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Anaerobic treatment of low-strength wastewaters at ambient temperature in upflow anaerobic sludge blanket (UASB) reactors

Submitted by

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering

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ABSTRACT

Anaerobic wastewater treatment is a well-established and proven technology for the treatment of various categories of industrial wastewaters. This technology has numerous advantages, such as low energy requirement, energy recovery as methane gas (CH_4), low costs of aeration and sludge handling, over aerobic counterparts. Most anaerobic wastewater treatments have been conducted within mesophilic (30°C - 40°C) or thermophilic (45°C - 60°C) temperature ranges. This is attributed to the fact that most of the biological reactions responsible for anaerobic biodegradation of organic matters proceed slower under psychrophilic (< 20°C) condition than under mesophilic and thermophilic conditions. However, municipal wastewater is generally discharged at low ambient temperature under temperate climatic conditions. Furthermore, municipal wastewaters belong to the category of low-strength wastewater that has a chemical oxygen demand (COD) concentration of about 1.0 g/L or lower. Therefore, a significant input of energy is required to heat a reactor to the treatment temperature. If anaerobic wastewater treatment without heating the reactor can be applied to low-strength wastewater, the cost of anaerobic wastewater treatment can be reduced, thereby making this technology an attractive option for the treatment of a variety of wastewaters. In this study, the technical feasibility of using an upflow anaerobic sludge blanket (UASB) reactor to treat low-strength wastewater at ambient temperature was investigated. Especially, the effects of temperature and hydraulic retention time (HRT) on the performance of a UASB reactor were investigated. Based on the results obtained, municipal wastewater was treated in a UASB reactor at ambient temperature. Furthermore, degasification with degassing membrane was applied to the UASB reactor to improve CH_4 recovery efficiency by collecting dissolved CH_4 (D-CH_4) from the reactor effluent. The degasification technology was compared with the other technologies for D-CH_4 collection.

We investigated the effects of temperature and HRT on the COD removal rate of a UASB reactor treating synthetic wastewater. We operated a bench-scale UASB reactor over 170 days. After COD removal efficiency reached a steady state, temperature of the reactor was changed from 35°C to 25°C and 15°C in a stepwise manner in the initial stage. In the latter stage, HRT was reduced from 10 h to 6.6 h and 3.3 h by altering the hydraulic loading rate without changing COD loading rate. In the initial stage, the total COD (T-COD) concentration of the influent was 1480 mg COD/L and

the concentration of dissolved fraction of COD (D-COD) in effluent was 120 mg COD/L, resulting in 92% of D-COD removal efficiency regardless of temperature. In the latter stage, D-COD removal efficiency was higher than 90%. It might be explained by the use of the synthetic wastewater without recalcitrant organic compounds, long HRT, and the large amount of biomass retained in the reactor.

The technical feasibility of using a UASB reactor to treat real municipal wastewater at ambient temperature was investigated. The UASB reactor was operated from January 2010 to June 2011. T-COD and D-COD concentrations in the wastewater were in the ranges of 70 mg/L - 310 mg/L and 50 mg/L - 160 mg/L, respectively. The rate of the particulate fraction of COD (P-COD) to T-COD in the influent remained relatively constant (0.56) throughout the operation. HRT was changed in the range of 2 h - 8 h in response to changes in the COD removal efficiency. Temperature, which was not controlled, varied from 6°C to 31°C. A 20-cm-high filter media was installed in the upper part of the UASB reactor on June 22, 2010, to avoid biomass washout. T-COD was not removed during the first winter. Between July and October 2010, the T-COD removal efficiency was in the range of 50% - 71%. The temperature ranged from 20°C to 31°C during this period, indicating that temperature was a critical factor for effective COD removal. Disintegration of the granules was observed during the operation and the average amounts of volatile suspended solids in the granular bed increased from 78 to 150 g per reactor by installation of the filter media to prevent biomass washout. Enhancement of biomass retention by the installation of the filter media and growth of biomass may contribute to the improvement in T-COD removal efficiency and increase in the CH_4 evolution rate into the UASB headspace during this period. The T-COD removal efficiency started to decrease at the beginning of November 2010 accompanying the temperature drop. This might be attributed to the low methanogenic activity at low temperature. Volatile fatty acids (mainly acetic acid) were detected in winter, but not in summer, indicating that acidogenic activity was not inhibited compared to methanogenic activity at low temperatures. These organic acids would be treated in aerobic post treatment. Subsequently, the T-COD removal efficiency gradually increased from 10% to around 60% in April 2011 owing to the gradual increase in temperature. We concluded that municipal wastewater could be anaerobically treated at ambient temperature with greater than 40% of T-COD removal efficiency except in winter (< 10°C). The COD removal efficiency was lower (< 71%) in this study than

those in UASB reactors treating high-strength wastewaters under mesophilic conditions in the previous studies. This might be because of the higher P-COD fraction of the municipal wastewater and the operation at ambient temperature in this study. We compared the operating parameters and T-COD removal efficiencies of the UASB reactor with ones treating low-strength wastewaters under psychrophilic conditions reported in the previous studies. The result indicates that the treatment of low-strength wastewaters at low temperatures results in low COD removal efficiencies. Therefore, an aerobic posttreatment is needed to achieve the appropriate T-COD removal efficiency.

When low-strength wastewaters are anaerobically treated at ambient temperature, it is important to consider D-CH_4. It is because the solubility of CH_4 in the liquid phase increases with decrease in temperature, which represents loss of energy that may be recovered and release of greenhouse gas into the environment. We employed a hollow-fiber membrane to recover residual D-CH_4 in the effluent of UASB reactors by degasification. The liquid outlet of the UASB reactor was connected to another reactor for degasification (a degassing membrane (DM) reactor). Firstly, a bench-scale UASB reactor equipped with the DM reactor was operated to treat synthetic wastewater at different temperatures and HRTs. Under 35°C and HRT of 10 h, average D-CH_4 concentration was reduced from 63 mg COD/L to 15 mg COD/L, resulting in an increase in the total CH_4 recovery efficiency from 89% to 97%. Average D-CH_4 concentration was as high as 104 mg COD/L at 15°C because of the higher solubility of CH_4 in the liquid and the average D-CH_4 concentration was reduced to 14 mg COD/L by degasification. Accordingly, the total CH_4 recovery efficiency increased from 71% to 97% at 15°C. Moreover, degasification tended to cause an increase in P-COD removal efficiency. In addition, the UASB reactor was operated at different HRTs. Although average D-CH_4 concentration in the UASB reactor was almost unchanged (ca. 70 mg COD/L), the D-CH_4 discharge rate from the UASB reactor increased with decreasing HRTs because of increase in the hydraulic loading rate. Because the D-CH_4 concentration could be reduced down to 12 mg COD/L by degasification at an HRT of 6.7 h, the CH_4 recovery rate was 1.5 times higher under degasification than under normal operation. Secondly, municipal wastewater was anaerobically treated with a UASB reactor at ambient temperature to investigate D-CH_4 recovery efficiency. D-CH_4, which was detected in the UASB effluent throughout the operation, could be successfully

collected with a degassing membrane over 18 months without membrane fouling. The ratio of the collection to recovery rates was 60% in summer and 100% in winter.

In summary, a UASB process is applicable to pretreatment of municipal wastewater at ambient temperature. T-COD removal efficiency was greater than 40% at temperatures higher than 10°C. Biomass retention is essential to reliable reactor operation. Since the ratio of D-CH_4 to CH_4 recovered from the UASB reactor was higher in municipal wastewater treatment than those in treatment of high-strength wastewater, D-CH_4 should be collected from the reactor effluent to prevent loss of energy and release of greenhouse gas. From an economic point of view, a further reduction in the energy required for degasification is needed.

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Chapter 1

Introduction

1 INTRODUCTION

1.1 ANAEROBIC DIGESTION (AD)

1.1.1 Microorganisms involved in anaerobic digestion (AD) process

Anaerobic digestion (AD) is a process used to treat the solid wastes and wastewaters, in which microorganisms break down into biodegradable materials in the absence of oxygen (O_2). This process is widely used as it reduces volume and mass of the input materials and generates useful by-products.

Microorganisms found in the wastewater can be divided into two groups according to their response to free molecular O_2 and their enzymatic ability to degrade substrate in the AD process. First group can be divided further into three groups as (1) strict aerobes, (2) facultative anaerobes, and (3) anaerobes, including the methane forming microorganisms (methanogens) (Gerardi et al., 2003). Strict aerobes do not exist in an anaerobic digester in which free molecular O_2 is absent. Facultative anaerobes are active in the presence or the absence of free molecular O_2.

Table 1.1: Groups of microorganisms according to their response to free molecular oxygen (O_2) (Gerardi et al., 2003)

Group	Significance
Strict aerobes	Degrade soluble organic compounds and contribute to filamentous sludge bulking
	Oxidize NO_2^- to NO_3^-
	Oxidize NH_4^- to NO_2^-
	Degrade soluble organic compounds
	Contribute to filamentous sludge bulking and floc formation
Facultative anaerobes	Degrade soluble organic compounds, and contribute to floc formation and denitrification
Anaerobes	Reduce SO_4^{2-} to H_2S (O_2 tolerant) Produce methane (CH_4) (O_2 intolerant)

The AD process occurs in four major stages. In the first stage, which is known as hydrolysis, solid complex organics, cellulose, proteins, and lipids are broken down into soluble organic compounds. In the second stage, the products in the first stage are converted into ammonia,

alcohol, and volatile fatty acids (VFAs) by exo-enzymes. Those are converted into acetic acid, propionic acid, hydrogen (H_2), carbon dioxide (CO_2), and other low molecular weight organic acids in the third stage. The microorganisms involve in this stage are known as acedogens or acid formers. In the final stage, two groups of methanogens involve into the reaction. The hydrogenotrophic methanogens convert H_2 and CO_2 to methane (CH_4) and acetotrophic methanogens convert acetate to CH_4 and bicarbonate. The schematic representation of the AD process is shown in the Figure 1.1. Next section provides a detailed description of the methanogens involved in the AD process.

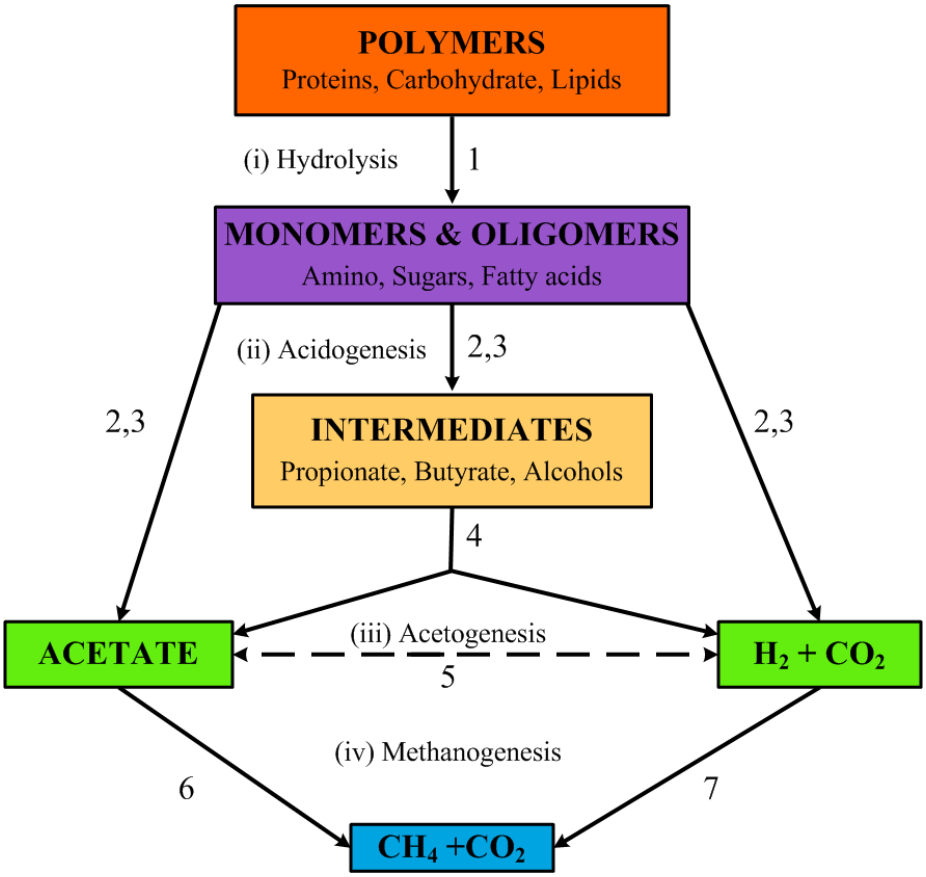


Figure 1.1: Anaerobic digestion (AD) of organic polymeric material. Italics indicate sub-processes: 1. Hydrolysis of complex and particulate organic materials (proteins, carbohydrate, and lipids), 2. Fermentation of amino acids and sugars, 3. Anaerobic oxidation of long-chain fatty acids and a1cohols, 4. Anaerobic oxidation of intermediary products such as short-chain fatty acids (except acetate), 5. Acetate production from carbon dioxide and hydrogen (homoacetogens), 6. Conversion of acetate to methane (acetotrophic methanogens), and 7. Methane production by reduction of carbon dioxide by hydrogen (hydrogenotrophic methanogens) (Gujer et al., 1983; Pavlostathis, 1991).

Methane forming microorganisms (methanogens)

Methanogens are found in habitats that are rich in degradable organic compounds. They obtain their energy for reproduction and cellular activity from the degradation of a relatively small number of simple substrates that include H_2, 1-carbon compounds, and acetate as the 2-carbon compound. Acetate is commonly split to form CH_4 while H_2 is combined with CO_2 to form CH_4 (known as acetotrophic cleavage). Each methanogen has a specific substrate or group of substrates that it can degrade (Table 1.2). Hydrogen can serve as a universal substrate for methanogens, and CO_2 functions as an inorganic carbon source in the forms of carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-).

Table 1.2: Species of methanogens and their substrates

Species	Substrates
Methanobacterium formicium	Carbon dioxide, formate, hydrogen
Methanobacterium thermoantotrophicum	Hydrogen, carbon dioxide, carbon monoxide
Methanococcus frisius	Hydrogen, methanol, methylamine
Methanococcus mazei	Acetate, methanol, methylamine
Methanosarcina bakerii	Acetate, carbon dioxide, hydrogen, methanol, methylamine

The use of acetate and hydrogen by methanogens produces majority of the CH_4 in an anaerobic digester. The fermentation of substrates such as acetate results in the production of CH_4 (Equation 1.1), and the reduction of CO_2 also results in the production of CH_4 (Equation 1.2).

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad 1.1$$

$$CO_2 + 4H_2 \rightarrow CH_4 + CO_2 \qquad 1.2$$

Acetotrophic cleavage of acetate and reduction of CO_2 are the two major pathways to CH_4 production, whereas, fermentation of propionate (CH_3CH_2COOH) and butyrate ($CH_3CH_2CH_2COOH$) are minor pathways to methane production. However, the fermentation of propionic acid to methane requires two different species of microorganisms and two microbial degradation steps (Equations 1.3 and 1.1).

$$4CH_4CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3CH_4 \quad 1.3$$

In the first reaction, methane and acetate are produced from the fermentation of propionate or butyrate by a volatile acidogen and a methanogen. In the second reaction, methane is produced from the cleavage of acetate by a methanogen. These reactions occur only if H_2 and formate are kept low (used) by methanogens. Accordingly, the accumulation of propionate or butyrate is a common indicator of stress in an anaerobic digester.

Butyrate is degraded to methane through two microbial degradation steps (Equations 1.4 and 1.1).

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 4CH_3COOH + CO_2 + CH_4 \quad 1.4$$

The hydrogenotrophic methanogens, the acetotrophic methanogens, and the methylotrophic methanogens are the three principal groups of methanogens. The hydrogenotrophic methanogens use H_2 to convert CO_2 to CH_4 (Equation 1.2). By converting CO_2 to CH_4, these organisms help to maintain a low partial H_2 pressure in an anaerobic digester that is required for acidogenic microorganisms.

The acetotrophic methanogens separate acetate into CH_4 and CO_2 (Equation 1.5). The CO_2 produced from acetate may be converted into CH_4 by hydrogenotrophic methanogens to CH_4 (Equation 1.2). Some hydrogenotrophic methanogens use CO to produce CH_4 (Equation 1.6).

$$CH_3COOH \rightarrow CO_2 + H_2 \quad 1.5$$

$$4CO + 2H_2 \rightarrow CH_4 + CO_2 \quad 1.6$$

The acetotrophic methanogens reproduce more slowly than the hydrogenotrophic methanogens and are adversely affected by the accumulation of H_2. Therefore, the maintenance of a low H_2 partial pressure in an anaerobic digester is favourable for the activity of acedogens and acetotrophic methanogens. Under a relatively high H_2 partial pressure, acetate and CH_4 production are reduced. The methylotrophic methanogens grow on substrates that contain the

methyl group (–CH_3). Examples of these substrates include methanol (CH_3OH) (Equation 1.7) and methylamines [$(CH_3)_3$–N] (Equation 1.8).

$$3CH_3OH + 6H \rightarrow 3CH_4 + 3H_2O \quad 1.7$$

$$4(CH_3)_3 - N + 6H_2O \rightarrow 9CH_4 + 3CO_2 + 4NH_3 \quad 1.8$$

The use of different substrates by methanogens results in different energy gains. For example, hydrogen-consuming CH_4 production results in more energy gain for methanogens than acetate degradation. Although the CH_4 production using H_2 is more effective process of energy capture by methanogens, in an anaerobic digester less than 30% of the CH_4 is produced by this method. Approximately 70% of the CH_4 produced in an anaerobic digester is derived from acetate. The reason for this is the limited supply of H_2 in an anaerobic digester.

1.1.2 Biogas

In the AD process, microorganisms degrade the organic matter into a mixture of gaseous biogas, which is collectively named as digester gas or biogas and sludge. Typical composition of the biogas is shown in the Table 1.3 (Ukpai and Nnabuchi, 2012). The composition of the biogas depends on the substrate composition (Table 1.5). Typically, biogas production in municipal anaerobic digesters is between 0.75 - 1.0 m^3/kg VS. The heat value of biogas is approximately 19 - 23 MJ/m^3, much lower than that of CH_4 (37 MJ/m^3) because of the dilution of CH_4 by CO_2.

Table 1.3: Composition of biogas (Ukpai and Nnabuchi, 2012)

Matter	Percentage by volume (%)
Methane (CH_4)	50 - 70
Carbon dioxide (CO_2)	30 - 40
Hydrogen (H_2)	1 - 10
Nitrogen (N_2)	1 - 3
Hydrogen sulphide (H_2S)	0.1
Oxygen (O_2)	0.1

Table 1.4: Mean composition and specific yields of biogas in relation to the kind of degraded substances (Gerardi et al., 2003)

Substance	Gas yield (m^3/kg-TS)	CH_4 content (Vol. %)	CO_2 content (Vol. %)
Carbohydrates	0.79	50	50
Fats	1.27	68	32
Proteins	0.70	71	29
Municipal solid waste	0.1 - 0.2	55 - 65	35 - 45
Biowaste	0.2 - 0.3	55 - 65	35 - 45
Sewage sludge	0.2 - 0.4	60 - 70	30 - 40
Manure	0.1 - 0.3	60 - 65	35 - 40

The yield and composition of the biogas can be estimated from the following equation, when the chemical composition of the substrate is known.

$$C_n H_a O_b + \left(n - \frac{a}{4} - \frac{b}{2}\right) H_2O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right) CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right) CO_2 \qquad 1.9$$

1.1.3 The upflow anaerobic sludge blanket (UASB) reactor

Dr. Gatze Lettinga and his colleagues developed the UASB process in the late 1970's. With the development of the UASB reactor, anaerobic systems gained interest as the secondary treatment in wastewater treatment. The simplest and oldest anaerobic process is the septic tank (Jewell, 1987). A detailed summary of the development of the UASB reactor is given in McCarty (2001). It further gained the attention of researchers with finding of the energy saving alternatives due to steep increase in energy prices in the 1970s (van Haandel et al., 1994). It is now extensively applied to treat industrial and domestic wastewaters (Hulshoff et al., 1986; Lettinga et al., 1991; Lettinga 1993; Kato et al., 1994). Figure 1.2 shows the schematic representation of the typical UASB reactor. In the UASB reactor, as the name implies, wastewater flows from the bottom of the reactor and then flows upward through the sludge bed. Sludge bed is composed of granules, which are aggregates of microorganisms formed during wastewater treatment. All biological processes take place within the sludge bed and responsible for the production of biogas. In the arrangement of biomass in granules, the different microbial populations selectively group in

layers on top of each other such as the outer layer contains mainly acidogens, sulfur reducing microorganisms, and hydrogen utilizing methanogens (Figure 1.3) (Satoh et al., 2007).

