# Lakehead
UNIVERSITY

OFFICE OF GRADUATE STUDIES

NAME OF STUDENT: Ke Xie

DEGREE AWARDED: M.Sc. Environmental Engineering

ACADEMIC UNIT: Faculty of Engineering

TITLE OF THESIS: Submerged Anaerobic Membrane Bioreactors for Kraft Evaporator Condensate Treatment: Feasibility and Membrane Fouling Studies

This thesis has been prepared

under my supervision

and the candidate has complied

with the Master's regulations.

Signature of Supervisor

NOV. 4, 2008

Date

*Your file Votre référence*
*ISBN: 978-0-494-47147-0*
*Our file Notre référence*
*ISBN: 978-0-494-47147-0*

# Submerged Anaerobic Membrane Bioreactors for Kraft Evaporator Condensate Treatment: Feasibility and Membrane Fouling Studies

By:
Ke Xie

Supervisor:
Dr. Baoqiang Liao

Environmental Engineering
Lakehead University
Thunder Bay, Ontario, Canada
October, 2008

# Abstract

In this study, the primary goal was to develop better treatment technologies for energy recovery from Kraft evaporator condensate (EC) using thermophilic and mesophilic submerged anaerobic membrane bioreactors (SAnMBRs). Specific objectives were to study the feasibility of using submerged AnMBRs for Kraft evaporator condensate treatment, to quantify the chemical oxygen demand (COD) removal efficiency and biogas production (chemical composition and rate), to characterize sludge properties, including particle size and extracellular polymeric substances (EPS), and to understand and control membrane fouling.

The feasibility of using a submerged anaerobic membrane bioreactor (AnMBR) for Kraft evaporator condensate treatment was studied at 37°C over a period of 7 months. Under the various tested organic loading rates, a high, stable chemical oxygen demand (COD) removal efficiency was achieved for three stages of influent CODs. The permeate was of high quality, and the resulting biogas, composed of 85% methane, was of excellent fuel quality. It was found that the bubbling of recycled biogas was effective for in-situ membrane cleaning, depending on the recycle flow rate of produced biogas. Toxic feed shocking, due to total reduced sulfur (TRS) compounds and a high pH (due to pH probe failure) resulted in deflocculation, which led to an increase in membrane filtration resistance caused by fine flocs.

The feasibility of using SAnMBRs for Kraft evaporator condensate treatment was also studied at 55°C. This was conducted during two runs, as influent toxicity terminated the first run. During the first run, a high COD removal efficiency was achieved, and the resulting biogas was, again, of high fuel quality. During the second run, a higher membrane fouling rate was present, and was related to the presence of a larger portion of fine colloidal particles. The experimental results from this study indicate that anaerobic treatment of Kraft evaporator condensate under thermophilic conditions for energy recovery and for subsequent reuse of high quality permeates is feasible in terms of COD removal and biogas production. However, pre-treatment may be needed to remove toxic

sulfur compounds, and membrane fouling caused by the large portion of fine particles may be a challenge.

The sludge properties and their effects on membrane fouling were also studied for both thermophilic and mesophilic SAnMBRs. The results show that the filtration behaviour of the two systems was significantly different, as the filtration resistance in the thermophilic SAnMBR was higher than that of the mesophilic system, despite operation under similar hydrodynamic conditions. A higher temperature and a relatively lower organic loading rate for the thermophilic SAnMBR promoted extracellular polymeric substances (EPS) to be released, a higher content of soluble microbial products (SMP) and biopolymer clusters (BPC), increased protein to polysaccharide ratio in the bound EPS, and smaller size flocs, giving rise to increased filtration resistance. Sludge properties, including SMP, BPC, bound EPS, and floc size, are the important parameters in governing sludge cake formation and membrane fouling in SAnMBR systems.

