	2200	2400	1300	1100	1000	600	700
0.18W/mL-1min	2700		1800	1550	2700	3800	4030	3900	2800	3500	2550	2670
0.33W/mL-1min	3600	4050	4450	3600	4200	4560	4630	4630	3600	4100	2700	2900
0.52W/mL-1min	2100	1700	1700	2200	2000	3100	3400	3500	2700	2900	2300	2500
Duration (days)	26	27	29	31	33	34	35	36	37	38	39	40
control	1050	1300	1400	1050	1200	1100	600	400	350	300	400	700
0.18W/mL-1min	2450	2900	2700	2450	2100	2900	2600	2350	2800	2500	2400	3540
0.33W/mL-1min	3100	2980	2800	3240	3000	3180	2600	2650	2300	2050	2100	3530
0.52W/mL-1min	2180	2700	1700	1850	1250	1300	1200	1000	1400	1300	1500	1800
Duration (days)	41	42	43	44	45	46	47	48	49	50	51	52
control	1220	1110	1390	590	1170	1170	1220	1400	1010	1200	1100	1000
0.18W/mL-1min	2860	3080	3190	3620	3720	3320	3270	3430	3120	3320	3010	2230
0.33W/mL-1min	3770	3350	3360	2680	4060	3910	3920	3670	3880	3700	3240	2570
0.52W/mL-1min	1800	1770	1400	1830	1440	2000	1885	1950	1940	1990	1930	1650
Duration (days)	53	54	55	56	57	58	59	60				
control	1100	790	790	720	990	890	910	880				
0.18W/mL-1min	2500	1890	2190	2100	2240	2190	2000	2050				
0.33W/mL-1min	2670	2480	2690	2350	2570	2660	2520	2820				
0.52W/mL-1min	1720	1650	1660	1320	1200	1580	1690	1640				

14.5 g COD/L.day: Biogas production (ml/d)

Duration (days)	1	2	3	4	5	6	7	8	9	10	11	12
control	970	1050	1100	770	970	980	950	940	970	980	1160	1470
0.18W/mL-1min	1990	2100	2245	1870	1970	2010	2040	2160	2030	2000	1630	2250
0.33W/mL-1min	2780	2720	2860	2810	3000	2860	2830	2590	2690	2650	1870	2970
0.52W/mL-1min	1660	1590	1130	1580	1380	1420	1500	1390	1470	1440	2020	2260
Duration (days)	13	14	15	16	17	18	19	20	21	22	23	24
control	1620	1720	2060	2000	1960	1830	1970	1890	1850	1580	1780	1870
0.18W/mL-1min	3220	2950	3620	4320	4970	2900	4930	2890	2650	4390	5060	3980
0.33W/mL-1min	3280	3090	3400	3720	4450	2940	3430	2900	3170	3980	4630	3580
0.52W/mL-1min	4100	3050	4020	4300	3590	3690	1950	2310	3100	3000	2980	2750
Duration (days)	25	26	27	28	29	30	31	32	33	34	35	37
control	1900	1600	1760	1660	1290	1650	1480	1190	1780	1790	2420	790
0.18W/mL-1min	3340	3420	3060	3200	3540	4300	3690	2200	2250	2890	2140	3290
0.33W/mL-1min	2970	2870	2790	2560	2780	2260	2900	2720	2340	2430	2560	2900
0.52W/mL-1min	2440	2560	2690	2880	2870	2430	2670	2490	2310	2310	2880	2690
Duration (days)	38	39	41	42	44	45	46	47	48	50	51	52
control	2108	2530	2100	2520	1780	1150	2120	1520	1290	1420	1100	1310
0.18W/mL-1min	3470	2140	2980	2430	3270	3120	2930	3320	3280	3370	3250	3520
0.33W/mL-1min	2890	2580	2560	2870	2809	2690	3040	2980	2260	1740	2430	2430
0.52W/mL-1min	2060	2690	2300	2540	2240	2300	2580	2660	2290	1700	2453	2540
Duration (days)	53	54	55									
control	1180	1090	1130									
0.18W/mL-1min	3390	3200	3100									
0.33W/mL-1min	3400	2430	3010									
0.52W/mL-1min	2035	2250	2450									