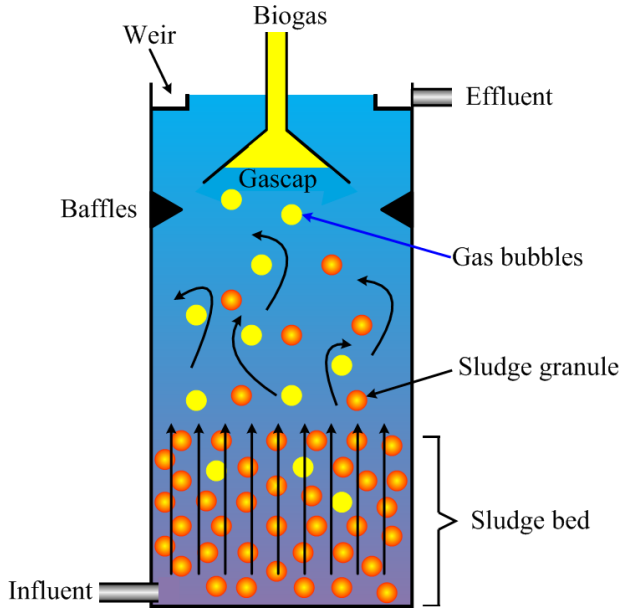


Figure 1.2: Schematic diagram of the upflow anaerobic sludge blanket (UASB) reactor.

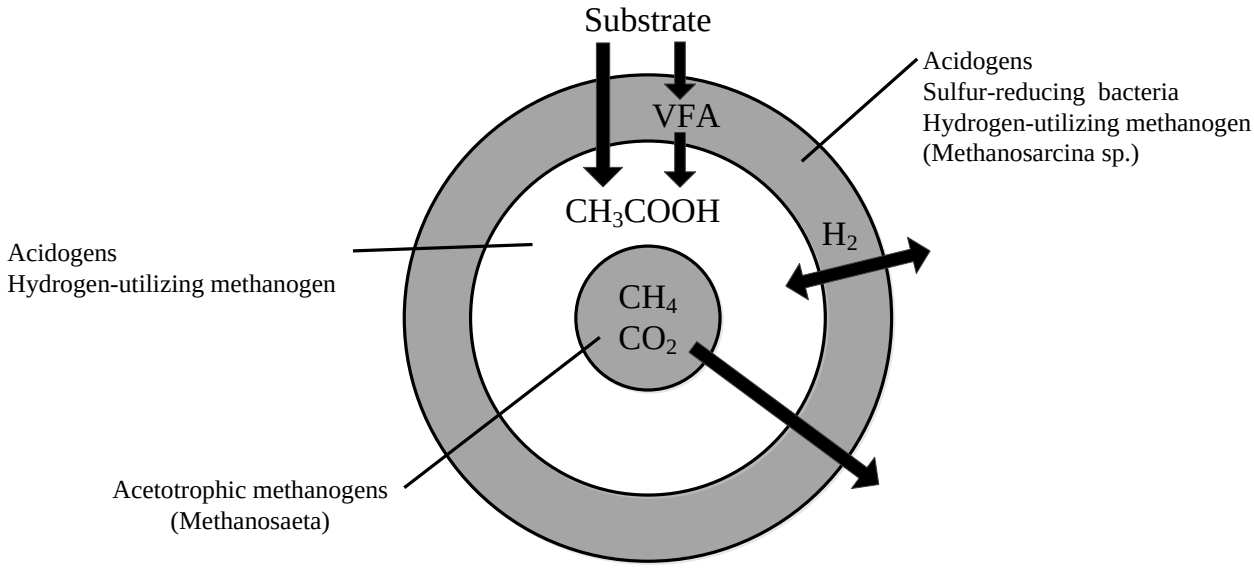


Figure 1.3: Layered structure of anaerobic granules (Guiot et al., 1992).

Acidogens and H_2 utilizing methanogens are in the middle layer and the core is dominated by acetotrophic methanogens. Generally, granules have a flattened spherical geometry with a

diameter of 1 - 3 mm. Due to their large particle size, the granules resist washout from the reactor, permitting high hydraulic loads. One gram of granular sludge organic matter (dry weight) can catalyze the conversion of 0.5 to 1 g COD/day to methane (Oh, 2012). Retention of active sludge within the UASB reactor enables good treatment performance at high organic loading rates. Natural turbulence caused by the influent flow and the biogas production provides good wastewater-biomass contact in UASB systems. At the top of the reactor, the water phase is separated from sludge solids, and gas is separated in a three-phase separator (also known as the gas-liquid-solids separator). Since, higher organic loads can be applied in UASB systems therefore; less reactor volume and space are required. Energy is produced as biogas.

1.1.4 Pros and cons of anaerobic digestion (AD)

There are many positive and negative aspects of AD. AD can be used to treat many biodegradable wastes, including wastes that are unsuitable for composting, such as meat and cooked food. It also helps to reduce the emission of greenhouse gases in number of key ways: Replacement of fossil fuels, reducing methane emission from landfills, and by displacing industrially produced chemical fertilizers.

AD has been known as a renewable energy-producing process, because in the process the biomasses (wood, crops, and garbage) which stored energy from the sun are used as energy sources. In addition, the nutrient-rich solids left after the digestion can be used as fertilizer, supplying vital nutrients to soils. The solid, fibrous component of digestate can be used as a soil conditioner. The liquor can be used as a substitute for chemical fertilizers, which require large amounts of energy to produce. The use of manufactured fertilizers is therefore more carbon intensive than the use of anaerobic digestate fertilizer. The methane in biogas gives the ability to be used it as a fuel, the combustion of which releases energy. In developing countries, biogas can be used as a low-cost fuel for cooking. It can also be utilized in modern waste management facilities where it can be used in gas engines to generate electricity. Biogas is a renewable fuel and electricity produced from it can be used to attract renewable energy subsidies. Effluent liquid can also be used for the production of functional polymers (e.g. bio plastics)**.** Bio plastics are environmentally friendly because, compared with traditional plastics, their production results in less CO_2 emission, which is thought to cause global warming. Those are also biodegradable,

meaning that the material returns to its natural state when buried in the ground. Anaerobic treatment processes are favourable as those consume little energy. At ambient temperature, the energy requirements are in the range 0.05 - 0.1 kWh/m^3. Moreover, compared to conventional systems anaerobic treatment processes require less space.

Although the anaerobic digesters provide many benefits, there are also some major drawbacks. Two major drawbacks of biogas systems are cost and maintenance. Cost will vary depending on the size of the operation. In addition, the large amount of biogas required to generate energy is not looked upon favourably. Biogas generates in a gaseous state and therefore has a low energy density in comparison to other fuels. The gases with economic value produced in an anaerobic digester are CH_4 and H_2. CH_4 can be used as a source of fuel. Anaerobic treatment is more susceptible to failure from changes in reactor conditions, as well as from difficulties during reactor operation even under stable conditions (Fongastitkul et al., 1994).

The following can be mentioned as advantages and disadvantages of anaerobic treatment, with special emphasis on UASB reactors:

Table 1.5: Advantages and disadvantages of the anaerobic processes

Advantages	**Disadvantages**
• Low production of sludge generated per organic removal • CH_4, recovered gas can be used as fuel (energy produced during the process in the form of methane can be also utilized) • Relatively simple construction and operation • High removal efficiency even at high loading rates • Application in small and large scale • Low nutrients and chemicals requirement	• Long start-up • High microbial sensitivity to some environmental conditions • Possible bad odors • Slow reaction in the cold climates • Low concentration in the effluent of the economy • CH_4 dissolved in the effluent

Substantial improvements have been made in tackling most of the alleged disadvantages of anaerobic treatment, with the result that only a few of the previously presumed drawbacks have remained. The next section provides a detailed account of related research carried out in the application of UASB reactors to treat low-strength wastewater highlighting the need for the present study.

1.2 ANAEROBIC TREATMENT OF LOW-STRENGTH WASTEWATERS AT AMBIENT TEMPERATURE

For stable digestion to proceed, it requires a balance between the production, and consumption of the intermediates in the stages of AD. Stage, in which waste conversion is slowest known as the rate-limiting stage, and both first and fourth stages are rate-limiting (Water Environment Federation 1987). In the first stage, conversion of complex organic compounds in to soluble organic compound is slow as lignin prevents the access of the enzymes, provide by the microorganisms. In addition, many of the complex organic compounds are not degradable. Stage 2 and 3 are not considered as rate-limiting stages as microorganisms involve in these stages grow fast and break down compounds quickly. According to the manual of Anaerobic Sludge Digestion, methanogens grow slowly and are relatively sensitive to environmental factors as well. Hence, in order to maintain the stable process, and to optimize the biogas yield it requires meeting the requirements of the methanogens. Certain physical as well as chemical requirements of the microorganisms should be maintained to achieve the high level of microorganism growth rate and sludge stabilization.

Temperature has significant effects on microorganisms, and lowering temperature is known to lead to a decrease in the maximum specific growth and substrate utilization rates (Trzcinski and Stuckey, 2010). Hence, the efficiency of the anaerobic process is highly dependent on the reactor temperature. Microorganisms grow faster at higher temperatures and increase the rate of digestion. As a result, retention time, and thus volume of the reactor depend on the temperature condition to be maintained in the reactor. In other words, there is a tradeoff between the rate of digestion and the temperature. Hydraulic retention time (HRT) indicates the time the waste remains in the reactor in contact with the biomass. The time required to achieve a given degree of treatment depends on the rate of microbial metabolism. Solid retention time (SRT), on the other hand, controls the microbial mass (biomass) in the reactor to achieve a given degree of

waste stabilization. SRT is a measure of the biological system's capability to achieve specific effluent standards and/or to maintain a satisfactory biodegradation rate of pollutants. Maintaining a high SRT produces a more stable operation, better toxic or shock load tolerance, and a quick recovery from toxicity. The permissible organic loading rate in the anaerobic process is also determined by the SRT. For the slow-growing microorganisms such as methanogens, care must be exercised to prevent their washout from the reactor in order to achieve a longer SRT. Elevated HRTs require a bigger reactor volume (volume = flow rate × HRT), which is costly. Wide varieties of high-rate anaerobic reactors have been able to maintain extremely high SRTs due to biomass immobilization. Such systems operate under short HRTs without any fear of biomass washout. The empirical HRTs for different anaerobic systems to achieve the same degree of treatment are presented in Table 1.6. High-rate treatment with short HRTs is necessary to treat the large volumes of low-strength wastewaters, while long SRTs are essential to maintain the slow growing anaerobic microbial populations in the treatment systems (Smith et al., 2012 and 2013). This is to keep capital costs and footprints of treatment systems sufficiently low.

Table 1.6: Hydraulic retention times (HRTs) of anaerobic systems needed to achieve 80% COD removal efficiency at temperatures > 20°C (Van Haandel and Lettinga, 1994)

Anaerobic system	HRT (hour)
Upflow anaerobic sludge blanket (UASB) reactor	5.5
Fluidized/expanded bed	5.5
Anaerobic filter	20
Anaerobic pond	144 days

Each type of microorganisms has an optimum temperature for growth. Psychrophilic, mesophilic and thermophilic are the most applied temperatures in AD systems (Mes de et al., 2003). Table 1.7 shows the corresponding temperatures for each bacteria group.

Table 1.7: Optimum temperature ranges for the growth of methanogens (Gerardi et al., 2003)

Bacteria group	Temperature range (°C)
Psychrophilic	10 - 20
Mesophilic	30 - 35
Thermophilic	50 - 60
Hyperthermophilic	> 65

However, most methanogens are known to be active in two temperature ranges: mesophilic range and thermophilic range (Figure 1.4).

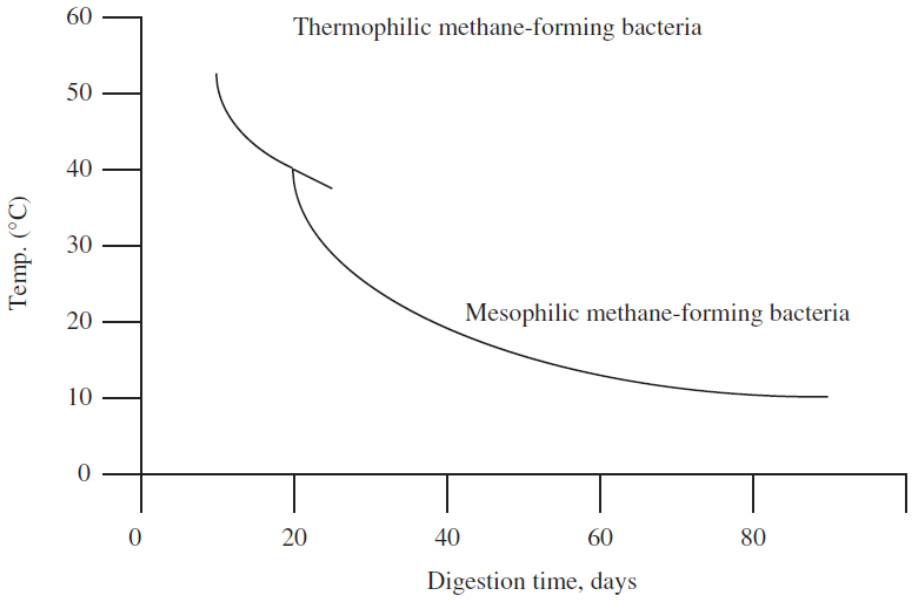


Figure 1.4: Variation of CH_4 production for operating conditions; Temperature and hydraulic retention time (HRT) (Gerardi et al., 2003).

At temperatures between 40°C and 50°C, methanogens are known to be inhibited. Optimum CH_4 production at municipal wastewater treatment plants is known to be achieved with temperature of approximately 35°C (Lew et al., 2004). As shown in Table 1.8, CH_4 production occurs over a wide range of temperature and according to the study of Lew et al. (2004), AD can occur at temperatures as low as 0°C (Lew et al., 2004). The recent emphasis of wastewater engineering community is the low-strength wastewater treatment at low temperatures. Anaerobic bacteria can adapt quite easily to low temperatures, and high rate anaerobic treatment has been achieved at psychrophilic conditions with chemical oxygen demand (COD) removals of 85% ~ 65% at 20°C, and of 55% - 65% at 13°C - 17°C (Lettinga et al.,1981). Low-strength wastewaters are discharged at ambient temperatures and heating high volumes of wastewater is not economically feasible as the potential energy recovery from low-strength wastewater is low. For example, according to Martin et al. (2011), influent COD concentrations higher than 4 g/L - 5 g/L, greater than those present in typical low-strength wastewaters, would be necessary to produce sufficient biogas to heat a reactor to mesophilic temperatures. Therefore, operation at ambient temperatures is essential for economical implementation of AD for low-strength wastewater treatment.

However, still there is a lack of insight into the AD process technology, especially at low temperatures. At low temperatures, the low hydrolysis rate, and a decrease in the degradable organic matter fraction were found to cause the deterioration of the overall anaerobic reactor performance (Elimitwalli et al., 2001). Therefore, more research is needed to understand the operation of AD of low-strength wastewaters at ambient psychrophilic temperatures, in particular, the effect of temperature and HRT on the COD removal.

Table 1.8: Temperature range for methane production for municipal anaerobic digesters

Temperature (°C)	**Methane production**
35	Optimum
32 - 34	Minimum
21 - 32	Little, digester going "sour"
< 21	Nil, digester is "sour"

A drop in temperature also results in change of the physical and chemical properties of the wastewater. For an instance, VFA formation occurs at low temperatures (when digester temperature falls below 32°C). However, still CH_4 production proceeds slowly. VFA production rate increases with the decrease in temperature and it may cause CH_4 production nonexistent. On the other hand, at low temperatures, the viscosity of liquids is also increased. Therefore, mixing is required, and sludge bed reactors become less easily mixed, particularly at low biogas production rates. This also causes particles to settle more slowly because of decreased liquid-solid separation at low temperatures. Moreover, the diffusion of soluble compounds may drop. In addition, the solubility of gaseous compounds increases as the temperature decreases below 20°C. This implies that the dissolved concentrations of CH_4, hydrogen sulphide (H_2S), and H_2 will be higher in the effluent of reactors operated at low temperatures than those from reactors operated at high temperatures. Agrawal et al. (1997) observed a 78% decrease in the gas production rate when the temperature reduced from 27°C to 10°C (Agrawal et al., 1997). In case of low-strength wastewater, dissolved methane (D-CH_4) discharged from the treatment process in the liquid phase represents a substantial portion of the total CH_4 generated (Smith et al., 2012). More importantly, methane is approximately 1.5 times more soluble at 15ºC compared to 35ºC, for a typical biogas methane content of 70% (Smith et al., 2012). It is reported that 30% and 50% of the CH_4 generated remained in the liquid phase during operation at 35ºC (Kim et al., 2011)

and at 15ºC (Smith et al., 2011), respectively. Some researchers have recognized significance of the D-CH_4. For example, Chynoweth et al. (1987) pointed out that loss of CH_4 (i.e., energy) was pronounced especially in digesters operated at high flow rates, and short HRTs because the effluent of the digester contains D-CH_4, for example about 50% or more of the saturation level. Pauss et al. (1990) emphasized the necessity of direct measurement of poorly soluble gases (e.g., CH_4 and H_2) in bulk liquid in anaerobic digesters to correctly determine the dissolved gas concentrations. In addition, a comparative analysis by Hartly et al. (2006) confirmed that CH_4 super-saturation resulted in significant loss of CH_4 in the effluent. These highlight the important role temperature has in methane solubility and, therefore, direct biogas methane recovery.

When treating a complex wastewater like domestic sewage, pH is usually in the optimum range without the need for chemical addition. However, the high increase of solubility of CO_2 indicates that a slightly lower reactor pH might prevail under psychrophilic conditions. On-line monitoring of the pH can be helpful in detecting system failure. Acetate is the major intermediate in the bioconversion of organic matter to CH_4, and CO_2. About 70% of the total CH_4 produced in AD originates from acetate (Gujer et al., 1983). Thus, the production of CH_4 from acetate is an important step in the AD process. It is accepted that methanogens from acetate can proceed well from pH 6 to pH 8. The pH of an anaerobic system is significantly affected by the CO_2 content of the biogas. In a properly operating anaerobic digester, pH between 6.8 and 7.2 occurs as VFAs are converted to CH_4 and CO_2. The release of CO_2 results in the production of carbonic acid, bicarbonate alkalinity, and carbonate alkalinity (Equation1.10).The release of ammonia results in the production of ammonium ions (Equation1.11).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad 1.10$$

$$NH_3 + H^+ \leftrightarrow NH_4^+ \quad 1.11$$

The equilibrium between carbonic acid, bicarbonate alkalinity, and carbonate alkalinity as well as ammonia and ammonium ions is a function of digester pH. Bicarbonate alkalinity is the primary source of carbon for methanogens. Normally, acid and ammonia production vary only slightly due to the buffering effect of carbon dioxide/bicarbonate (CO_2/HCO_3^-) and ammonia/ammonium (NH_3/NH_4^+), which are formed during fermentation. Thus, the pH normally stays constant between 7 and 8.

Table 1.9: Optimum pH of some methanogens

Genus	pH
Methanoshaera	6.8
Methanothermus	6.5
Mathanogenium	7.0
Methanolacinia	6.6 - 7.2
Methanomicrobium	6.1 - 6.9
Methanospirillium	7.0 -7.5
Methanococcoides	7.0 - 7.5
Methanohalobium	6.5 - 7.5
Methanolobus	6.5 - 6.8

There are two groups of bacteria in terms of pH optima, namely acidogens and methane-producing microorganisms (methanogens). The acidogens prefer a pH of 5.5 - 6.5, while methanogens prefer a range of 7.8 - 8.2. In an environment, where both cultures coexist, the optimal pH range is 6.8 - 7.4. Moreover, the value and stability of the pH in an anaerobic reactor are extremely important because methanogenesis only proceeds at a high rate when the pH is maintained in the neutral range (6.3 - 7.8) (van Haandel et al., 1994). Thereupon, VFA is a substrate to evaluate the effect of operational parameters on the kinetics of anaerobic sludge. All in all, accumulation of VFAs, mainly due to increase in dissolved CO_2 and H_2 concentrations, often causes decrease in pH, which leads to process failure in an anaerobic digester. Voolapalli and Stuckey (1998) reported a method to prevent pH drop and provide thermodynamically favourable conditions (e.g., relatively low H_2 and CO_2 partial pressures) in anaerobic digesters by recovering dissolved H_2 and CO_2 in bulk liquid using a submerged silicone membrane (Voolapali et al., 1998). However, the effects of degasification on reactor performance and total biogas recovery efficiency have not been revealed.