# Acknowledgments

I would like to express my sincere appreciation and deepest gratitude to my supervisor, Dr. Baoqiang Liao, for his enthusiastic guidance, endless encouragement, and experienced advice throughout this thesis. His guidance and patience was most helpful when this project experienced any difficulties. At the same time, I would like to show my great appreciation for his help on my study, research, and my life in Canada, as this has improved my English level and my research abilities.

Financial support arranged by Dr. B. Liao through Natural Sciences and Engineering Research Council of Canada (NSERC) discovery grant is highly appreciated. Special thanks go out to Abitibi-Bowater Inc. (Thunder Bay, Ontario) and Tembec Industries Inc. (Temiscaming, Quebec) whose contributions allowed us to carry out this experiment.

Unaffected gratitude is expressed to Dr. Hongjun Lin for his continuous help during the experiment and the preparation of this thesis. Wholehearted thanks are given to Mr. Daniel Bertoldo for his support and help during the project and the completion of this thesis.

In addition, heartfelt thanks are extended to the professors and the graduate students in the Department of Chemical Engineering and Environment Engineering, especially Dr. Lionel Catalan, Dr. Aichen Cheng, and Dr. Wa Gao for their helpful comments and their great patience during my graduate study at Lakehead University. I am full of gratitude to the reading committee for their time and effort. Their experience and knowledgeable expertise were of great assistance to this thesis. Special acknowledgement must be given to the staff of the instrumentation lab, Allan MacKenzie, Ain Raitsakas and Keith Pringnitz, of Lakehead University.

Finally, I would like to show my sincere appreciation to all the persons who have offered me help during my study in Lakehead University. They made my life much more enjoyable during my academic study.

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# List of Nomenclature

| | |
|---|---|
| AC | Activated Carbon |
| AD | Anaerobic Digestion |
| AFM | Atomic Force Microscope |
| AnMBR | Anaerobic Membrane Bioreactor |
| ANOVA | Analysis of Variance |
| AOX | Adsorbable Organic Halides |
| APHA | American Public Health Association |
| BOD | Biological Oxygen Demand |
| BPC | Biopolymer Clusters |
| BSA | Bovine Serum Albumin |
| CER | Cation Exchange Resin |
| CLSM | Confocal Laser Scanning Microscopy |
| COD | Chemical Oxygen Demand |
| CSTR | Continuously Stirred Tank Reactor |
| D(0.1) | Less than or equal to 10 % of the measured particles |
| DL | Detectable Limit |
| EC | Evaporator Condensate |
| ED | Electrodialysis |
| EDTA | Ethylenediaminetetraacetic Acid |
| EDX | Energy Diffusive X-ray Analyzer |
| EPA | Environmental Protection Agency |
| EPS | Extracellular Polymeric Substances |
| F/M | Food/Microorganisms |
| FTIR | Fourier Transform Infrared |
| GMF | Granular Membrane Filtration |
| HAP | Hazardous Air Pollutants |
| HRT | Hydraulic Retention Time |
| ICP | Inductively Coupled Plasma |
| $J$ | Membrane Flux |
| LPM | Litres Per Minute |
| MACT | Maximum Achievable Control Technology |
| MBR | Membrane Bioreactor |
| MCAB | Membrane-Coupled Anaerobic Bioreactor |
| MF | Membrane Filtration |
| MLSS | Mixed Liquor Suspended Solids |
| MW | Molecular Weight |
| MWCO | Molecular Weight Cut-Off |
| NCASI | National Council on Air and Stream Improvement |
| NF | Nanofiltration |
| NSERC | Natural Sciences and Engineering Research Council of Canada |
| NTA | Nitrilotriacetic Acid |
| OLR | Organic Loading Rate |
| PAC | Powdered Activated Carbon |