According to Henry's law, the solubility of a gas in a liquid at a particular temperature is proportional to the pressure of that gas above the liquid. A theoretical and experimental study carried out by Friedmann and Märkl (1993, 1994) showed that higher solubility of the produced gases, like CO_2, H_2S, and NH_3 pronounce at an elevated pressure. It causes changes in pH with a significant effect on the kinetics of biogas production (Jördening and Winter, 2005). The effect is different for each gas component and as a result, the composition of the produced biogas will change when increasing hydrostatic pressure. At a higher hydrostatic pressure the transport

capacity of the product gases from the liquid phase to the gas phase decreases and, therefore, the concentration of these gases in the liquid phase will increase additionally. Figure 1.5 shows the relative change in the composition of produced biogas as a function of pressure for a particular experiment carried out.

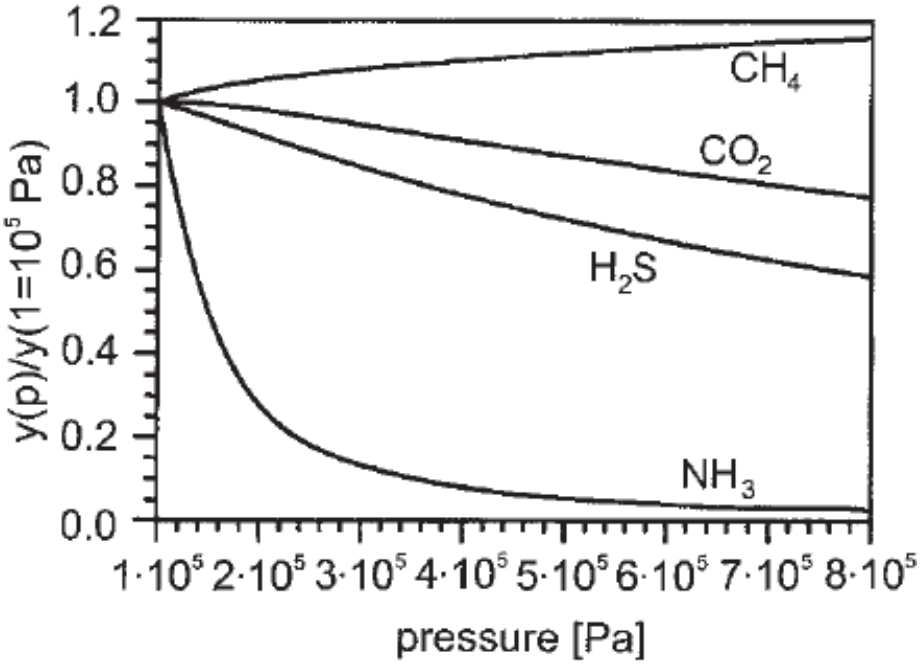


Figure 1.5: Relative change in the composition of the produced biogas due to an alteration in the absolute pressure (Experiments conducted with 16 L stirred tank reactor) (Jördening and Winter, 2005).

1.3 AIMS OF THIS STUDY

The main objective of this research is to investigate the technical feasibility of using a upflow anaerobic sludge blanket (UASB) to treat low-strength wastewater at ambient temperature and specific objectives are as follows;

1) To introduce a degassing membrane (DM) technology for an anaerobic wastewater treatment process

2) Application of degasification with DM to the UASB reactor to improve methane (CH_4) recovery efficiency by collecting dissolved methane (D-CH_4) from the effluent and to study the effects of temperature and hydraulic retention time (HRT) on the performance of a UASB reactor treating synthetic wastewater

3) To study the application of DM to remove residual D-CH_4 gas in an UASB reactor treating municipal wastewater at ambient temperature

These objectives can contribute in understanding the effect of operating parameters, especially temperature and HRT on the performance of a UASB reactor, and will enable us to propose effective approach to be used in cold regions to treat low-strength wastewater with high biogas recovery.

1.4 ORGANIZATION OF THIS THESIS

The organization of the dissertation is as follows. The thesis consists of five chapters. Chapter one describes the background of the study and provides a detailed literature review pertaining to the research area. It will provide the reader an impression regarding the need of this kind of study.

Chapter 2 discusses the results of a bench-scale UASB reactor equipped with a degassing membrane to recover the dissolved biogas. In this study, degassing membrane was installed inside the upper part of the UASB reactor and was completely submerged to recover dissolved gas in the bulk liquid.

Chapter 3 presents the methodologies used in the experimental study conducted in assessing the reactor performance in treating synthetic wastewater at different temperatures and HRTs. In this experimental set-up, a reactor for degasification was connected to the liquid outlet of the UASB reactor to collect the residual dissolved methane. Results and findings obtained from the experiments are discussed.

Chapter 4 presents the performance of the UASB reactor in treating sewage wastewater and discusses the application results of degassing membrane to remove residual dissolved methane gas in an UASB reactor treating low-strength wastewater at low temperature.

Last chapter, Chapter 5 concludes this thesis, highlighting the main contributions of this research along with some recommendations on future research directions.

Chapter 2

Introduction of a degassing membrane technology for an anaerobic wastewater treatment process

2 INTRODUCTION OF A DEGASSING MEMBRANE TECHNOLOGY FOR AN ANAEROBIC WASTEWATER TREATMENT PROCESS

2.1 INTRODUCTION

There is an increasing interest in developing renewable energy technologies. Anaerobic digestion (AD) has been known as a renewable energy-producing process because in the process the biomass (e.g., wood, crops, garbage and high-strength wastewaters), which stores energy from the sun, are used as energy sources (Lettinga et al., 2001; Satoh et al., 2007; Ariesyady et al., 2007a, b). The methane (CH_4) in biogas produced in the AD processes can be used as a fuel.

Anaerobic digesters with high solid retention time compared to hydraulic retention time (HRT) (high rate systems) are used to treat high-strength wastewaters. In especial, an upflow anaerobic sludge blanket (UASB) reactor is considered to be effective in treating high-strength wastewaters. In a UASB reactor, the biogas is produced in the liquid phase (bulk liquid). Most biogas is released to the gas phase (headspace), but some remains dissolved in the bulk liquid. Significance of the dissolved CH_4 (D-CH_4) has been recognized by some researchers (Keller and Hartley, 2003; Cakir and Stenstrom, 2005; Lettinga et al., 2001; Hatamoto et al., 2010; Matsuura et al., 2010). Chynoweth et al. (1987) pointed out that loss of CH_4 (i.e., energy) was pronounced especially in digesters operated at high flow rates and short HRTs because the effluent of the digester contains D-CH_4, for example about 50% or more of the saturation level. Pauss et al. (1990) emphasized the necessity of direct measurement of poorly soluble gases (e.g., CH_4 and hydrogen (H_2) gas) in bulk liquid in anaerobic digesters to correctly determine dissolved gas concentrations, because CH_4 and H_2 were 12 and 70 times oversaturated as compared with the theoretical values, respectively. In addition, a comparative analysis by Hartly et al. (2006) confirmed that CH_4 super-saturation resulted in significant loss of CH_4 in the effluent.

The degassing membrane (DM) can remove dissolved H_2 (D-H_2) and CO_2 (D-CO_2) as well as D-CH_4. Reduction of D-H_2 concentration in the liquid phase makes volatile fatty acids (VFA) oxidation reactions thermodynamically favourable and reduction of D-CO_2 concentration prevents pH drop. Accumulation of VFA also causes decrease in pH, which leads to process failure in an anaerobic digester. Voolapalli and Stuckey (1998) reported a method to prevent pH drop and provide thermodynamically favorable conditions (e.g., relatively low H_2 and CO_2 partial pressures) in anaerobic digesters by recovering D-H_2 and D-CO_2 in bulk liquid using a

submerged silicone membrane. However, the effects of degasification on reactor performance and total biogas recovery efficiency have not been revealed.

Therefore, we operated a bench-scale UASB reactor equipped with a DM to recover the dissolved biogas. Reactor performance (i.e., Chemical Oxygen Demand (COD) removal and CH_4 production rates) was monitored over 150 days and compared under different operational conditions (i.e., with or without degasification). In addition, we discussed the effect of degasification on COD removal and D-CH_4 recovery efficiencies.

2.2 MATERIALS AND METHODS

2.2.1 Experimental setup

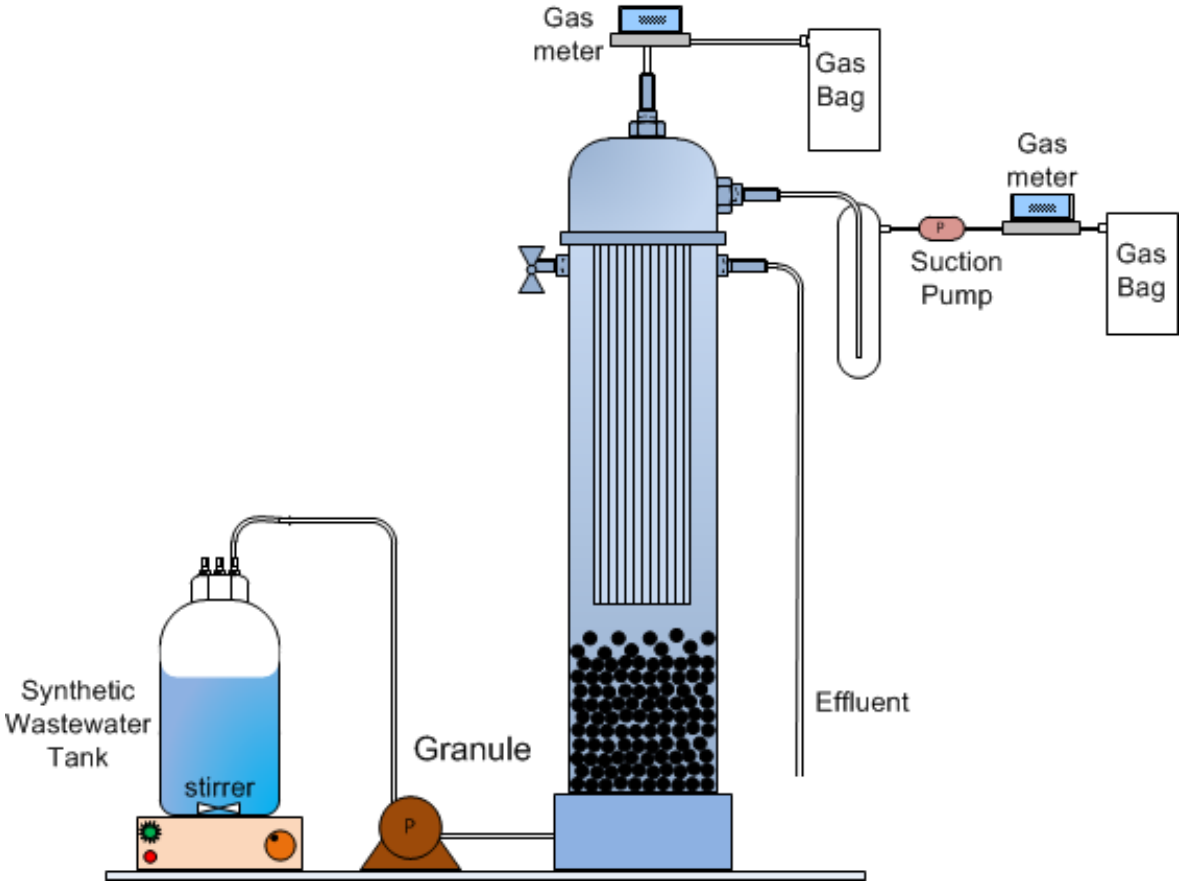


Figure 2.1: Experimental setup

A bench-scale UASB reactor (height, 30 cm; diameter, 7 cm; working volume, 1.1 L) was operated (Figure 2.1). The reactor was inoculated with 0.3 L of anaerobic granular sludge, which

had 28 g/L of total solids and 22 g/L of volatile solids, obtained from a full-scale UASB reactor treating the wastewater from an isomerized sugar-processing plant. A three-layer composite hollow fiber membrane (MHF) (Mitsubishi Rayon Co., Ltd., Tokyo, Japan) was installed inside the upper part of the UASB reactor and was completely submerged to recover dissolved gas in the bulk liquid. Its internal and external diameters are 200 μm and 280 μm, respectively, and the total membrane area is 1.7 m^2. The reactor was equipped with a water jacket to maintain a constant temperature of 35°C. The reactor was fed with a well mixed synthetic wastewater (Satoh et al., 2007) at an average organic loading rate of 1,450 mg total COD/L/day and HRT of 10 h. The synthetic medium contained powdered skim milk (1,000 mg/L) as carbon and energy sources, $NaHCO_3$ (1,000 mg/L), K_2HPO_4 (250 mg/L), $(NH_4)_2HPO_4$ (28 mg/L), inorganic salts (27 mg/L) and trace metals (0.2 mg/L). pH in the bulk liquid was maintained at around 7.0. After the gas production reached steady state, dissolved gas in the bulk liquid was recovered through the DM using an air pump (Model APN-110KV-1, Iwaki Co., Ltd., Tokyo, Japan). Trans-membrane pressure was set at 50 kPa and 70 kPa (absolute pressure) from day 85 to day 91 and from day 135 to day 143, respectively, with a vacuum gauge. The operation without degasification was referred as normal operation in the text.

2.2.2 Sample analysis

Gas composition

All gas compositions (CH_4, CO_2, N_2, and H_2) in the headspace and the membrane were measured by a gas chromatography system (GC-14B, Shimadzu Co., Kyoto, Japan) equipped with a thermal-conductivity detector and a Shincarbon-ST column. Dissolved gas compositions were measured using the headspace method. A 50 mL liquid sample collected from the reactor was injected into a sealed vial filled with 100% argon gas and shaken vigorously for 5 min to allow transfer of the gas in the liquid sample into the headspace. The sample was then allowed to stand for 30 min at room temperature for the equilibration of the gas and liquid phases, after which the headspace gas was measured by gas chromatography. Standard liquid samples containing a known concentration of each standard gas were prepared as described below.

Dissolved gas composition

A 125 mL vial was filled with 50 mL of distilled water. Argon gas was blown into the distilled water for 5 min to remove any air in the liquid and gas phases and sealed with a butyl rubber

septum. One hundred percent CH_4, CO_2, or H_2 gas (1 mL), corresponding to 820 μmol of each gas, was injected into each prepared vial. Next, each vial was shaken and allowed to stand before measurement of the headspace gas-by-gas chromatography.

Dissolved gas concentrations in the sample liquid were calculated based on the ratio of the gas amounts in the sample and the standard sample.

COD measurements

Reactor performance was assessed through COD measurements. All concentrations of total COD (T-COD) and the dissolved fraction of COD (D-COD) after passage through 0.45 μm membranes (Advantec Co., Ltd., Tokyo, Japan) were measured using the Hach Method 8000 (Hach Corporation, Loveland, Colorado). All VFA (formate, acetate, propionate, lactate, I-butyrate, and N-butyrate) concentrations were determined with a high-performance liquid chromatography system (LC-10AD, Shimadzu Co., Kyoto, Japan) equipped with a Shimadzu Shim-pack SCR-102H column (0.008 X 0.3 m) after passage through a 0.2 μm membrane.

Oxidation-reduction potential (ORP) and pH

The oxidation-reduction potential (ORP) and pH were determined with an ORP and pH electrode, respectively.

2.3 RESULTS AND DISCUSSION

A bench-scale UASB reactor was operated at 35ºC for 150 days, and the influent T-COD, effluent T-COD, and effluent D-COD concentrations in the reactor were measured. The influent T-COD concentration during steady-state operation was approximately 1,450 mg/L. At the beginning of the study, the effluent T-COD and D-COD concentrations were high (Figure 2.2). The effluent COD concentrations started to decrease at day 50. After 70 days, the COD removal efficiency reached steady state. The degasification process was applied to recover the dissolved biogas in the liquid phase on day 85. The average effluent D-COD concentrations (± standard deviation) were 250 ± 30 and 140 ± 40 mg/L during the normal and degassing operations (days 70 to 84 and 85 to 91), respectively. Average COD removal efficiencies were 83% and 90% during the normal and degassing operations. The total VFA concentration was 100 mg-C/L on

day 50 and decreased throughout UASB reactor operation. It was 50 mg-C/L on day 64 and < 5 mg-C/L after day 85. Thus, there was no effect of degasification on degradation of VFAs.

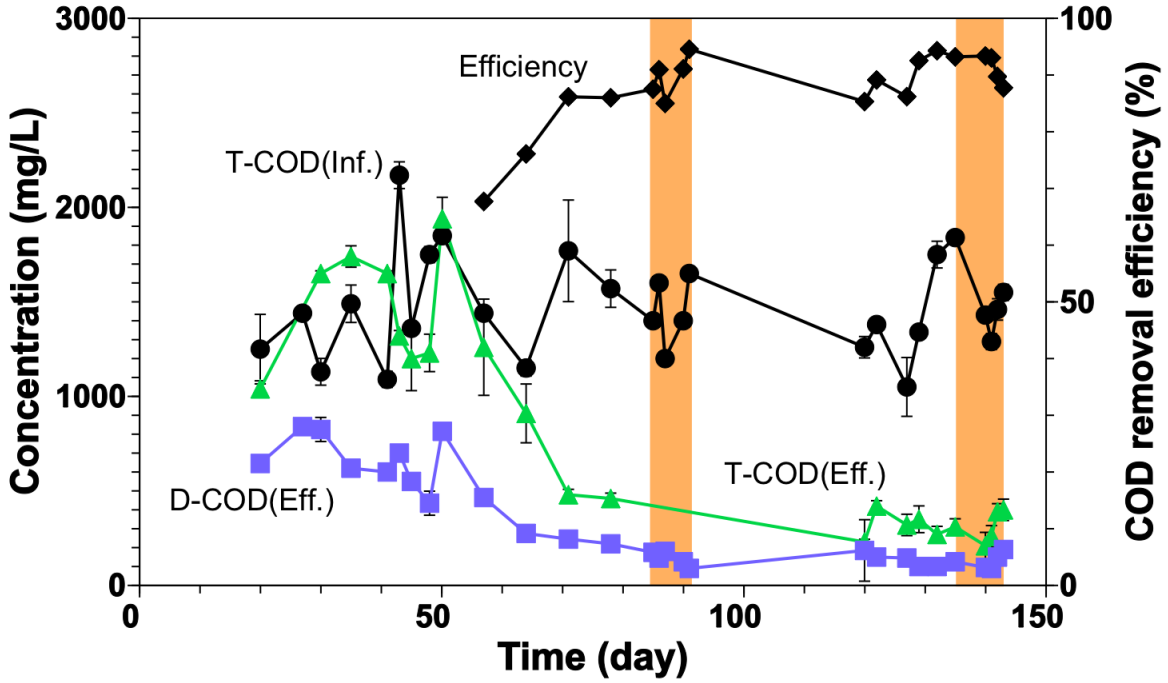


Figure 2.2: Variations in total chemical oxygen demand (T-COD) and dissolved chemical oxygen demand (D-COD) concentrations in the effluent of the UASB (upflow anaerobic sludge blanket) reactor. Shaded areas indicate the periods during which the reactor was operated at trans-membrane pressures of 50 or 70 kPa. The gray line indicates COD concentration in the influent.

The total biogas production rate during normal operation (i.e., rate of biogas evolution into headspace) was approximately 1,500 mL/L-reactor/day, whereas it was approximately 1,700 mL/ L-reactor/day during the degassing operation (1,200 mL/L-reactor/day of headspace biogas and 500 mL/L-reactor/day of suction biogas). The increase in the total biogas production was attributed to an increase in the COD removal efficiency. At the trans-membrane pressure of 70 kPa (days 135 to 143), the average COD removal efficiency was 91%. These results indicate that the degasification process actually improved the COD removal efficiency, although the efficiency remained low. It is likely that the degasification successfully reduced the D-H_2 concentration in the bulk liquid and provided thermodynamically favorable conditions for the degradation of organic compounds by anaerobic microorganisms (Voolapalli and Stuckey, 1998). The D-H_2 concentration in the bulk liquid was too low to be determined using the headspace method. Instead, H_2 levels in the suction gas were measured and averaged 140 ± 120

ppm, which indicates the direct removal of D-H_2 in the bulk liquid. However, the degassing operational period in this study was too short for steady state to be reached with respect to biogas composition and COD.

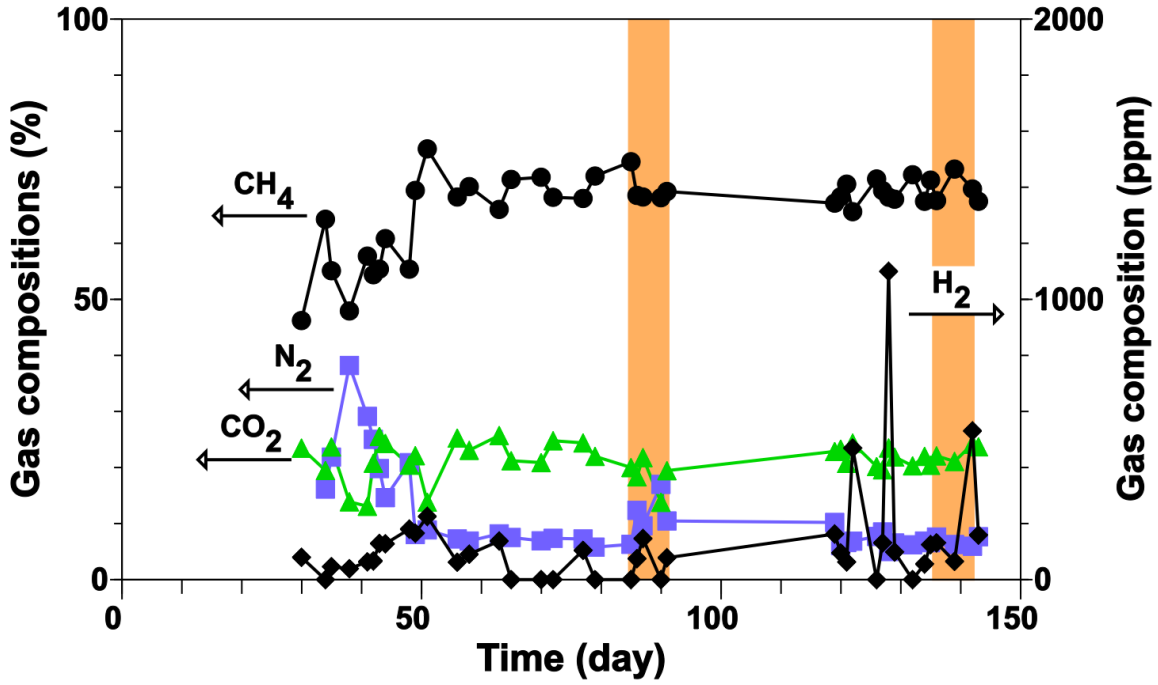


Figure 2.3: Variations in methane (CH_4), nitrogen (N_2), and carbon dioxide (CO_2) gas concentrations in the headspace of the UASB (upflow anaerobic sludge blanket) reactor. Shaded areas indicate the periods during which the reactor was operated at trans-membrane pressures of 50 or 70 kPa.

Therefore, further research is necessary to investigate the effects of degasification on reactor performances (e.g., COD removal efficiency, CH_4 recovery rate) over an extended period. Figure 2.3 shows the gas compositions in the headspace of the reactor over time. After 60 days the gas composition remained almost constant. Average measured gas compositions in the headspace were 66 ± 7% of CH_4, 21 ± 3% of CO_2, and 11 ± 7% of N_2. The H_2 contents were 80 ± 68, 60 ± 62, 240 ± 350, and 178 ± 177 ppm on days 70 to 84, days 85 to 91, days 92 to 134, and days 135 to 143, respectively. Thus, degasification did not affect the headspace gas compositions significantly.

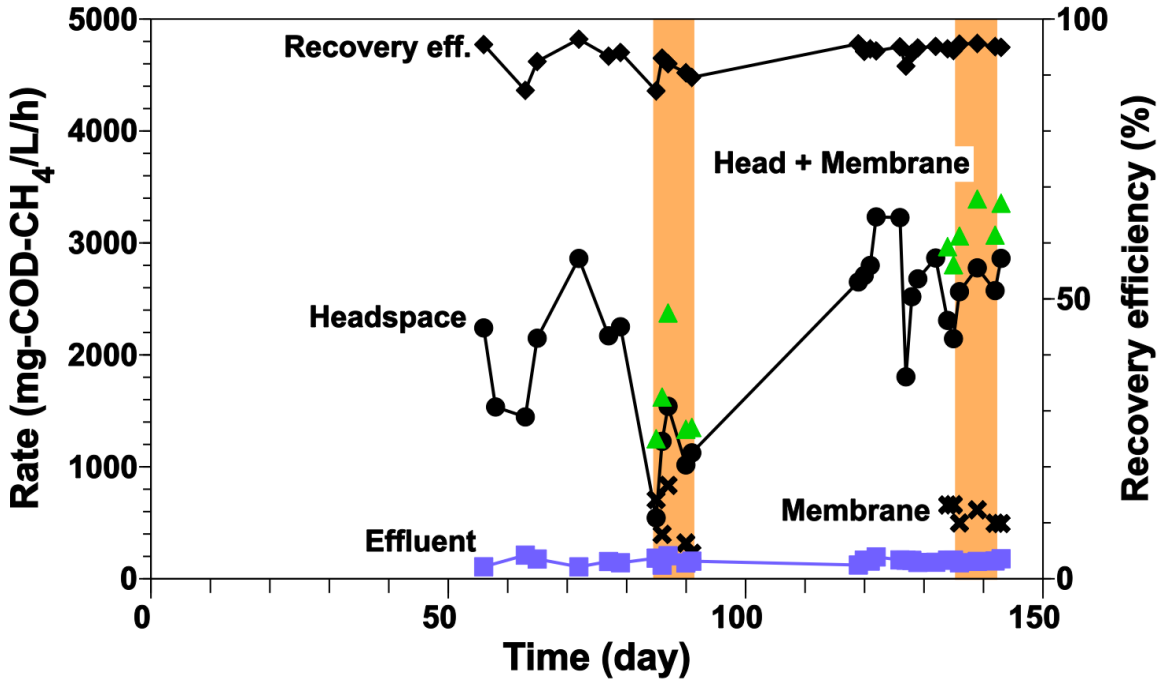


Figure 2.4: Production rates of methane gas (CH_4) evolved into the headspace. Methane gas recovered from the membrane and discharged in the effluent and CH_4 recovery efficiency in the UASB (upflow anaerobic sludge blanket) reactor.

Figure 2.4 shows the production rates of CH_4 gas evolved into the headspace, recovered from the membrane, and discharged into the effluent. It also illustrates CH_4 recovery efficiency in the UASB reactor. Figure 2.5 summarizes the average values of these CH_4 production rates. During normal operation, the average CH_4 evolution rate into the headspace was 1,750 ± 840 mg-COD/L-reactor/day. The D-CH_4 was discharged into the effluent at a rate of 160 ± 40 mg-COD/L-reactor/day. Thus, CH_4 loss into the effluent accounted for 8% of the total CH_4 produced (defined as the sum of CH_4 in the headspace, membrane, and effluent). During the degassing operation at 50 kPa, CH_4 could be collected from the membrane at an average rate of 440 ± 270 mg-COD/L-reactor/day. Contrary to expectations, the CH_4 discharging rate into the effluent was found to be almost the same as during normal operation; that is, the average D-CH_4 concentration (69 ± 12 mg-COD/L) was comparable to that during normal operation (73 ± 14 mg-COD/L). Thus, the CH_4 recovery efficiency (defined as the ratio of CH_4 in the headspace plus membrane to the total CH_4 production) during normal operation (92%) was comparable to that during the degassing operation (91%). The average CH_4 evolution rate into the headspace decreased to 1,230 ± 230 mg-COD/L-reactor/day during the degassing operation.

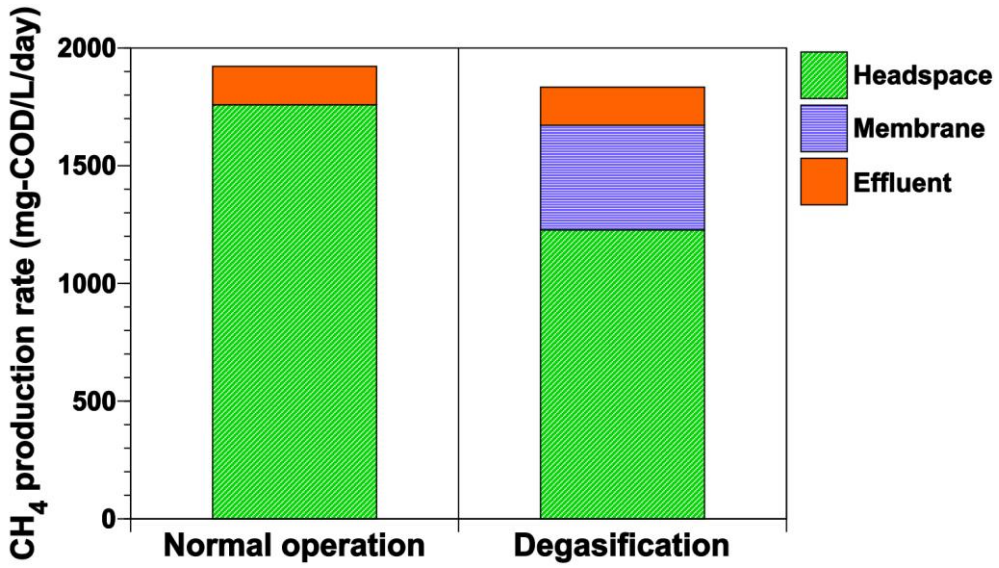


Figure 2.5: Average production rates of methane gas (CH_4) entering the headspace, collected from the membrane, and remaining in the effluent of the UASB (upflow anaerobic sludge blanket) reactor.

These results clearly show that CH_4 levels evolved in the headspace and collected from the membrane during the degassing operation were almost the same as the CH_4 evolved into the headspace during normal operation. Based on these findings, it can be concluded that (1) the D-CH_4 was successfully recovered from the DM, but (2) CH_4 in the headspace was redissolved into the bulk liquid in the reactor because of the CH_4 equilibrium between the liquid and gas phases. Therefore, in future studies, the DM reactor could be operated separately from the UASB reactor to prevent redissolution of CH_4 (Bandara et al., 2011). The CH_4 collection efficiency (defined as the ratio of CH_4 in the membrane to the CH_4 in the headspace plus membrane) was 26% (Matsunaga et al., 2012). This value was lower than the N_2O collection efficiency in an anammox (anaerobic ammonium oxidation) reactor (48%) as a result of lower trans-membrane pressure.

2.4 CONCLUSIONS

A degassing membrane (DM) was added to a UASB reactor to both recover D-H_2 in the bulk liquid and to improve COD removal efficiency. The D-H_2 could be recovered through a DM and such degasification could improve the COD removal efficiency. However, the degassing operational periods in this study were too short to verify the effect of degasification on overall process performance. Therefore, in future studies the DM reactor can be operated separately from the UASB reactor to prevent redissolution of CH_4.

Chapter 3

Removal of residual dissolved methane gas in an upflow anaerobic sludge blanket reactor treating low-strength wastewater at low temperature with degassing membrane

3 REMOVAL OF RESIDUAL DISSOLVED METHANE GAS IN AN UPFLOW ANAEROBIC SLUDGE BLANKET REACTOR TREATING LOW-STRENGTH WASTEWATER AT LOW TEMPERATURE WITH DEGASSING MEMBRANE

3.1 INTRODUCTION

Anaerobic processes are an attractive technology for wastewater treatment. Low biomass generation and low or zero energy requirements are the main advantages of anaerobic wastewater treatment. Most studies on anaerobic wastewater treatment have been conducted within mesophilic (30°C - 40°C) or thermophilic (50°C - 60°C) temperature ranges (Dhaked et al., 2010; Lettinga et al., 2001). However, low-strength wastewater, such as domestic and food-processing wastewater, is often discharged at ambient temperatures (15°C - 20°C) and heating the wastewater to maintain mesophilic conditions for anaerobic treatment introduces large energy requirements. It is known that anaerobic processes are not capable of achieving efficient organic removals when treating low-strength wastewaters at temperatures below the mesophilic range. Many industrial and domestic wastewaters have chemical oxygen demands (CODs) of less than 1,500 mg/L, and many of these wastewaters have seasonal low temperatures. Successful anaerobic treatment of such wastewaters without the addition of heat will have a significant effect in reducing the energy requirements and cost of wastewater treatment. Therefore, in this study a upflow anaerobic sludge blanket (UASB) reactor was operated over 170 days to investigate the reactor performance (i.e., COD removal and methane (CH_4) production rates) in treating low-strength wastewater under different operational conditions.

Improvements in reactor design and operational conditions have helped to overcome many of the disadvantages of anaerobic wastewater treatment that limited its application to high-strength wastewater treatment at mesophilic or thermophilic temperatures and have allowed for successful operation of anaerobic wastewater treatment reactors at low temperatures (Dhaked et al., 2010; Lettinga et al., 1999, 2001; Trzcinski and Stuckey, 2010; Luostarinen and Rintala, 2005; Madden et al., 2010; Xing et al., 2009; McKeown et al., 2009). In addition, several studies have focused on anaerobic wastewater treatment of low-strength wastewaters at lower temperatures (Elmitwalli et al., 2003; Angenent et al., 2001; Gomec et al., 2008; Matsushige et al., 1990). A drop in temperature causes a change in the physical and chemical properties of wastewater, and this can significantly affect the reactor performance. For instance, dissolved methane gas (D-CH_4) might play an important role in energy recovery efficiency of the reactor;

however, to date, the role of D-CH_4 has been overlooked. Discharge of residual D-CH_4 in the reactor effluent represents a loss of energy that may be recovered; in addition, D-CH_4 is a source of CH_4, a greenhouse gas, that may be released into the environment (Hartley and Lant, 2006; Hatamoto et al., 2010; Matsuura et al., 2010). This knowledge is particularly important when low-strength wastewaters are anaerobically treated at low temperature, because the solubility of CH_4 in the liquid phase increases with a decrease in temperature. Few studies have investigated the removal of D-CH_4 in anaerobic wastewater treatment processes by biological oxidation, physical gasification based on gas liquid equilibrium, and mixing with gas or a paddle (Hartley and Lant, 2006; Hatamoto et al., 2010; Matsuura et al., 2010; Pauss et al., 1990a,b). However, the recovery efficiency of D-CH_4 was low and/or the recovered CH_4 gas composition was low in these processes. Hence, another technology is required for the removal of D-CH_4 (Voolapalli and Stuckey, 1998).

In this study, we employed a hollow-fiber membrane to recover residual D-CH_4 in the effluent of an anaerobic wastewater treatment reactor by degasification. A bench-scale upflow anaerobic sludge blanket (UASB) reactor was operated, and the liquid outlet of the UASB reactor was connected to another reactor for degasification. After achieving stable COD removal efficiency, the D-CH_4 discharged from the UASB reactor was recovered by the degassing membrane (DM) reactor. In addition, we investigated the effects of temperature and hydraulic retention time (HRT) of the UASB reactor on the efficiency of degasification.

3.2 MATERIALS AND METHODS

3.2.1 Experimental setup

A bench-scale UASB reactor with a working volume of 1.3 L (height, 40 cm; diameter, 7 cm) was operated. Figure 3.1 shows an overview of the experimental apparatus. The reactor was inoculated with 0.3 L of anaerobic granular sludge obtained from a full-scale UASB reactor treating the wastewater from an isomerized sugar-processing plant.

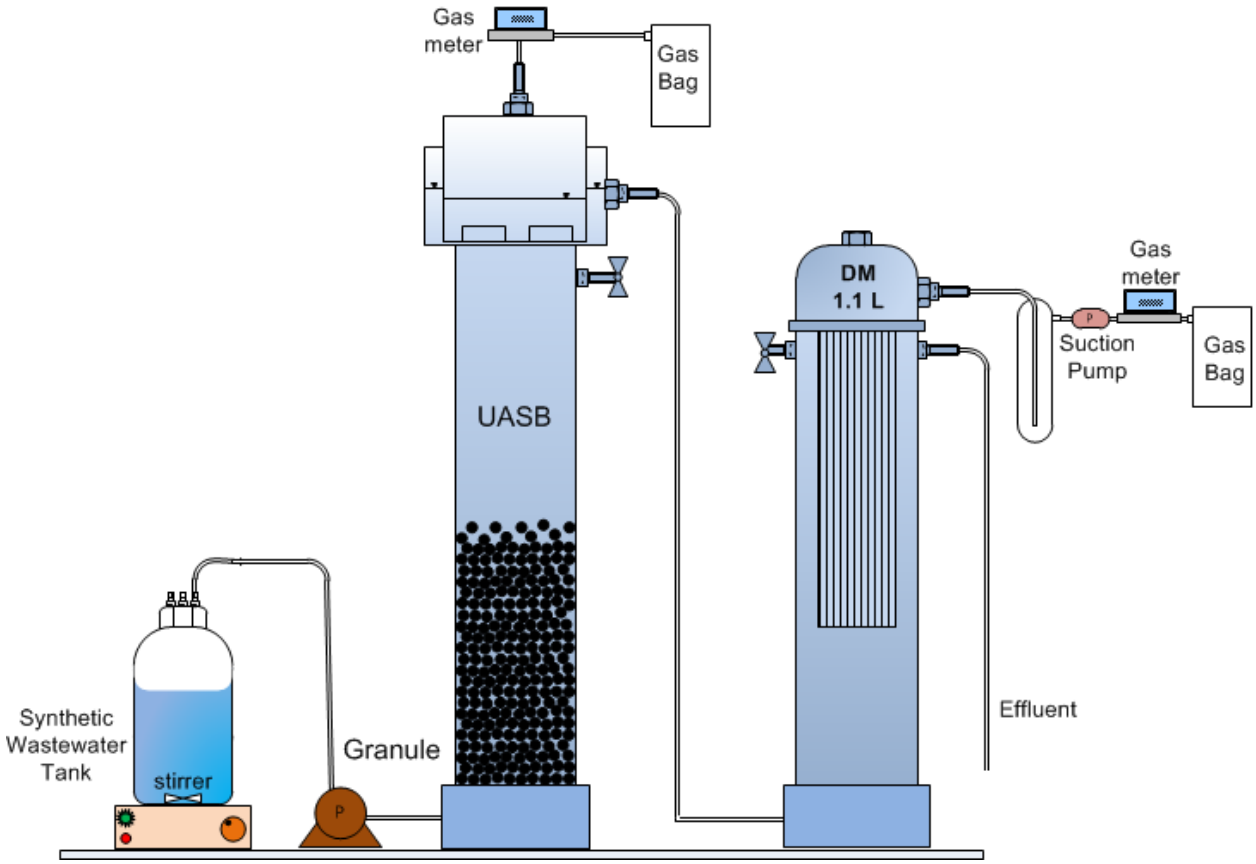


Figure 3.1: Experimental setup.

The UASB reactor was equipped with a water jacket to maintain a temperature of 35°C, 25°C, and 15°C. It was fed with a well mixed synthetic wastewater (Satoh et al., 2007). The synthetic wastewater contains milk powder (1,000 mg/L), $NaHCO_3$ (1,000 mg/L), K_2HPO_4 (250 mg/L), and the mineral solution. The composition of synthetic wastewater and milk powder is given in Table 3.1. On average organic loading rate was 3,500 mg total COD/L/day and HRT was 10 h, 6.66 h, and 3.33 h. pH in the bulk liquid was maintained at around 7 after 51 days. The experiment was divided into 7 experimental phases based on operating conditions (i.e., HRT and temperature) as given in the Table 3.2.

After gas production reached a steady state, dissolved gas in the liquid was collected by the DM. A reactor for degasification (height, 30 cm; diameter, 7 cm; working volume, 1.1 L) was connected to the liquid outlet of the UASB reactor to collect the residual D-CH_4 in the UASB effluent by degasification. A hollow-fiber membrane module (a multi-layered composite hollow-fiber membrane; MHF0504MBFT) provided by the Mitsubishi Rayon Co., Ltd. (Tokyo, Japan)

was installed in the DM reactor. The DM reactor was completely filled with the wastewater treated in the UASB reactor. The liquid in the DM reactor was not mixed. The characteristics of the DM module are summarized in Table 3.3. The dissolved biogas diffuses into the lumen of the hollow fibers of the DM under vacuum generated using a vacuum pump (Model APN-110KV- 1; Iwaki Co., Ltd., Tokyo, Japan). Although gas molecules can pass through the non-porous layer of the membrane, liquids cannot. Thus, the DM effectively separates dissolved gas from the liquid. The DM reactor was operated at same temperatures as the UASB reactor. Trans-membrane pressures were set at 50 kPa and 80 kPa (absolute pressure) by using a vacuum gauge, and HRTs of the DM reactor were altered in accordance with variations in the HRTs of the UASB reactor (Table 3.2). The operation of the DM reactor without degasification is referred to as normal operation.