| | |
|---|---|
| PN | Protein |
| PS | Polysaccharide |
| PV | Pervaporation |
| PVDF | Polyvinylidene Fluoride |
| $R_c$ | Cake Layer Resistance |
| $R_m$ | Membrane Resistance |
| $R_p$ | Pore Blocking Resistance |
| $R_t$ | Total Hydraulic Resistance |
| RO | Reverse Osmosis |
| SAnMBR | Submerged Anaerobic Membrane Bioreactor |
| SEM | Scanning Electron Microscope |
| SMP | Soluble Microbial Products |
| SRT | Solids Retention Time |
| SS | Suspended Solids |
| TMP | Transmembrane Pressure |
| TMP mill | Thermo-Mechanical Pulp |
| TMR | Transmembrane Total Resistance |
| TOC | Total Organic Carbon |
| TRS | Total Reduced Sulfur |
| TSS | Total Suspended Solids |
| UAF | Upflow Anaerobic Filter |
| UASB | Upflow Anaerobic Sludge Blanket |
| UF | Ultrafiltration |
| VFA | Volatile Fatty Acids |
| VSS | Volatile Suspended Solids |
| $\Delta P$ | Change of Pressure |
| $\Delta p_T$ | Transmembrane Pressure |
| $\eta$ | Dynamic Viscosity |

# Chapter 1
# General Introduction

## 1.1 Treatment of Kraft Evaporator Condensate Overview

As a resource-intensive industry, pulp and paper manufacturing has played a crucial role in Canada's economy, while also causing problems for the environment and human health. In the United States, pulp and paper mills are now considered the third largest industrial polluter (Springer, 1986). In Canada, it has been estimated that this industry is responsible for 50% of all waste dumped into the nation's waters (Sinclair, 1990). The pollution problems from the pulp and paper industry should be tackled in a cost-effective manner, such that the economic health of the industry is sustained and the well-being of the environment and human health are maintained.

Evaporator condensates from Kraft mills have been receiving great attention since the late 1970s because of the elevated concerns on the negative impact of waste streams and mephitic odours (mainly due to reduced sulfur compounds [TRS]) on the environment and human beings. Kraft evaporator condensates may constitute only 5% of the total mill effluent volume, but may account for as much as 40% of the total BOD discharged from a bleached Kraft mill (Blackwell et al., 1979). As an alternative to conventional end-of-pipe wastewater treatment, some mills are considering reusing the evaporator condensates as process water by closing up the evaporation process water system. This system constitutes a significant organic load to the effluent treatment system (Bérubé and Hall, 1996; Milet and Duff, 1998). By reusing the Kraft condensates, the contaminant load to the existing combined mill effluent treatment system can be decreased, reducing energy and raw water requirements, and potentially reducing the impact of discharging treated wastewater to the environment. Additionally, some legislation offers a number of incentives for internal process water treatment and reuse (Vice and Carroll, 1998).

Generally, in the major pulp and paper production process, the Kraft (sulfate) process, a treatment of wood chips at 160 – 180°C in a "white liquor" solution (composed of

sodium sulfide and sodium hydroxide) occurs, after which approximately 55% of the original wood is dissolved in what is now known as "black liquor." The black liquor from the digester contains approximately 15 wt% solid content, which is far too low for combustion, leading to an insufficient energy supply for the mill. To raise the solid content in the black liquor to 75 wt%, which is required for incineration and on-site energy recovery, the liquor is to be evaporated using a sequence of concentrators (Marklund). Evaporator condensates are therefore designated as the waste stream from the digester and black liquor evaporators. Generally, the condensates prior to treatment are called "foul condensates", and, after treatment and subsequent reuse in the mill, are called "clean (or green) condensates".

Kraft condensates have the characteristics of high-strength, high-temperature, and low volume (Blackwell et al., 1979; Lapara and Alleman, 1999). The main contaminants of concern in Kraft condensates are methanol and total reduced sulfur (TRS) compounds, which include hydrogen sulfide ($H_2S$), methyl mercaptan ($CH_3SH$), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). The reduced sulfur compounds are responsible for most of the strong odor of the condensates, and also impart toxicity to the condensates (Blackwell et al., 1979; Environment Canada; and Blackwell et al., 1980). Foul condensates contain a major portion of the total mill TRS (Sarkanen et al., 1970).

Methanol is the predominant BOD component in evaporator condensates. Due to its toxicity to humans, the U.S. EPA classifies methanol as a hazardous air pollutant (Roche, 1995). The original draft of the EPA's Cluster Rules (Roche, 1995), which has subsequently been revised (Swan, 1995), stated that any stream which contains greater than 500 mg/L of methanol should be treated such that 90% of the methanol is removed prior to wastewater treatment. All vaporous emissions from such a stream should also be collected and treated. A survey of U.S. Kraft mills (NCASI, 1995) indicates that, on average, 75% of the total condensate volume is currently reused within the mills, and the mean methanol concentration of these reused condensates is 680 mg/L. The remaining 25% of the condensate streams, which were sent either to the effluent treatment plant or to a steam stripper, had a mean methanol concentration of 2360 mg/L. Whether the

driving force is the reduction of the methanol load to the effluent treatment system or the restriction on the use of contaminated streams, an effective condensate treatment process will likely be required in the future.

There are two main approaches in treating and reutilizing evaporator condensates: (a) physical processes, and (b) biological processes. The former are mostly represented by the steam stripping process. Steam stripping has been a common treatment technology due to the relatively low installation and operating costs of this type of system in the past decade. In a steam stripper system, the foul condensate is filtered and fed to a stripping column. In the column, the condensate is heated with steam to remove vapors, including methanol and TRS compounds, which includes hydrogen sulfide and trace amounts of dimethyl disulfide, dimethyl sulfide, and methyl mercaptan. Water vapor is removed from the column overhead using a condenser, which recovers and processes the vapor. The stripped condensate leaves the bottom of the column and can be reused in the pulping process or sent to the waste treatment system (Crutcher and Bullock, 1999). Approximately one in five Kraft mills in the U.S. uses a steam stripper for removing BOD and TRS (NCASI, 1994). The methanol concentration in and out of the surveyed strippers averaged 4830 and 610 mg/L, respectively. Since the operational costs of a steam stripper are proportional to the volume of liquid to be treated, they are more cost effective when treating low volume, high-strength streams (Milet and Duff, 1998). The stripped overhead gas will go to an incinerator, kiln, or boiler where the mixture is burned. However, there are frequent flameout problems at the incinerator, due to the low fuel value of this stream. This problem can result in permit violations due to the emission of unburned gases (Burgess et al., 2002).

The second approach involves the development of new biological treatment processes to curtail the release of toxic condensates form the pulp and paper mill, particularly hybrid or dual systems that capitalize on the advantages afforded by both anaerobic and aerobic digestion (Murray, 1992). In contrast to steam stripping, the operating cost of biological treatment is proportional to the strength of the stream to be treated, due to the costs associated with nutrients, aeration, and sludge handling. The biological oxidation of

condensate contaminants may, therefore, be a more cost-effective technology than steam stripping, especially if large volume, low-strength condensate streams are to be treated.

Aerobic and anaerobic processes treating industrial wastewaters have been conducted commonly at mesophilic temperatures (35°C – 40°C). Since the last decade, thermophilic methods (at a temperature range of 55°C to 60°C) in treating industrial wastewaters have gained great attention due to the high contaminants removal efficiency in comparison with conventional mesophilic processes. In addition to operational temperature differences, the biomass growth also varies, including suspended biomass, biofilm, and granula. As membrane technologies advance, membranes have been gradually applied in bioreactor systems, emerging as an important treatment technology. For instance, in aerobic processes treating evaporator condensates, membranes could be used as a means of aeration which enhances the aeration efficiency (Zheng, 2008). In anaerobic processes, membranes could be used as filtration unit so that biomass can be fully retained within the reactor, decoupling the hydraulic retention time (HRT) and solids retention time (SRT).