Table 3.1: The components and the concentration of synthetic wastewater and milk powder

Synthetic wastewater

Component	Concentration (mg/L)
Milk powder	1,000
$NaHCO_3$	1,000
K_2HPO_4	250
$(NH_4)_2HPO_4$	28
KCl	28
NH_4Cl	32
$FeCl_2 \cdot 4H_2O$	16
$MgSO_4 \cdot 7H_2O$	32
$MnSO_4$	0.2
$CuCl_2 \cdot 2H_2O$	0.2
$CoCl_2 \cdot 6H_2O$	0.2
Ni	0.2
Zn	0.2

Milk powder (Nutrient 100 g)	
Energy	505 Kcal
Protein	11.8 g
Lipid	25.9 g
Sugar	57.2 g
Sodium	140 mg
Calcium	380 mg
Phosphorus	210 mg
Water	2.8 mg
Ash	2.3 g

Table 3.2: Summary of operational conditions

Phase	Influent T-COD concentration (mg/L)	T-COD loading rate (mg/L/h)	HRT of UASB (hour)	HRT of DM (hour)	Temperature (°C)	Trans-membrane pressure (kPa)
1.1	1,650 ± 132	150 ± 10	10.9 ± 0.2	9.2 ±0.2	35	0
1.2	1,580 ± 95	150 ± 4	10.3 ± 0.4	8.7 ± 0.3	35	50
1.3	1,620 ± 48	160 ± 10	10.0 ± 0.3	8.5 ± 0.3	35	80
1.4	1,640	160	10.4	8.8	35	0
2.1	1,530 ±21	150 ± 7	10.2 ± 0.4	8.6 ± 0.4	25	0
2.2	1,410 ± 13	140 ± 5	10.1 ± 0.3	8.5 ± 0.3	25	80
2.3	1,390	140	10.2	8.6	25	0
3.1	1,390 ±0	130 ± 7	10.3 ± 0.6	8.7 ± 0.5	15	0
3.2	1,340 ± 18	130 ± 4	10.1 ± 0.2	8.5 ± 0.2	15	80
3.3	1,400	140	10.0	8.5	15	0
4	1,460 ± 47	150 ± 4	10.0 ± 0.1	8.4 ± 0	35	0
5.1	810 ± 30	110 ± 23	5.5 ± 1.0	4.7 ± 0.8	35	0
5.2	880 ± 55	89 ± 5	6.6 ± 0	5.6 ± 0	35	80
5.3	950 ± 4	96 ± 1	6.6 ± 0	5.6 ±0	35	0
6.1	450 ± 48	45 ± 5	3.3. ± 0	2.8 ± 0	35	0
6.2	480 ± 5	48 ± 1	3.3 ± 0	2.8 ± 0	35	80
6.3	500	50	3.3	2.8	35	0
7	1,510 ±46	150 ± 5	9.9 ± 0.1	8.4 ± 0	35	0

Table 3.3: Characteristics of the degassing membrane module

Item	Characteristics
Non-porous layer for degassing	Polyethylene
Porous layer	Polyurethane
Outer diameter of a hollow fiber	280 µm
Inner diameter of a hollow fiber	200 µm
Thickness	40 µm
Length	360 mm
Number of hollow fiber	5,500
Total membrane area	1.7 m^2
Membrane volume	0.4 L

D-CH_4 collection efficiency was calculated as a ratio of D-CH_4 concentration collected by the DM to D-CH_4 discharged from the UASB reactor. The D-CH_4 concentration in the DM was calculated as the difference between the D-CH_4 concentrations discharged from the UASB and

DM reactors. Total CH_4 recovery efficiency was calculated as a ratio of the CH_4 recovery rate (mg COD/L/ day) to the total CH_4 production rate (mg COD/L/ day). The CH_4 recovery rate is defined as the sum of the CH_4 evolution rate in the UASB headspace and CH_4 collection rate in the DM. The total CH_4 production rate is defined as the sum of the CH_4 evolution rate, CH_4 collection rate, and CH_4 discharge rate from the DM reactor.

3.2.2 Sample analysis

COD measurement methods

The concentration of total COD (T-COD) and dissolved fraction of COD (D-COD) were measured using the Hach method (Method 8000) after filtering through 0.45-μm-pore-size membrane (Advantech Co., Ltd., Tokyo, Japan). After dilution of samples at adequate dilution rates, 2 mL of diluted samples was added to the COD reagent. After that, samples were kept at 150°C for 2 hours. After 2 hours, the samples were mixed instantly. Then samples were cooled to room temperature about 15 minutes. Particulate COD (P-COD) was calculated as T-COD minus D-COD.

Volatile fatty acid (VFA) measurement methods

VFA (lactic acid, formic acid, acetic acid, propionic acid, n-butyrate, and i-butyric acid) concentrations in the UASB were determined by a high-performance liquid chromatography system (LC-10AD system; Shimadzu Co., Kyoto, Japan) equipped with a Shimadzu Shim-pack CR-102H column (0.8 by 30 cm) after 10 times dilution, and filtration through 0.2-μm-pore-size membrane. Stationary phase is P-toluenesulfonic acid (5 mM), Bis-Tris (20 mM), and EDTA (100 μM) in the mixed solution. Mobile phase is a P-toluenesulfonic acid (5 mM). For the standard sample, the stock solution including lactic acid, formic acid, acetic acid, propionic acid, n-butyrate, and i-butyric acid (each 1000 mg-C/L) was diluted with 100 times.

pH measurement

The pH was measured using pH meter (Horiba, Ltd. D-51, Range pH 0.00 ~ pH 14.00), in the artificial wastewater tank, and inside UASB reactor.

Measurement of headspace gas

The gas composition of the headspace in the UASB reactor was measured by a gas chromatography system (GC-14B; Shimadzu Co., Kyoto, Japan) column. The biogas volumes were measured at ambient temperature.

Measurement of dissolved gas

The dissolved gas compositions were measured by using the headspace method. Liquid samples (50 mL) were obtained from the UASB and DM reactors and were injected with a syringe into a sealed vial (125 mL) that was prefilled with 100% argon gas. We then added 1 mL of 20 mM mercury (II) chloride to the vial to inhibit biological reactions. The vial was vigorously shaken for 5 min to allow for diffusion of the dissolved gas in the liquid sample into the headspace. The liquid sample was allowed to stand for 30 min at room temperature to equilibrate the gas and liquid phases. Then, the composition of the headspace gas was determined using gas chromatography. The standard liquid sample with known concentration of each standard gas was prepared as follows. A vial (125 mL) was filled with 50 mL of distilled water. Argon gas was blown into the distilled water in the vial for 5 min to remove air in the liquid and gas phases. The vial was then sealed with a butyl rubber septum. Next, we injected 1 mL of 100% of each gas, corresponding to 820 μmol at 25^{O}C, to the vial. The vial was shaken and allowed to stand for 30 min, and then, the composition of the headspace gas was determined by gas chromatography. The concentrations of dissolved gases in the sample liquid were calculated based on the ratio of the amount of gas in the sample to that in the standard sample. All measurements were conducted at a constant temperature of 25ºC.

On the base on these results, D-CH_4 collection efficiency was calculated as a ratio of D-CH_4 concentration collected by the DM to D-CH_4 discharged from the UASB reactor. The D-CH_4 concentration in the DM was calculated as the difference between the D-CH_4 concentrations discharged from the UASB and DM reactors. Total CH_4 recovery efficiency was calculated as a ratio of the CH_4 recovery rate (mg COD/L/ day) to the total CH_4 production rate (mg COD/L/ day). The CH_4 recovery rate is defined as the sum of the CH_4 evolution rate in the UASB headspace and CH_4 collection rate in the DM. The total CH_4 production rate is defined as the sum of the CH_4 evolution rate, CH_4 collection rate, and CH_4 discharge rate from the DM reactor.

3.3 RESULTS AND DISCUSSION

3.3.1 Performance of the upflow anaerobic sludge blanket (UASB) reactor

The bench-scale UASB reactor was operated at different temperatures and HRTs for 170 days, and concentrations of influent T-COD and effluent T-COD and D-COD in the UASB reactor were measured (Figure 3.2). The average T-COD concentration (± standard deviation) of the influent was 1,480 ± 240 mg COD/L from startup to day 128 (by Phase 4), after which the influent T-COD concentrations decreased to 870 ± 65 mg COD/L. Even at the beginning of the reactor operation, D-COD removal efficiency was high (Figure 3.2), probably because of the high amount of biomass, although the influent and effluent T-COD concentrations fluctuated. The average effluent D-COD concentration was 120 ± 40 mg COD/L by day 128, resulting in a D-COD removal efficiency as high as 92 ± 2%.

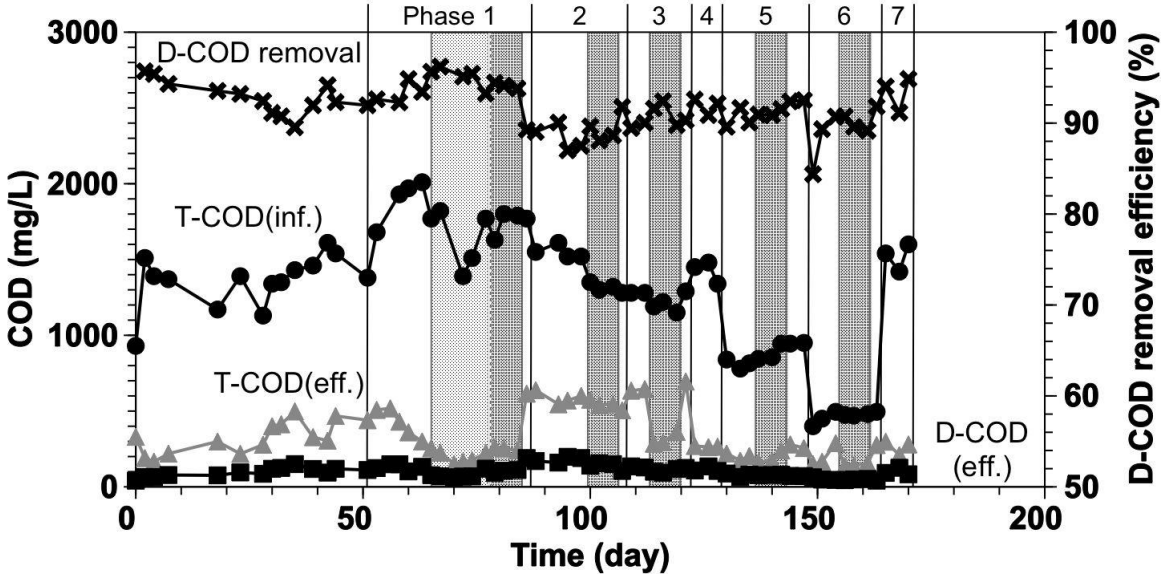


Figure 3.2: Concentration of influent total chemical oxygen demand (T-COD) and effluent T-COD and dissolved fraction of COD (D-COD) in the upflow anaerobic sludge blanket (UASB) reactor, and D-COD removal efficiency of the UASB reactor. Operational conditions in each phase are summarized in Table 3.2.

Total VFA concentration in the UASB reactor was less than 68 mg COD/L for 170 days (data not shown). The dominant VFA was acetate, with a maximal concentration of 53 mg COD/L and average concentration of 28 ± 14 mg COD/L for 170 days. The second dominant VFA was propionate (9 ± 6 mg COD/L); the concentrations of other VFAs (lactate, formate, i-butyrate, and n-butyrate) were less than 1 mg COD/L.

3.3.2 Performance of the degassing membrane (DM) reactor

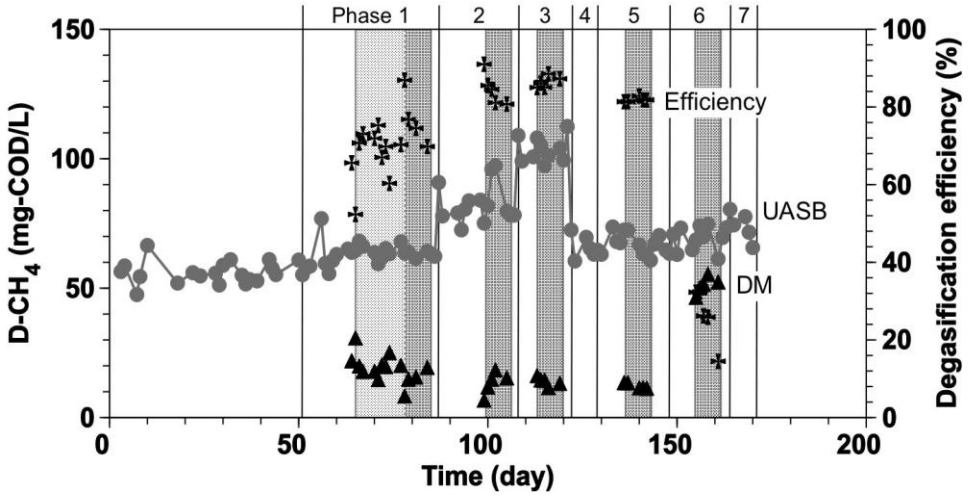


Figure 3.3: Dissolved methane (D-CH_4) concentrations in the upflow anaerobic sludge blanket (UASB) and degassing membrane (DM) reactors, and D-CH_4 collection efficiency of the DM reactor. The gray area represents a degasification period. Operational conditions in each phase are summarized in Table 3.2.

Since the reactor performance (e.g., the dissolved chemical oxygen demand (D-COD) removal efficiency of the UASB reactor) became stable after adjusting the pH to 7.6 after day 51, degasification was conducted at a trans-membrane pressure (absolute pressure) of 50 kPa from day 64 (Phase 1.2) to recover residual D-CH_4 in the UASB effluent. The average D-CH_4 concentration was 61 ± 6 mg COD/L during normal operation (Phase 1.1); in contrast, it was 20 ± 4 mg COD/L in the effluent of the DM reactor during the degasification period (Phase 1.2) (Figure 3.3). The difference between the D-CH_4 concentrations in the effluents of the UASB and DM reactors indicated that the DM successfully collected D-CH_4 during the degasification period. The trans-membrane pressure was further reduced by 20 kPa (absolute pressure) at day 78 (Phase 1.3) to reduce the residual D-CH_4 in the UASB effluent. The D-CH_4 concentration was 15 ± 5 mg COD/L in the DM reactor effluent in Phase 1.3 (Figure 3.3). Based on these results, D-CH_4 collection efficiency was calculated to be 73 ± 8% in Phase 1. To check for reproducibility of the efficiency of degasification, vacuum was discontinued at day 85 (Phase 1.4). The average D-CH_4 concentration was 63 ± 1 mg COD/L in the DM reactor effluent in Phase 1.4, and this concentration was comparable to that before degasification (Phase 1.1) (Figure 3.3). These results clearly indicated that D-CH_4 was successfully collected by degasification with the DM.

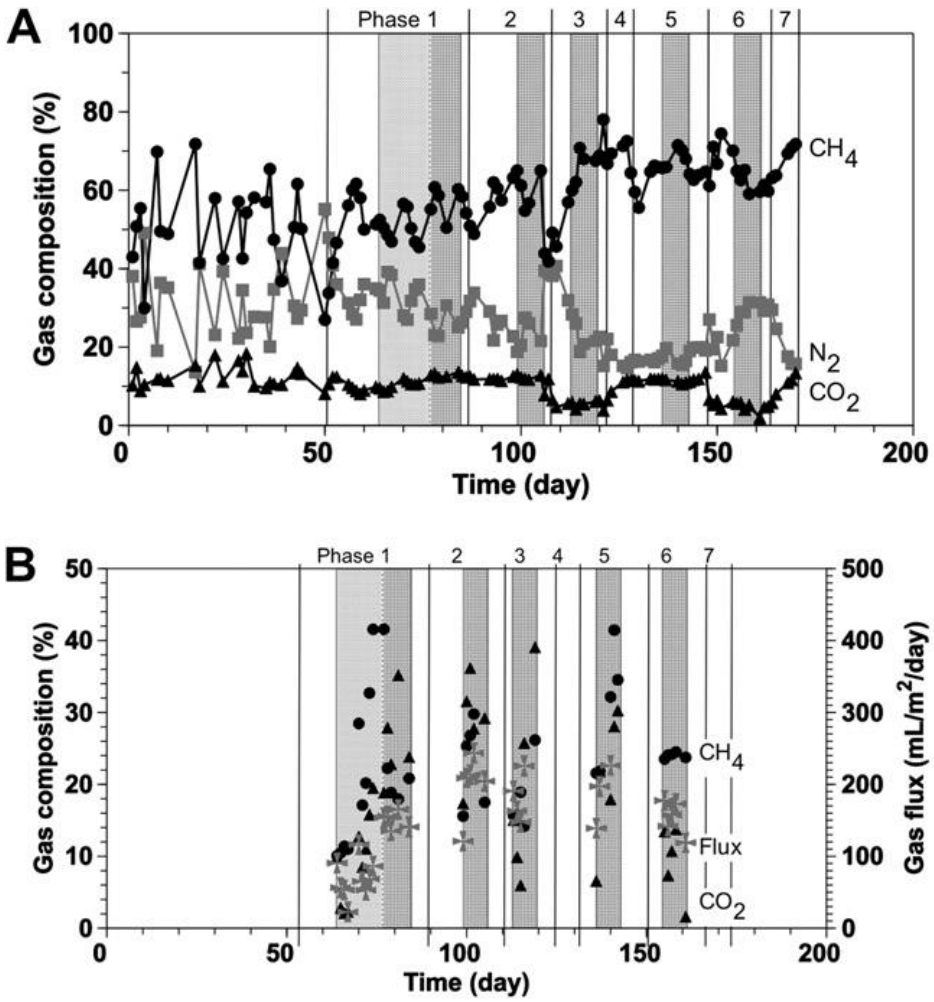


Figure 3.4: Gas compositions in the headspace of the upflow anaerobic sludge blanket (UASB) reactor (A) and inside the lumen of the hollow fibers of the degassing membrane (DM), and gas flux into the hollow fibers of the DM (B). The gray area represents the degasification period. Operational conditions in each phase are summarized in Table 3.2.

Discharge of residual D-CH_4 in the effluent of wastewater treatment reactors contributes to an increase in atmospheric CH_4, which is 21 times more potent than CO_2 as a greenhouse gas (Hartley and Lant, 2006). In addition, the D-CH_4 discharge represents a loss of energy that is generated in anaerobic wastewater treatment processes. Therefore, recovery of D-CH_4 from the effluent of the anaerobic wastewater treatment reactors is a prerequisite for the discharge of the effluent into the environment. Gas compositions in the headspace of the UASB reactor (Figure 3.4A) and inside the lumen of the hollow fibers of the DM (Figure 3.4B) are shown in Figure 3.4. Although gas compositions fluctuated until day 50, they became relatively stable thereafter because of pH adjustment to 7.6. Average CH_4 compositions in the UASB headspace during the degasification period (Phases 1.2 and 1.3) were 51 ± 4% and 58 ± 5%, respectively, and they

were 49 ±12% and 56 ± 3% during normal operation (Phases 1.1 and 1.4, respectively) (Figure 3.4A). Thus, degasification did not significantly affect the CH_4 composition in the UASB headspace. Average compositions of CH_4 and CO_2 collected through the DM during the degasification period were 22 ± 13% and 10 ± 7%, respectively, in Phase 1.2, and 20 ± 2% and 27 ± 6%, respectively, in Phase 1.3 (Figure 3.4B).

Oxygen (O_2) was detected in the biogas collected through the DM; this indicated the ingress of air into the dissolved gas collection line. The percentage of Nitrogen (N_2) plus O_2 in the collected biogas varied from 39% to 87% in Phase 1. The ratios of N_2 to O_2 were 3.9 or higher, and these ratios were greater than the ratio of N_2 to O_2 in air (79/21 or 3.76). This was because the dissolved biogas itself contained N_2 but not O_2. If air had been excluded from the collected biogas, the average CH_4 composition in the collected gas would have been 63 ± 15% in Phase 1.2, which would have been comparable to that in the UASB headspace.