Even though both aerobic and anaerobic treatment processes have been successfully used for Kraft evaporator condensate treatment (Barton et al., 1996 and 1998), there are a number of drawbacks associated with the conventional aerobic and anaerobic treatments. High energy costs associated with aeration and the potential stripping of methanol by aeration are the major concerns of aerobic treatment. Anaerobic treatment has the advantage over aerobic treatment in terms of energy recovery and lower sludge yield; however, both aerobic and anaerobic treatment may suffer from biomass separation problems, including sludge bulking and deflocculation. Therefore, aerobic membrane bioreactor (MBR) (Dias et al. 2005, Bérubé and Hall, 2000) and external cross-flow anaerobic membrane bioreactor (AnMBR) technologies (Minami et al., 1994; Brockmann and Seyfried, 1996) have been developed for Kraft evaporator condensate treatment. While the external cross-flow AnMBR is a very promising technology for Kraft evaporator condensate treatment in terms of energy recovery (net energy gain) and elimination of biomass separation problems, the complete recirculation of mixed liquor at

a high velocity to minimize membrane fouling will consume a significant amount of energy and thus reduce the net gain of energy. In addition, the shear force from the recirculation pump will break flocs and reduce biological activity. The other type of AnMBR is a submerged AnMBR which uses biogas for in-situ bubbling for membrane cleaning. The concept of submerged AnMBRs has received great attention in the last few years, considering its low energy consumption as compared to external cross-flow AnMBRs. There are few studies that use submerged AnMBRs for wastewater treatment (Hu and Stuckey, 2006 and 2007). However, to the best of our knowledge, there is no study reported yet on the use of submerged AnMBR technology for Kraft evaporator condensate treatment.

## 1.2 Literature Review

In Kraft condensates management, biological treatment systems are normally operated at temperatures in the range of 15°C – 40°C, where mesophilic microorganisms are predominant. However, the temperature of foul condensates originating from Kraft evaporators and digesters is around 50°C – 70°C. This would require the condensates to be cooled prior to treatment. A novel concept is the biological treatment of evaporator condensates at higher temperatures (45°C - 60°C), where thermophilic microorganisms are responsible for degrading the dissolved organic matter.

The purpose of this literature review was to retrospect what is known about the aerobic and anaerobic processes involved in Kraft evaporator condensates management, and what is known about the operating conditions and fouling mechanisms of the membrane bioreactors for pulp and paper wastewater treatment.

### 1.2.1 Aerobic Processes

Barton et al. (1996) studied the treatment of mill condensates using aerobic and anaerobic bioreactors at the mesophilic temperature range. They found that biotreatment of the foul condensates were feasible to an acceptable quality for reuse in the mill.

Milet and Duff (1998) improved the treatment of Kraft evaporator condensates in a sequencing batch reactor by successfully applying a self-cycling fermentation control strategy. This self-cycling fermentation technique is based on the changes in the oxygen uptake rate of microorganisms under varying conditions of substrate supply. When treating the evaporator condensates, 64% of the influent COD of 1740 mg/L was removed.

When Kraft condensate treatment is conducted under thermophilic conditions, the re-use of condensates could also result in significant energy savings since the heat content of the condensates could be recovered. The possibility of using high temperature biological treatments to remove contaminants from combined Kraft pup mill effluent has been investigated in a number of laboratory scale studies. Tripathi and Allen (1998), Tai (1998), as well as Flippen and Eckenfelder (1994) all reported that the chemical oxygen demand (COD) removal efficiencies decreased at operating temperatures above 35°C, while Graczyk (1984), Barre et al. (1996) and Rintala and Lepisto (1993) reported similar or even better COD removal efficiencies at operating temperatures above 35°C. Consequently, there is no clear advantage in treating combined Kraft pulp mill effluent at elevated temperatures. Yet, unlike the removal of general COD from combined Kraft pulp mill effluent, the biological removal of COD caused by methanol and TRS compounds has been documented to be more efficient at temperatures in excess of 35°C. Using pure cultures grown on methanol as a sole substrate, Brooke et al. (1989) observed a higher growth yield at temperatures exceeding 45°C. Similarly, Snedecore and Cooney (1974), observed a higher growth yield at temperatures above 45°C for a mixed culture of bacteria grown on methanol as a sole substrate. Also, bacteria capable of biologically oxidizing reduced sulfur compounds have been reported to thrive at temperatures exceeding 50°C (Brock, 1978). Unfortunately, there is very little information available regarding the removal kinetics of methanol from condensates (Barton et al. 1996).