Several approaches for removal and/or recovery of D-CH_4 in wastewater treatment processes have been investigated. Hatamoto et al. (2010) used an encapsulated down-flow hanging sponge (DHS) reactor to biologically oxidize the D-CH_4; although this technique enabled oxidization of 95% of the D-CH_4, no D-CH_4 was recovered as CH_4 gas. In contrast, Matsuura et al. (2010) employed a two-stage Down-flow Hanging Sponge Reactor (DHS) reactor for post-treatment of the effluent from a UASB reactor treating municipal sewage to recover and oxidize D-CH_4. The first stage reactor could recover D-CH_4 with 77% recovery efficiency. However, CH_4 compositions in the recovered biogas were relatively low because of an inherent limitation of this method the D-CH_4 is released from a liquid in the DHS reactor by physical gasification based on the gas liquid equilibrium. Another approach for removing D-CH_4 involved mixing the liquid in an anaerobic wastewater treatment reactor with gas or a paddle. Hartley and Lant (2006) applied intermittent gas mixing by micro-aeration with biogas containing air, and this resulted in the release of D-CH_4 into the gas phase of the reactor. However, the CH_4 composition in the recovered biogas was lower than that in the reactor headspace in the absence of aeration, because the gas used for aeration diluted the biogas. Recovered biogas with low CH_4 concentration is unsuitable for subsequent energy generation processes. Pauss et al. (1990a) mixed the liquid phase in reactors with a paddle or by recirculating the supernatant liquid to enhance the evolution of D-CH_4 and gas bubbles attached to solid particles from the liquid phase to gas phase.

However, in this method, the D-CH_4 concentration would theoretically never be lower than the saturation concentration of D-CH_4. Another possible process is to apply vacuum directly to the reactor. It does not seem to be realistic, because the reactor must be closed completely and a pressure tight case.

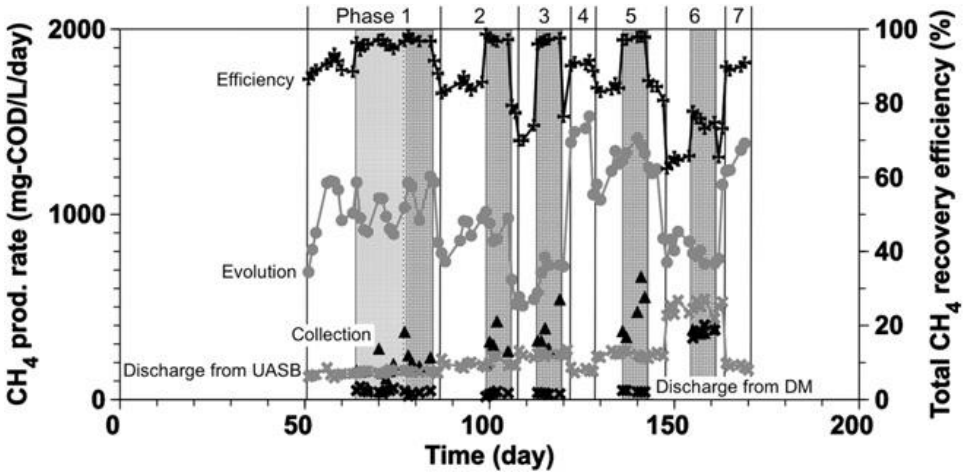


Figure 3.5: Rates (mg COD/L/day) of CH_4 evolution in the upflow anaerobic sludge blanket (UASB) headspace, CH_4 collection from the degassing membrane (DM), and CH_4 discharge from the UASB and DM reactors, as well as total CH_4 recovery efficiency. The gray area represents a degasification period. Operational conditions in each phase are summarized in Table 3.2.

In order to check the mass balance of CH_4, the CH_4 evolution rate in the UASB headspace, CH_4 collection rate from the DM, and CH_4 discharge rate from the DM reactor were calculated using the CH_4 concentrations and flow rates of wastewater and biogas described above. Figure 3.5 shows the rates of CH_4 discharged from the UASB reactor and total CH_4 recovery efficiency.

The average CH_4 evolution rates were 1,000 ± 94 mg COD/L/day and 1,120 ± 110 mg COD/L/day during the degasification period (Phases 1.2 and 1.3, respectively). These rates were comparable to those during normal operation (960 ± 220 mg COD/L/day in Phase 1.1 and 1,010 ± 230 mg COD/L/day in Phase 1.4). Thus, degasification did not significantly affect the CH_4 evolution rate in the UASB reactor. In contrast, the average CH_4 discharge rates were lower during the degasification period (49 ± 10 mg COD/L/day in Phase 1.2 and 35 ± 11 mg COD/L/day in Phase 1.3) than during normal operation (140 ± 14 mg COD/L/day in Phase 1.1 and 150 ± 3 mg COD/L/day in Phase 1.4) because of the collection of D-CH_4 with the DM. The D-CH_4 discharge rate accounted for 11 ± 3% of the total CH_4 production rate during the normal operation (Phase 1.1), whereas it was 2.6 ± 0.8% during the degasification period (Phase 1.3).

The average CH_4 collection rates were 180 ± 85 mg COD/L/day in Phase 1.2 and 210 ± 26 mg COD/L/day in Phase 1.3 (Figure 3.5). On the basis of these results, the total CH_4 production rates were calculated to be 1,090 ± 230 mg COD/L/day in Phase 1.1 and 1,160 ± 230 mg COD/L/day in Phase 1.4. In contrast, these rates were slightly higher (1,220 ± 140 mg COD/L/day in Phase 1.2 and 1,370 ± 130 mg COD/L/day in Phase 1.3) during the degasification period, probably because of CH_4 production in the DM reactor. Accordingly, D-CH_4 collection efficiencies were 68 ± 7% and 77 ± 7% in Phases 1.2 and 1.3, respectively, and total CH_4 recovery efficiencies increased up to 96 ± 1% and 97 ± 1% during the degasification period (Phases 1.2 and 1.3, respectively), as compared to those during normal operation (89 ± 3% in Phase 1.1 and 90 ± 2% in Phase 1.4).

3.3.3 The effect of temperature

Dissolved methane (D-CH_4)

The UASB and DM reactors were operated at low temperatures (25ºC and 15ºC in phases 2 and 3, respectively). The average D-CH_4 concentrations in the UASB reactor were 63 ± 4 mg COD/L at 35°C throughout Phase 1, 82 ± 7 mg COD/L at 25°C throughout Phase 2, and 104 ± 5 mg COD/L at 15°C throughout Phase 3 (Figure 3.3). The increase in D-CH_4 concentrations at lower temperatures was attributed to an increase in the solubility of CH_4 in the liquid phase with decreasing temperature. Corresponding with the increase in D-CH_4 concentration, average D-CH_4 discharge rates increased from 150 ± 12 mg COD/L/day at 35°C to 200 ± 20 mg COD/L/day at 25°C and 250 ± 13 mg COD/L/day at 15°C, thereby indicating that the loss of D-CH_4 from the UASB reactor was more significant at lower temperatures.

Degasification enabled successful collection of D-CH_4 by the DM regardless of temperature. The D-CH_4 concentrations decreased to 13 ± 4 mg COD/L at 25°C (Phase 2.2) and 14 ± 2 mg COD/L at 15°C (Phase 3.2) in the DM reactor. The ratio of D-CH_4 concentration to CH_4 composition in the UASB headspace increased with decreasing temperature. Therefore, the CH_4 collection rates showed a relative increase from 210 ± 26 mg COD/L/day at 35°C (Phase 1.3) to 300 ± 84 mg COD/L/day at 25°C (Phase 2.2) and to 370 ± 100 mg COD/L/day at 15°C (Phase 3.2). Accordingly, total CH_4 recovery efficiency increased from 71% in Phase 3.1 to 97% at 15°C by

degasification (Phase 3.2), and D-CH_4 collection efficiencies increased with a decrease in temperature from 77 ± 7% at 35°C to 85 ± 4% at 25°C and 86 ± 2% at 15°C.

CH_4 evolution and CH_4 recovery rate in the UASB reactor

CH_4 evolution rates in the UASB headspace decreased with a decrease in temperature (Figure 3.5); 1,000 ± 170 mg COD/L/day throughout Phase 1, 860 ± 140 mg COD/L/day throughout Phase 2, and 650 ± 100 mg COD/L/day throughout Phase 3. D-COD removal efficiency was not considerably decreased at lower temperatures (94%, 89%, and 91% in Phases 1.3, 2.2, and 3.2 respectively). This finding indicated that microbial CH_4 production activity was maintained even at low temperatures probably because of the presence of sufficient amount of biomass and high bioavailability of influent organic materials. Hence, the decrease in the CH_4 evolution rate might be due to an increase in the solubility of CH_4 in the liquid phase (Lettinga et al., 2001).

The CH_4 recovery rates at 25°C (1,230 ± 54 mg COD/L/day in Phase 2.2) and at 15°C (1,060 ± 150 mg COD/L/day in Phase 3.2) were higher than the CH_4 evolution rate at 35°C during normal operation (1,000 ± 170 mg COD/L/day throughout Phase 1). Thus, it can be concluded that the degasification technology enables us to recover CH_4 in a UASB process at low temperature without heating, and the amount of CH_4 produced in the UASB process is comparable to that produced in a conventional process under mesophilic conditions. In general, many types of wastewaters are discharged at low ambient temperatures under temperate climatic conditions. To treat such wastewaters under mesophilic condition, their temperature must be increased to the optimal mesophilic range. This requires a significant amount of energy, and the high-energy cost is a heavy economic burden on such wastewater treatment systems (Lettinga et al., 2001). A UASB process that does not require heating is economically attractive (Angenent et al., 2001; Dhaked et al., 2010). However, the degasification technology also consumed much energy in this study (42 J/s). The maximal CH_4 collection rate of 660 mg COD/L/day (Figure 3.5) was comparable only to 0.14 J/s, assuming that 1 L of CH_4 has the energy of 35,800 J. Future studies must aim to reduce the energy required for degasification so that the degasification technology may be applied in real wastewater treatment processes.

COD removal efficiency

Concentrations of influent T-COD and effluent T-COD and D-COD in the UASB reactor are shown in Figure 3.2. Although the D-COD removal efficiency was slightly decreased at lower temperatures (Phases 2 and 3), it was still higher than 87%, and the effluent D-COD concentration was less than 200 mg COD/L (Figure 3.2). In contrast, the P-COD concentration in the DM reactor, which was calculated as the difference between the effluent T-COD and D-COD concentrations, increased at lower temperatures, indicating a decrease in P-COD removal efficiency. At lower temperatures, particles might settle more slowly because of lower liquid-solid separation efficiency, which in turn may be attributed to higher liquid viscosity and/or attachment of gas bubbles onto the particles. Interestingly, the P-COD removal efficiency in the DM reactor was improved by degasification in Phase 3. This finding may be explained by the fact that a decrease in the dissolved gas concentration in the liquid in the DM reactor caused by degasification, followed by redissolution of the gas bubbles attached to the particles, caused the particles to efficiently settle down. The degasification technology might improve the efficiency of particle separation in a clarifier for a UASB reactor. To verify the reproducibility of temperature effects, the temperature in the UASB reactor was set at 35°C again at day 123. The average D-COD removal efficiency (92 ± 1%) and the D-CH_4 concentration (66 ± 5 mg COD/L) in Phase 4 were comparable to those in Phase 1 (94 ± 2% and 63 ± 4 mg COD/L, respectively). This finding indicated that changes in chemical parameters (e.g., the D-CH_4 concentration and the CH_4 evolution rate in the UASB reactor) in Phases 2 and 3 were attributed to lower temperatures.

3.3.4 The effect of hydraulic retention time

The UASB reactor was again operated at 35°C but at lower COD concentrations (the concentrations throughout Phase 5 and Phase 6 were two-third and one-third, respectively, of that in Phase 4) (Figure 3.2 and Table 3.2). In order to keep the COD loading rate of the UASB reactor constant, HRTs in Phase 5 (6.7 h) and Phase 6 (3.3 h) were also reduced to two-third and one-third, respectively, of the HRT in phase 4 (10 h) by increasing the wastewater feed rate. The average D-CH_4 concentration in the UASB reactor was ca. 70 mg COD/L in Phases 4 to 7 because of the identical solubility of CH_4 at a constant temperature (35°C). The average D-CH_4 concentration was ca. 90% of the theoretical saturation concentration of D-CH_4 at 35°C (Hartley

and Lant, 2006). An increase in the wastewater feed rate resulted in an increase in the CH_4 discharge rate from the UASB reactor (Figure 3.5). The D-CH_4 discharge rates were 160 ± 12 mg COD/L/day in Phase 4, 240 ± 15 mg COD/L/day throughout Phase 5, and 500 ± 35 mg COD/L/day throughout Phase 6. The average CH_4 collection rate was 480 ± 130 mg COD/L/day in Phase 5.2, and this was much higher than that in Phase 1.3 (210 ± 26 mg COD/L/day) because of the higher D-CH_4 concentration. The corresponding total CH_4 recovery efficiency was 98% and the CH_4 recovery rate was 1,830 ± 160 mg COD/L/day, which was 1.5 times higher than that in normal operation at the same HRT in Phase 5.1 (1,220 ± 100 mg COD/L/day). These results indicate that the UASB process with degasification is a promising technology for effective CH_4 recovery in low-strength wastewater treatment. Because of the economical benefits offered by the UASB process, its application to low-strength wastewater treatment has recently attracted much attention (Angenent et al., 2001; Elmitwalli et al., 2003; Gomec et al., 2008; Matsushige et al., 1990). At an HRT of 3.3 h, D-CH_4 remained at a high concentration (51 ± 3 mg COD/L, and hence, the total CH_4 recovery efficiency was as low as 76 ± 2% during the degasification period (Phase 6.2). This was probably because of insufficient HRT to collect D-CH_4; however, the average CH_4 collection rate was still high (370 ± 10 mg COD/L/day). The average biogas collection rates calculated by excluding the amount of air from the collected biogas (i.e., biogas flux through the DM) were 150 ± 14 mL/m^2/day in Phase 1.3 and 150 ± 24 mL/m^2/day in Phase 6.2 (Figure 3.4B), indicating that the decrease in biogas flux due to membrane fouling was negligible in this study.

3.4 CONCLUSIONS

A bench-scale UASB reactor was operated at different temperatures and HRTs for 170 days. Low-strength wastewater could be treated with a UASB reactor at low temperatures and short HRTs. D-COD removal efficiency was higher than the 90% irrespective of the temperature due to the use of synthetic wastewater without recalcitrant organic compounds, long HRT, and the large amount of biomass retained.

Particularly under temperate climate conditions, many low and medium strength wastewaters are discharged at low ambient temperatures (<18°C). On the other hand, practically all full-scale applications of anaerobic wastewater treatment so far are restricted to wastewater with

temperatures exceeding 18ºC. Hence, in general, a significant amount of energy is required to bring the wastewater temperature up to the optimal mesophilic range (30ºC - 40ºC) than 18ºC. This puts a heavy burden on the economy of the wastewater system.

A bench-scale upflow anaerobic sludge blanket (UASB) reactor equipped with the degassing membrane (DM) reactor was operated to treat synthetic wastewater. The system was operated at different temperatures and HRTs. D-CH_4 was successfully collected by degasification with the DM. Under lower temperatures or shorter HRTs, the D-CH_4 concentrations increased; therefore, the D-CH_4 collection efficiencies increased. Moreover, the P-COD concentration was decreased by degasification. These results indicated that degasification is a promising technology for improving CH_4 recovery and P-COD removal efficiencies of the UASB process for treating low-strength wastewater at low temperature. Conclusions were drawn with using synthetic wastewater and this procedure would be better tested with real wastewater.

Chapter 4

Anaerobic treatment of municipal wastewater at ambient temperatures and recovery of dissolved methane

4 ANAEROBIC TREATMENT OF MUNICIPAL WASTEWATER AT AMBIENT TEMPERATURES AND RECOVERY OF DISSOLVED METHANE

4.1 INTRODUCTION

Anaerobic treatment is an attractive option for the biological treatment of municipal wastewater (Elefsiniotis et al., 1996; Kayranli and Ugurlu, 2011; Latif et al., 2011; Lew et al., 2011). In temperate regions, the ambient temperature of municipal wastewaters is considerably lower than the optimum value for anaerobic treatment processes (Dhaked et al., 2010; Latif et al., 2011). To operate anaerobic treatment processes under mesophilic conditions (30°C - 40°C), a significant input of energy is required to heat the influent wastewaters, resulting in a loss of energy. Thus, the operation of an anaerobic bioreactor for municipal wastewater treatment at ambient temperature in temperate regions offers economic advantages over the operation under mesophilic or thermophilic (50°C - 60°C) conditions.

Anaerobic treatment of low-strength wastewaters at ambient or low temperatures has recently been successfully demonstrated (A'lvarez et al., 2008; Kayranli and Ugurlu, 2011; Latif et al., 2011; Lew et al., 2011; Urban et al., 2007). However, further studies are required to anaerobically treat low-strength municipal wastewaters at low temperatures. Domestic sewage is a complex substrate with only a small fraction of readily degradable matter in anaerobic conditions, making the hydrolysis become the limiting step of the overall process in many cases. Specifically, chemical oxygen demand (COD) removal rate and methane (CH_4) production rate are low owing to lower microbial activity under psychrophilic (< 20°C) conditions (Dhaked et al., 2010; Latif et al., 2011). There is limited research that considered seasonal variability. Usually, anaerobic treatment plants unable to equalize the seasonal variations. The economic feasibility of the long-term low-temperature anaerobic treatment relies on sufficient microbial activity to ensure reliable wastewater treatment. However, little is known about psychrophilic methanogenesis. In some systems mesophilic methanogenic communities that adapt to low temperatures contributed to methanogenesis, in contrast, specific psychrophilic methanogenic communities carried out methanogenesis in others. (Dhaked et al., 2010). Greater insights into the relationship between process performance and microbial characteristics in the anaerobic treatment of municipal wastewaters at low temperature are required to achieve stable COD removal and biogas production.

It is also important to consider dissolved methane gas (D-CH_4) in the anaerobic treatment of municipal wastewaters. D-CH_4 in anaerobic treatment effluent is not usually recovered, which results in greenhouse gas emission from the anaerobic treatment process and loss of a potential energy resource (Urban et al., 2007). The loss of D-CH4 is enhanced at lower temperatures because of the increase in CH_4 solubility at reduced temperatures (Bandara et al., 2011). Thus, it is the case with the anaerobic treatment of municipal wastewaters at low temperatures. In these processes, as much D-CH_4 as possible from the anaerobic treatment effluent should be collected. Several studies have investigated the collection of D-CH_4 from the anaerobic treatment of wastewaters by physical gasification based on gas liquid equilibrium and mixing with gas or a paddle (Hatamoto et al., 2010; Matsuura et al., 2010; Hartley and Lant, 2006; Pauss et al., 1990a). However, the collection efficiency of D-CH_4 was low and/or the recovered CH_4 gas concentration was low using these technologies. Our previous research demonstrated that degasification with a degassing membrane (DM) could effectively collect D-CH_4 without reducing its concentration in the anaerobic treatment of a low-strength synthetic wastewater at low temperature (Bandara et al., 2011). The DM only allows gas molecules to pass through the non-porous layer of the DM (Bandara et al., 2011; Matsunaga et al., 2012). Thus, the DM effectively separates dissolved gases from the liquid. In the present research study, we operated a bench-scale upflow anaerobic sludge blanket (UASB) reactor, of which the liquid outlet was connected to the DM reactor, to treat raw municipal wastewater at ambient temperature (from 6 ºC to 31 ºC) over 18 months. The aim of this study is therefore to investigate the effect of seasonal variations on the performance of the anaerobic digestion (AD). Additionally, the D-CH_4 collection efficiency by degasification was investigated.

4.2 MATERIALS AND METHODS

4.2.1 Experimental setup

A upflow anaerobic sludge blanket (UASB) reactor (height, 80 cm; diameter, 5 cm; working volume, 2.6 L) was operated from January 2010 to June 2011 (Figure 4.1). The reactor was inoculated with 0.7 L of anaerobic granular sludge obtained from the bench-scale UASB reactor operated in our laboratory (Bandara et al., 2011). It had total and volatile solids concentrations of 24 g/L and 18 g/L, respectively. The UASB reactor was fed with domestic wastewater obtained from the Souseigawa municipal wastewater treatment plant in Sapporo, Japan (Okabe et al.,

1999). The concentrations (average ± standard deviation) of total chemical oxygen demand (T-COD) and the dissolved fraction of COD (D-COD), and pH in the wastewater were 173 ± 38 g/L, 78 ± 17 g/L, and 7.2 ± 0.2, respectively. The hydraulic retention time (HRT) was changed in response to changes in the COD removal efficiency (Figure 4.2b). The temperature, which was not controlled, varied from 6°C to 31°C. A 20-cm-high filter media (polyester nonwoven fabric sheets; Japan Vilene Co., Ltd., Tokyo, Japan) was installed in the upper part of the UASB reactor on June 22, 2010, to avoid biomass washout.

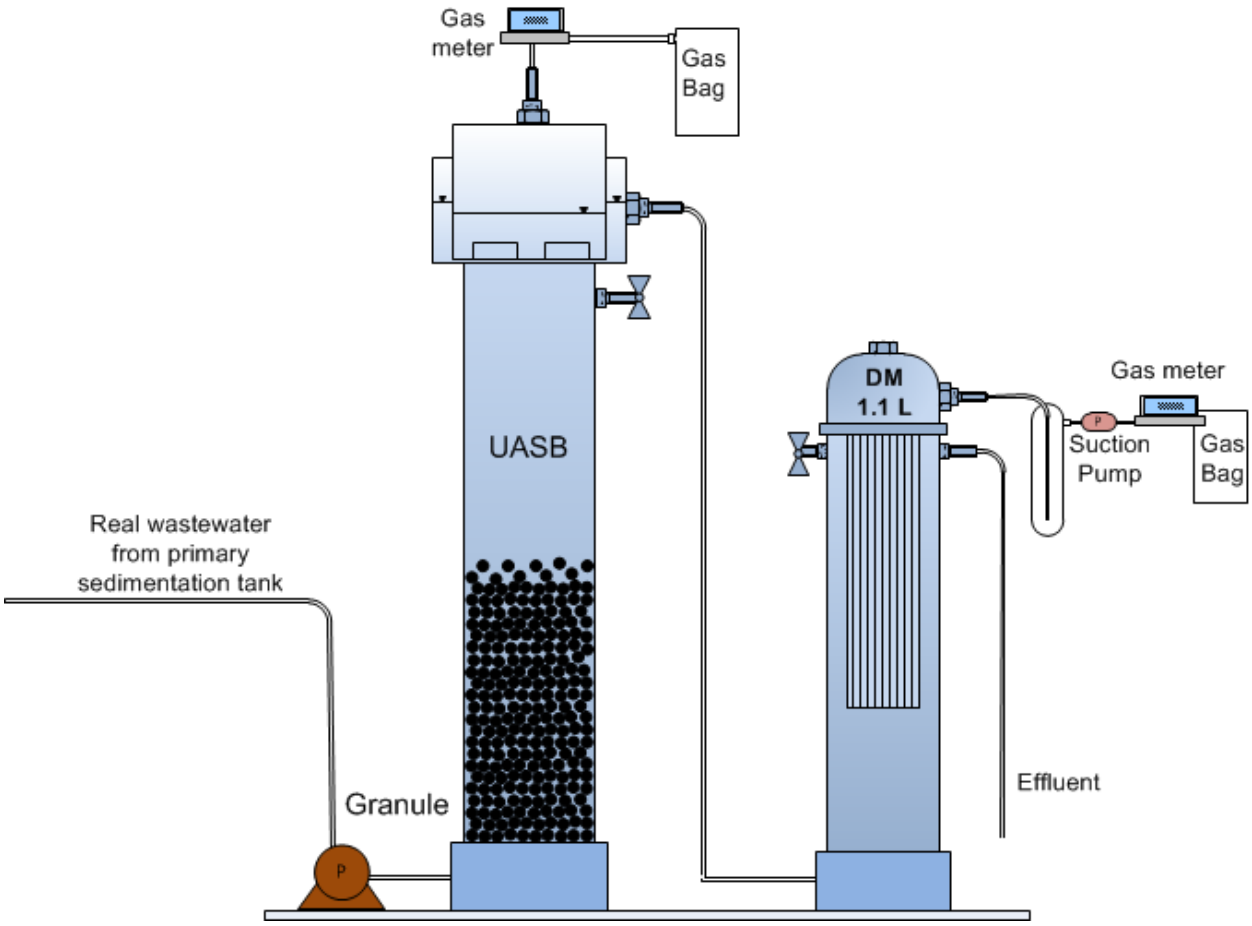


Figure 4.1: Experimental setup.

A DM reactor was connected to the effluent of the UASB reactor treating sewage wastewater to collect the residual D-CH_4 in the effluent according to the above study. The characteristics of the DM were described in detail previously. D-CH_4 was collected into the lumen of the hollow fibers of the DM using a vacuum pump and the trans-membrane pressure was set to 80 kPa using a

vacuum gauge. A trans-membrane pressure of 97 kPa was also tested after April 25, 2011, to investigate the effect of trans-membrane pressure on D-CH_4 collection efficiency.

4.2.2 Sample analysis

CH_4 gas concentrations in the headspace of the UASB reactor was measured by using a gas chromatography system (Bandara et al., 2011). Dissolved gas concentrations were measured using the headspace method. The concentrations of T-COD and D-COD in the influent and effluent were measured using a Hach method (Method 8000) (Bandara et al., 2011). Particulate fraction of COD (P-COD) concentration was estimated by subtracting the D-COD concentration from the T-COD concentration. The oxidation–reduction potential (ORP) and pH were directly determined by using an ORP and a pH electrode, respectively.

On the basis of these measurements and liquid flow rates, the rates (mg COD/day) of CH_4 evolved into the UASB headspace ($R(CH_4)_{evo}$), D-CH_4 discharged from the UASB reactor ($R(D\text{-}CH_4)_{UASB}$), D-CH_4 collected with the DM ($R(D\text{-}CH_4)_{col}$), and D-CH_4 discharged from the DM reactor ($R(D\text{-}CH_4)_{dis}$) were calculated. Furthermore, the D-CH_4 collection efficiency was calculated as;

$$D-CH_4\ collection\ efficiency = \frac{R(D-CH_4)_{col}}{R(D-CH_4)_{UASB}}$$

The CH_4 recovery efficiency was calculated as;

$$CH_4\ recovery\ efficiency = \frac{R(CH_4)_{rec}}{T-R(CH_4)} = \frac{R(CH_4)_{evo}+R(D-CH_4)_{col}}{R(CH_4)_{evo}+R(D-CH_4)_{col}+R(D-CH_4)_{dis}}$$

where $R(CH_4)_{rec}$ is the CH_4 recovery rate (mg COD/day) defined as the sum of $R(CH_4)_{evo}$ and $R(D\text{-}CH_4)_{col}$, and T-$R(CH_4)$ is the total CH_4 production rate (mg COD/day) defined as the sum of $R(CH_4)_{evo}$, $R(D\text{-}CH_4)_{col}$, and $R(D\text{-}CH_4)_{dis}$.

4.3 RESULTS AND DISCUSSION

4.3.1 Performance of the UASB reactor

COD removal efficiency

The bench-scale UASB reactor was operated at ambient temperature from January 2010 to June 2011. Changes in T-COD and D-COD concentrations in the influent, T-COD concentration in the effluent, and T-COD removal efficiency of the UASB reactor were observed (Figure 4.2a). The influent T-COD and D-COD concentrations were in the ranges of 70 g/L - 310 g/L and 50 g/L - 160 g/L, respectively. Based on the COD results, the municipal wastewater used in this study could be classified as a low-strength domestic wastewater (Tchobanoglous et al., 2003). The average (± Standard deviation) of the influent P-COD/T-COD ratio remained relatively constant (0.56 ± 0.05) throughout the operation.

Temperature, hydraulic retention time (HRT), and pH in the UASB reactor are shown in Figure 4.2b. Temperature varied from 6°C to 31°C during the operation. HRT was adjusted in the range of 2 h - 8 h in response to changes in the COD removal efficiency. The pH in the UASB reactor became lower than that in the influent after July 2010.

T-COD was not removed during the first winter (Figure 4.2a). Between July and October 2010, the T-COD removal efficiency was in the range of 50% - 71%. The temperature ranged from 20°C to 31°C during this period (Figure 4.2b), indicating that temperature was a critical factor for effective COD removal. Although disintegration of the granules was observed during the operation, the average amounts of volatile suspended solids (VSS) in the granular bed increased from 78 ± 15 g to 150 ± 40 g per reactor by installation of the filter media on June 22, 2010 because of prevention of biomass washout. This is a common problem with the anaerobic treatment of low-strength wastewaters for short HRT (Latif et al., 2011). Enhancement of the retention and growth of biomass by the installation of the filter media may have contributed to the improvement in T-COD removal efficiency (Figure 4.2a) and increase in methane (CH_4) gas evolution rates into the headspace of the UASB reactor (see Figure 4.2c) between July and October 2010. The T-COD removal efficiency started to decrease at the beginning of November 2010 accompanying the temperature drop. This might be attributed to the low methanogenic activity at low temperatures (Dhaked et al., 2010).

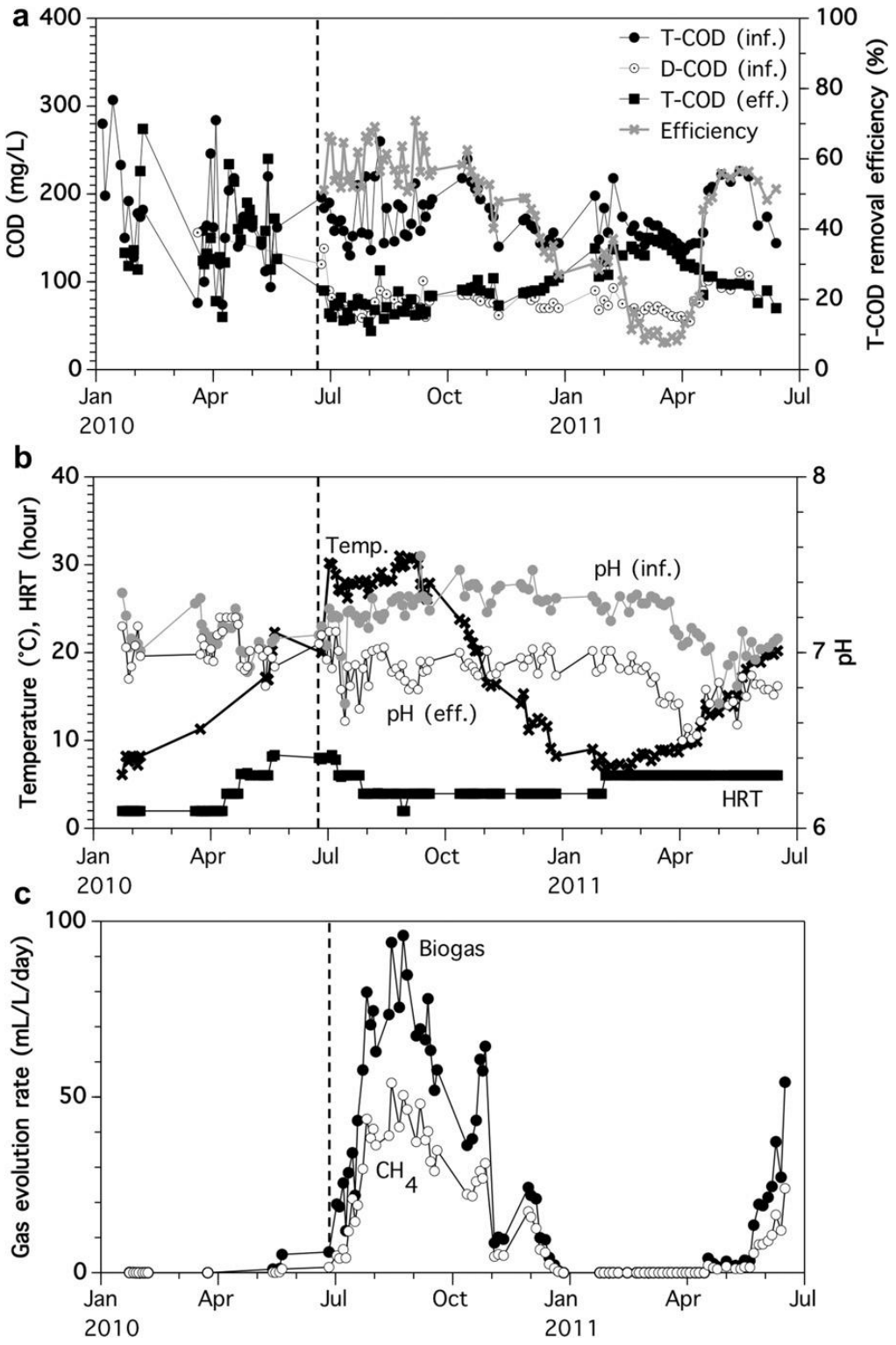


Figure 4.2: a). Concentrations of influent T-COD and D-COD and effluent T-COD of the upflow anaerobic sludge blanket (UASB) reactor, and the T-COD removal efficiency of the UASB reactor from May 2010. b). Variation in temperature, hydraulic retention time (HRT), and pH in the UASB reactor. c). Variation in biogas production and methane.

Volatile fatty acids (VFAs) (mainly acetic acid) were detected in winter, but not in summer, indicating that acidogenic activity was not inhibited compared to methanogenic activity at low temperatures. Subsequently, the T-COD removal efficiency gradually increased from 10% to around 60% in April 2011 owing to the gradual increase in temperature. The COD removal efficiency was lower (< 71%) in this study than those in UASB reactors treating high-strength wastewaters under mesophilic conditions (Latif et al., 2011). This might be because of the higher P-COD fraction of the municipal wastewater used in this study and the operation at ambient temperature (Figure 4.2 a and b) (A'lvarez et al., 2008).

Table 4.1: A summary of the operating parameters and T-COD removal efficiencies of upflow anaerobic sludge blanket (UASB) reactors treating low-strength wastewaters under psychrophilic conditions

Influent COD concentration (mg/L)*	**Temperature (°C)**	**HRT (hour)**	**T-COD rem. eff. (%)**	**Reference**
70 - 310	6 - 31	2 - 8	8 -71	This study
690 ± 133	10	84 ± 20	51 ± 16	Luostarinen and Rintala, 2005
1,500 ± 2,200	20	18 - 12	50 - 80	Sayed et al., 1984
115 - 595	13 - 25	4 - 7	64 - 72	Uemura and Harada, 2000
1,247 ± 220	15.5	8	23	Sawajneh et al., 2010
350 - 500	20	48	60 - 75	Singh, 1998
350 - 600	32 - 6	48 - 3	70 - 90	Singh, 2003
2,350 - 550	32 - 6	48 - 3	30 - 87	Singh, 2002
500	35.8 - 10.8	80, 10	60 - 80	Langenoff, 2000
1,576 (±367)	10 - 28	6	42 - 78	Lew, 2011
627	19 - 28	4	30 - 74	Barbosa, 1989
200 - 500	25 - 13	4.7	73 - 83	Uemura, 2000
590 - 335	25 - 22	5 - 7	70	Souza, 2011
640 ± 127	30	6 - 16	70 - 40	Elimitwalli et al., 2007

* COD concentrations are indicated as the lowest value - the highest value or as average ± standard deviation

Table 4.1 summarizes the operating parameters and T-COD removal efficiencies of UASB reactors treating low-strength wastewaters under psychrophilic conditions reported in the previous studies. These results indicate that the treatment of low-strength wastewaters at low temperatures results in low COD removal efficiencies. Therefore, an aerobic post-treatment is needed to achieve the appropriate T-COD removal efficiency (Khan et al., 2011).

Biogas production

The biogas production rate and CH_4 evolution rates in the UASB reactor are presented in Figure 4.2c. From January to May 2010, no biogas was evolved into the UASB headspace because of the low T-COD removal efficiency (< 5%) (Figure 4.2a). Biogas was evolved in summer. The CH_4 concentration in the UASB headspace was 50% ± 11% from July to October, which is comparable to or lower than those when treating high-strength wastewaters (Bandara et al., 2011; Latif et al., 2011). Biogas evolution ceased again in the second winter season. Thereafter, biogas evolution occurred as temperature increased from May 2011.

4.3.2 Performance of the degassing membrane (DM) reactor

Figure 4.3a shows D-CH_4 concentrations discharged from the UASB and DM reactors. D-CH_4 concentrations discharged from the DM reactor were clearly lower than those from the UASB reactor, indicating the DM successfully collected the residual D-CH_4 in the effluent of the UASB reactor. The average D-CH_4 concentrations discharged from the UASB and DM reactors were 51 ± 12 mg COD/L and 22 ± 4 mg COD/L from July to October 2010, and 48 ± 9 mg COD/L and 16 ± 34 mg COD/L from December 2010 to March 2011, respectively. The average biogas flux through the DM was 55 ± 10 mL/m^2/day during the operating period. This indicates that membrane fouling of the DM was insignificant for 18 months. An increase in trans-membrane pressure on April 25, 2011, resulted in a further decrease in the concentration of D-CH_4 discharged from the DM reactor.

$R(CH_4)_{evo}$, $R(D\text{-}CH_4)_{col}$, and $R(D\text{-}CH_4)_{dis}$ were calculated in order to investigate the mass balance of CH_4 in this system. Figure 4.3b shows $R(CH_4)_{evo}$, $R(D\text{-}CH_4)_{col}$, and $R(D\text{-}CH_4)_{dis}$, and the CH_4 recovery efficiency. From January to May 2010, no CH_4 was evolved from the UASB reactor. From July to October 2010, $R(CH_4)_{evo}$, $R(D\text{-}CH_4)_{col}$, and $R(D\text{-}CH_4)_{dis}$ were 210 ± 110 mg COD/L, 280 ± 100 mg COD/L, and 330 ± 140 mg COD/L, respectively. Their average rates were 0 mg COD/L, 125 ± 20 mg COD/L, and 180 ± 35 mg COD/L, respectively, from mid-December 2010 to March 2011. An absence of CH_4 evolution was attributed to the decrease in organic matter degradation rate at lower temperatures (Figure 4.2a and b). The average CH_4 recovery efficiency was 59 ± 9% from July to October 2010 and 41 ± 6% from mid-December 2010 to March 2011. The average ratio of $R(D\text{-}CH_4)_{col}$ to $R(CH_4)_{rec}$ was 60 ± 12% from July to

October 2010, but it was 100% during winter because no biogas was evolved into the UASB headspace.

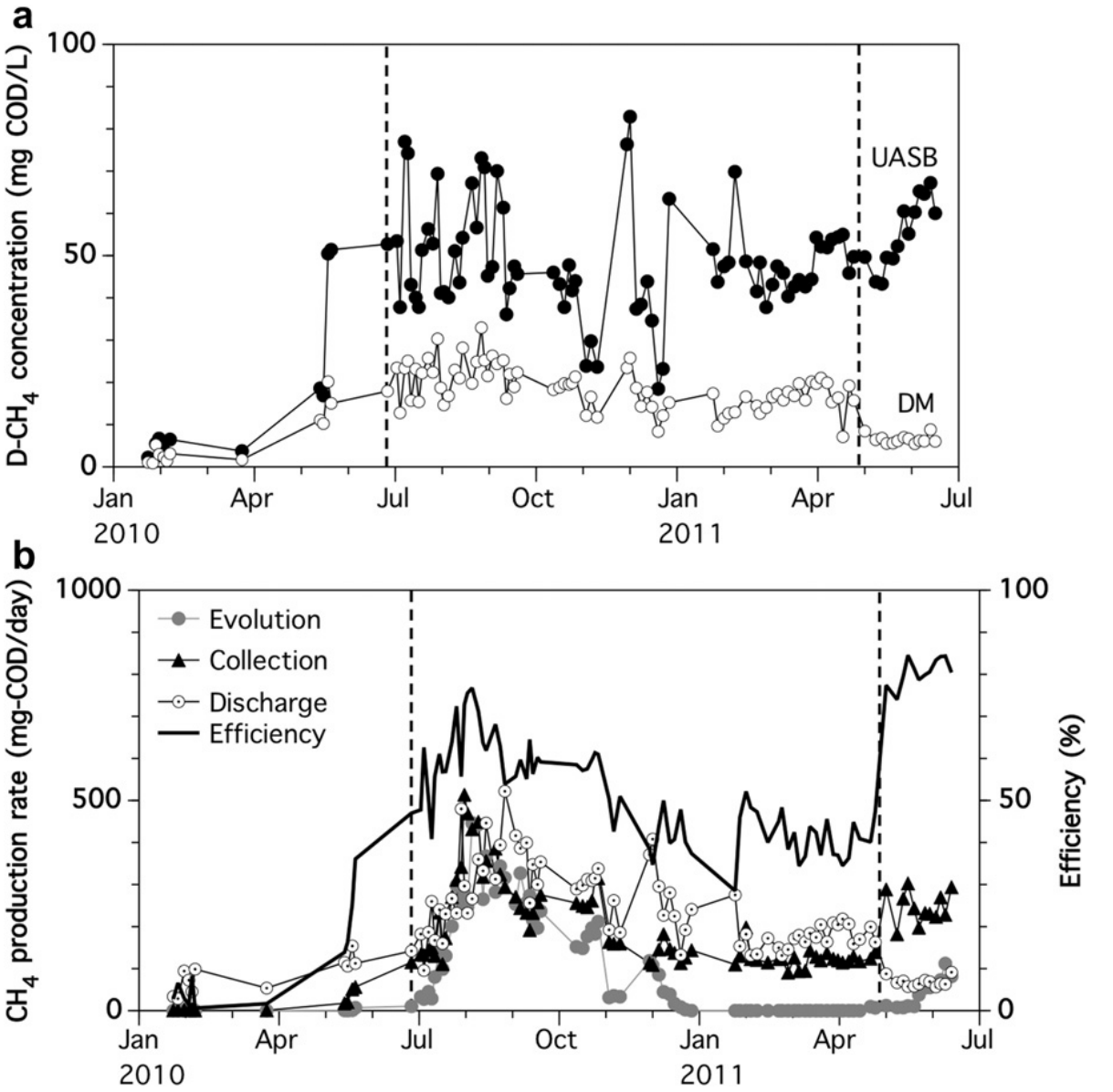


Figure 4.3: a). Variation in the D-CH_4 concentration discharged from the UASB and DM reactors. The dotted lines indicate the days when the filter media was installed (June 2010) and trans-membrane pressure was increased to 97 kPa (April 2011). b). CH_4 evolution rate in the UASB reactor, D-CH_4 collection and discharge rates in the DM reactor, and CH_4 recovery efficiency. The dotted lines indicate the days when the filter media was installed (June 2010) and trans-membrane pressure was increased to 97 kPa (April 2011).

These values were greater than those in the UASB and DM reactors treating high-strength wastewater (<35%) (Bandara et al., 2011). Thus, we concluded that degasification technology is

advantageous, especially when low-strength wastewater is treated under ambient conditions in comparison to mesophilic conditions (Khan et al., 2011). However, a reduction in energy for degasification should be investigated in future studies.

T-R(CH_4) decreased with decreasing temperature (Figure 4.3b). This is attributed to the decrease in the organic matter degradation rate associated with a drop in temperature (Figure 4.2a and b) (Dhaked et al., 2010; Latif et al., 2011). As shown in Figure 4.3b, at low temperatures (<10°C), $R(CH_4)_{evo}$ was almost zero and $R(D\text{-}CH_4)_{dis}$ was 180 ± 35 mg COD/L from mid- December 2010 to March 2011. D-CH_4 concentrations in the DM reactor were 29 ± 9 mg COD/L from July to October 2010 and 32 ± 9 mg COD/L from mid-December 2010 to March 2011, because the solubility of D-CH_4 increased with decreasing temperature. Consequently, the D-CH_4 collection efficiency increased relatively from 57 ± 7% to 66 ± 8% with a decrease in temperature. The remaining D-CH_4 concentrations in the effluent from the DM reactor were similar to those from the treatment of high-strength synthetic wastewaters (Bandara et al., 2011) because the same type of DM and the same trans-membrane pressure were applied. Increasing the trans-membrane pressure (after April 25, 2011) improved the D-CH_4 collection efficiency (Figure 4.3b). Thus, trans-membrane pressure was a critical operating parameter for the DM.

4.4 CONCLUSIONS

In this study, municipal wastewater was anaerobically treated with a bench-scale UASB reactor at ambient temperature (6°C - 31°C) over 18 months. The data presented here indicated that municipal wastewaters could be treated anaerobically at ambient temperature. We could achieve maximum of 70% T-COD removal efficiency in treating municipal wastewater. If ambient temperature was higher than 10ºC, T-COD removal efficiency of municipal wastewater was higher than 40% without heating.

Degassing membrane (DM) technology was applied to treat sewage wastewater at ambient temperature in order to test the technical feasibility of degassing to real wastewater. Results showed that DM is useful for collecting D-CH_4 especially under psychrophilic conditions. From an economic point of view, a further reduction in the energy is required for degasification is needed.

Chapter 5

Conclusions and Recommendations

5 CONCLUSIONS AND RECOMMENDATIONS

The main aim of this research was to investigate the technical feasibility of using an upflow anaerobic sludge blanket (UASB) reactor to treat low-strength wastewater at ambient temperature.

A degassing membrane (DM) was installed in a UASB reactor to both recover D-H_2 in the bulk liquid and to improve COD removal efficiency. Degasification could improve the COD removal efficiency.

DM reactor was operated separately from the UASB reactor to prevent redissolution of CH_4. D-CH_4 was successfully collected by degasification with the degassing membrane (DM). Under lower temperatures or shorter HRTs, the D-CH_4 concentrations increased; therefore, the D-CH_4 collection efficiencies increased. Moreover, the P-COD concentration was decreased by degasification. These results indicated that degasification is a promising technology for improving CH_4 recovery and P-COD removal efficiencies of the UASB process for treating low-strength wastewater at low temperature. We also studied the effects of temperature and hydraulic retention time (HRT) on the performance of a UASB reactor. It was possible to treat low-strength wastewaters at ambient temperature using a UASB reactor. During the operational period, D-COD removal efficiency was greater than 90% at 15ºC.

Municipal wastewater was then treated in a UASB reactor at ambient temperature (6°C - 31°C) over 18 months. Analysis of results suggests that it was possible to treat the municipal wastewater anaerobically at ambient temperature. We could achieve maximum of 70% T-COD removal efficiency in treating municipal wastewater. If ambient temperature was higher than 10ºC, T-COD removal efficiency of municipal wastewater was higher than 40% without heating. Degassing membrane was useful in collecting D-CH_4 especially under psychrophilic conditions. From an economic point of view, a further reduction in the energy is required for degasification is needed.

Chapter 6

References

6 REFERANCES

Agrawal, L., Haraha, H., & Okui, H. (1997). Treatment of Dilute Wastewater in a UASB Reactor at a Moderate Temperature: Performance Aspects. *Journal of Fermentation and Bioengineering, 83*(2), 179-184.

A'lvarez, J., Armstrong, E., Gomez, M., & Soto, M. (2008). Anaerobic treatment of low-strength minicipal wastewater by a two-stage pilot plant under psychrophilic conditions. *Bioresour. Technol., 99*, 7051-7062.

Angenent, L., Banik, G., & Sung, S. (2001). Anaerobic Migration Blanket Reactor Treatment of Low-Strength Wastewater at Low Temperatures. *Water Environment Research, 73*, 567-574.

Ariesyady, H., Ito, T., & Okabe, S. (2007a). Functional bacterial and archaeal community structures of major trophic groups in full- scale anaerobic sludge digester. *Water Research, 41(7)*, 1554-1568.

Ariesyady, H., Ito, T., Yoshiguchi, K., & Okabe, S. (2007b). Phylogenetic and functional diversity of propionate-oxidizing bacreria in an anaerobic digester sludge. *Applied microbiology and biotechnology, 75(3)*, 673-683.

Bandara, W., Satoh, H., Sasakawa, M., Nakahara, Y., Takahashi, M., & Okabe, S. (2011). Removal of residual dissolved methane gas in an upflow anaerobic sludge blanket reactor treating low-strength wastewater at low temperature with degassing membrane. *Water Research, 45 (11)*, 3533-3540.

Barbosa, R., & Sant'anna Jr, G. (1989). Treatment of raw domestic sewage in an UASB reactor. *Water Research, 23(12)*, 1483-1490.

Cakir, F., & Stenstrom, M. (2005). Greenhouse gas production: A comparison between aerobic and anaerobic wastewater treatment technology. *Water Research, 39*(17), 4197-4203.

Chynoweth, D., & Isaacson, R. (1987). Anaerobic digestion of biomass. *Elesevier Applied Science, New York, USA*, 219-231.

Dhaked, R., Singh, P., & Singh, L. (2010). Biomethanation under psychrophilic conditions. *Water Management, 30*, 2490-2496.

Elefsiniotis, P., Wareham, D., & Oldham, W. (1996). Particulate organic carbon solubilization in an acid-phase upflow anaerobic sludge blanket system. *Environmental Science & Technology, 30 (5)*, 1508-1514.

Elmitwalli, T., & Otterpohl, R. (2007). Anaerobic biodegradability and treatment of grey water in upflow anaerobic sludge blanket (UASB) reactor. *Water Research, 41*(6), 1379–1387.

Elmitwalli, T., van Lier, J., Zeeman, G., & Lettinga, G. (2003). Treatment of domestic sewage at low temperature in a two-anaerobic step system followed by a trickling filter. *Water Science and Technology, 48 (11-12)*, 199-206.

Elmitwalli, T., Zeeman, G., & Lattinga, G. (2001). Anaerobic treatment of domestic sewage at low Temperature. *Water Science and Technology, 44(4)*, 33-40.

Federation, W. E. (1987). *Manual of anaerobic Sludge Digestion, operation and Maintenance, Second edition.*

Fongastitkul, P., Mavinic, D., & Lo, K. (1994). A two-phased anaerobic digestion process: Concept, process failure and maximum system loading rate. *66(3)*, 243-254.

Friedmann, H., & Märkl, H. (1993). The influence of increased hydrostatic pressure on biogas production. *GWF Water / Waste Water, 12*, 689–698.

Friedmann, H., & Märkl, H. (1994). The influence of product gases on microbiological methane formation. *GWF Water / Waste Water, 6*, 302–311.

Gerardi, M. H. (2003). *The Microbiology of Anaerobic Digesters.* John Wiley & Sons, Inc.

Gomec, C., Letsiou, I., Ozturk, I., Eroglu, Y., & Wilderer, P. (2008). Identification of archaeal population in the granular sludge of an UASB reactor treating sewage at low temperatures. *Journal of Environmental Science and Health, Part A 43 (13)*, 1504-1510.

Guiot, S., Pauss, A., & Costerton, J. (1992). A structured model of the anaerobic granule consortium. *Water Sci. Technol., 25 (7)*, 1-10.

Gujer, W., & Zehnder, A. (1983). Conversion process in anaerobic digestion. *Water Science and Technology 15*, 127-167.

Hartley, K., & Lant, P. (2006). Eliminating non-renewable CO2 emissions from sewage treatment:An anaerobic migrating bed reactor pilot plant study. *Biotechnology and Bioengineering, 95(3)*, 384-398.

Hatamoto, M., Koshiyama, Y., Kindaichi, T., Ozaki, N., & Ohashi, A. (2010). Enrichment and identifiifaction of methane-oxidizing bacteria by using down-flow hanging sponge bioreactor under low methane concentration. *Annals of Microbiology*.

Hulshoff Pol, L., & Lettinga, G. (1986). New technology for anaerobic treatment. *Water Science and Techology 18(12)*, 41-53.

Jewell, W. (1987). Anearobic sewage treatment. *Environmental Science and Technology 21(1),* 14-21.

Jördening, H.-J., & Winter, J. (2005). *Environmental Biotechnology: Concepts and Application.* WileyPublishers.

Kato, M., Field, J., Kleerebezem, R., & Lettinga, G. (1994). Treatment of low strength soluble wastewater in UASB reactors. *Ferment. Bioengrg. 80(5),* 499-506.

Kayranli, B., & Ugurlu, A. (2011). Effects of temperature and biomass concentration on the performance of anaerobic sequencing batch reactor treating low strength wastewater. *Desalination, 278*(1-3), 77-83.

Keller, J., & Hartley, K. (2003). Greenhouse gas production in wastewater treatment: process selection is the major factor. *Water Sci. & Technolo., 47 (12),* 43-48.

Khan, A., Gaur, R., Tyagi, V., Khursheed, A., Lew, B., Mehrotra, I., & Kazmi, A. (2011). Sustainable options of post treatment of UASB effluent treating sewage: A review. *Resources, Conservation & Recycling, 55*(12), 1232-1251.

Kim, J., Kim, K., Ye, H., Lee, E., Shin, C., McCarty, P., & Bae, J. (2011). Anaerobic fluidized bed membrane bioreactor for wastewater treatment. *Environ. Sci. Technol., 45,* 576-581.

Langenhoff, A., & Stuckey, D. (2000). Treatment of dilute wastewater using an anaerobic baffled reactor: effect of low temperature. *Water Research, 34*(15), 3867–3875.

Latif, M., Ghufran, R., Wahid, Z., & Ahmad, A. (2011). Integrated application of upflow anaerobic sludge blanket reactor for the treatment of wastewaters. *Water Research, 45 (16),* 4683-4699.

Lettinga, G., & Hulshoff Pol, L. (1991). UASB-process design for various types of watewater. *Water Science and Technology,* 87-107.

Lettinga, G., de Man, A., van der Last, A., Wiegant, W., van Knippenber, K., Frijns, J., & van Buuren, J. (1993). Anaerobic treatment of domestic wastewater . *Water Science and Technology 27(9),* 67-73.

Lettinga, G., Rebac, S., & Zeeman, G. (2001). Challenge of psychrophilic anaerobic wastewater treatment. *Trends in Biotechnology, 19(9),* 363-370.

Lettinga, G., Rebac, S., Parshina, S., Nozhevnikova, A., Lier, J., & Stems, A. (1999). High-Rate Anaerobic Treatment of Wastewater at Low Temperatures. *Applied and Environmental Microbiology, 65*(4), 1696–1702.

Lettinga, G., Roersma, R., Grin, P., de Zeeuw, W., Hulshof Pol, L., van Velsen, L., . . . Zeeman, G. (1981). Anaerobic treatment of sewage and low strength waste water. *The 2nd International symposium on Anaerobic Digestion* (pp. 271-291). Travemunde: Germany.

Lew, B., Lustig, I., Beliavski, M., Tarre, S., & Green, M. (2011). An integrated UASB-sludge digester system for raw domestic wastewater treatment in temperate climates. *Bioresource Technology, 102*, 4921-4924.

Lew, B., Tarre, S., Belavski, M., & Green, M. (2004). UASB reactor for domestic wastewater treatment at low temperatures: a comparison between a classical UASB and hybrid UASB-filter reactor. *Water Sci Technol. 49(11-12)*, 295-301.

Luostarinen, S., & Rintala, J. (2005). Anaerobic on-site treatment of black water and dairy parlour wastewater in UASB-septic tanks at low temperatures. *Water Research, 39 (2-3)*, 436-448.

Madden, P., Chinalia, F., Enright, A., Collins, G., & O'Flaherty, V. (2010). Perturbation-independent community development in low-temperature anaerobic biological wastewater treatment bioreactors. *Biotechnology and Bioengineering, 105 (1)*, 79-87.

Martin, I., Pidou, M., Soares, A., Judd, S., & Jefferson, B. (2011). Modelling the energy demands of aerobic and anaerobic membrane bioreactors for wastewater treatment. *Environ. Technol., 32 (9-10)*, 921-932.

Matsunaga, K., Kindaichi, T., Ozaki, N., Ohashi, A., Nakahara, Y., & Sasakawa, M. (2012). Development of Anammox Reactor Equipped with a Degassing Membrane to Improve Biomass Retension. *Water Sci & Technol., 66 (2)*, 451-456.

Matsushige, K., Inamori, Y., Mizuochi, M., Hosomi, M., & Sudo, R. (1990). The effects of temperature on anaerobic filter treatment for low-strength organic wastewater. *Environmental Technology, 11 (10)*, 899-910.

Matsuura, N., Hatamoto, M., Sumino, H., Syutsubo, K., Yamaguchi, T., & Ohashi, A. (2010). Closed DHS system to privent dissolved methane emission as greenhouse gas in anaerobic wastewater treatment by its recovery and biological oxidation. *Waster Science & Technology, 61(9)*, 2407-2415.

McCarty, P. (2001). The development of anaerobic treatment and its future. *44(8)*, 149-156.

McKeown, R., Scully, C., Mahony, T., Collins, G., & O'Flaherty, V. (2009). Long-term (1243 days), low-temperature (4-15°C), anaerobic biotreatment of acidified wastewaters:

Bioprocess performance and physiological characteristics. *Water Research, 43 (6)*, 1611-1620.

Mes de, T., Stams, A., Reith, J., & Zeeman, G. (2003). Methane Production by Anaerobic digestion of wastewater and Solid Wastes. In T. Mes de, A. Stams, J. Reith, & G. Zeeman, *Bio-methane & Bio-hydrogen. Status and Perspectives of Biological Methane and therlands* (pp. 58–102).

Oh, J. (2012). *Performance evaluation of the pilot-scale static granular bed reactor (SGBR) for industrial wastewater treatment and biofilter treating septic tank effluent using recycled rubber particles.*

Okabe, S., Satoh, H., & Watanabe, Y. (1999). In situ analysis of nitrifying biofilms as determined by in situ hybridization and the use of microelectrodes. *Applied and Environmental Microbiology, 65 (7)*, 3182-3191.

Pauss, A., Andre, G., Perrier, M., & Guiot, S. (1990a). Liquid-to-gas mass transfer in anaerobic processes: Inevitable transfer limitations of methane and hydrogen in the biomethanation process. *Applied and Environmental Microbiology, 56(6)*, 1636-1644.

Pauss, A., Samson, R., & Guiot, S. (1990b). Continuous measurement of dissolved H2 in an anaerobic reactor using a new hydrogen/air fuel cell detector. *Biotechnol. Bioengng, 35*, 492-501.

Pavlostathis, S., & Giraldo-Gomez, E. (1991). Kinetics of anaerobic treatment: a critical review. *Environmental Control 21(5,6)*, 411-490.

Satoh, H., Miura, Y., Tsushima, I., & Okabe, S. (2007). Layered structure of bacterial and archaealcommunities and their in situ activities in anaerobic granules. *Applied and Environmantal Microbiology, 73(22)*, 7300-7307.

Sawajneh, Z., Al-Omari, A., & Halalsheh, M. (2010). Anaerobic treatment of strong sewage by a two stage system of AF and UASB reactors. *Water Science and Technology, 61 (9)*, 2399−2406.

Sayed, S., Dezeeuw, W., & Lettinga, G. (1984). Anaerobic treatment of slaughterhouse waste using a flocculant sludge UASB reactor. *Agricultural Wastes, 11 (3)*, 197−226.

Singh, K., & Viraraghavan, T. (2002). Effect of Temperature on Bio-Kinetic Coefficients in UASB Treatment of Municipal Wastewater. *Water, Air, and Soil Pollution, 136*(1-4), 243-254.

Singh, K., & Viraraghavan, T. (2003). Impact of temperature on performance, microbiological, and hydrodynamic aspects of UASB reactors treating municipal wastewater. *Water Sci Technol., 48*(6), 211-217.

Singh, K., & Virarghavan, T. (1998). Start-Up and Operation of UASB Reactors at 20°C for Municipal Wastewater Treatment. *Journal of Fermentation and Bioengineering, 85(6),* 609-614.

Smith, A., Sherlos, S., & Raskin, L. (2013). Psychrophilic anaerobic membrane bioreactor treatment of domestic wastewater. *Water Research, 47 (4)*, 1655-1665.

Smith, A., Stadler, L., Love, N., Skerlos, S., & Raskin, L. (2012). Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater A critical review. *Bioresoure Technology, 122*, 149-159.

Souza, C., & Chernicharo, C. (2001). Methane losses in UASB reactors treating domestic wastewater: mass balance and possible improvements. *Water Sci. & Technology, 64*(11), 2259-2264.

Tchobanoglous, G., Burton, L., & Stensel, H. (2003). *Wastewater Engineering: Treatment and Reuse* (Vols. 4th, ed.). New York: McGraw-Hill.

Trzcinski, A., & Stuckey, D. (2010). Treatment of municipal solid waste leachate using a submerged anaerobic membrane bioreactor at mesophilic and psychrophilic temperatures - Analysis of recalcitrants in the permeate using GC-MS. *Water Research, 44 (3)*, 671-680.

Uemura, S., & Harada, H. (2000). Treatment of sewage by a UASB reactor under moderate to low temperature conditions. *Bioresource Technology, 72 (3)*, 275−282.

Ukpai, P., & Nanbuchi, M. (2012). Comparative study of biogas production from cow dung, cow pea and cassava peeling using 45 liters biogas digester. *Advances in Applied Science Research, 3 (3)*, 1864-1869.

Urban, I., Weichgrebe, D., & Rosenwinkel, K. (2007). Anaerobic treatment of municipal wastewater using the UASB-technology. *Water Science and Technology, 56 (10)*, 37-44.

van Haandel, A., & Lettinga, G. (1994). *Anaerobic sewage treatment. Practical duide for regions with a hot climate.* Chichester. UK.: John Wiley and sons Ltd.

Voolapalli, R., & Stuckey, D. (1998). Stability enhancement of anaerobic digestion through membrane gas extraction under organic shock loads. *Journal of Chemical Technology and Biotechnology, 73(2)*, 153-161.

Xing, W., Zuo, J., Dai, N., Cheng, J., & Li, J. (2009). Reactor performance and microbial community of an EGSB reactor operated at 20 and 15°C. *Journal of Applied Microbiology, 107 (3)*, 848-857.