Some works have been published on this subject (Barton et al., 1996; Bérubé and Hall, 1999a, 1999b, 2000; Dias et al., 2005). In Bérubé and Hall, a series of laboratory and pilot-scale experiments were conducted to treat synthetic condensates, which were rich in

methanol. Good methanol removal efficiencies were obtained at a temperature range of 55°C to 60°C. Welander et al. (1999) obtained high removals of methanol and chemical oxygen demand (COD) using anaerobic followed by aerobic biological treatment at 55°C. Although anaerobic treatment showed a better operating economy, it was more sensitive to inhibitory compounds and it was suggested that the recovery time after upsets may be long.

Bérubé and Hall (1999a) investigated the feasibility of biologically removing the methanol from condensates at a high temperature. Synthetic condensate was used in their studies, which contained methanol (500 mg/L), dimethyl sulphide (37 mg/L) and dimethyl disulphide (25 mg/L). The experiment was operated at a 12 hr HRT and a 20 day SRT. An ultrafiltration membrane was operated with a cross-flow velocity of approximately 3 m/s and a trans-membrane pressure of approximately 2 atmospheres (207 kPa; 30 psi). Their results showed a zero order rate of methanol removal at 1.4 mg/L/min and specific methanol utilization rate of 0.8 $day^{-1}$. The zero order decrease in the concentration of methanol in the MBR indicated that methanol was not limiting or inhibiting in the range of concentrations examined (Bérubé and Hall, 2000). At the optimum operating temperatures of 55°C and 60°C, the concentration of methanol in the membrane bioreactor was reduced to less than 0.5 mg/L during each batch cycle. Beyond 60°C, both the methanol removal and specific utilization rates declined sharply. The inhibited growth beyond 60°C indicates that the mixed culture was thermotolerant rather than thermophilic, whereas by definition, thermophilic bacteria thrive at temperatures above 60°C (Brock 1978). In general, Bérubé and Hall (1999a) observed a maximum methanol specific utilization rate of 0.8 $day^{-1}$ which is higher than values reported for biological treatment systems operated at a mesophilic (30°C - 35°C) or intermediate (35°C - 45°C) temperature range. Tai (1998) reported specific utilization rates of 0.69 $day^{-1}$ and 0.44 $day^{-1}$ for methanol removal from a bleached Kraft pulp mill combined effluent in a laboratory scale activated sludge treatment system, operating at temperatures of 35°C and 45°C, respectively. Barton et al. (1996) measured a specific methanol utilization rate of approximately 0.45 $day^{-1}$ in a batch treatment system treating combined Kraft mill condensates at 33°C. The results from Bérubé and Hall (1999a) suggest the

operation at elevated temperatures not only reduces the need for cooling of the condensates before treatment, but may also result in a high contaminant removal rate. Also, the effects of real condensates on methanol removal kinetics were investigated in Bérubé and Hall (1999b).

Bérubé and Hall (1999b) investigated the effects of the Kraft evaporator condensate matrix on methanol removal in a high temperature membrane bioreactor. They observed a lower specific methanol utilization rate (0.55 $day^{-1}$) for the treatment of real condensate in a MBR in comparison with that observed when treating synthetic condensate (0.81 $day^{-1}$). However, this was still more then 20% higher than previously by Barton et al. (1996) who reported a utilization rate of 0.45 $day^{-1}$ in a batch activated sludge system treating combined evaporator condensate at 33°C. The reduction in the specific methanol utilization rate was not a result of inhibition from compounds present in the real condensate matrix. The reduction was due to a shift in the composition of the microbial community present in the MBR mixed liquor. When treating synthetic condensate, the microbial community appeared to consist exclusively of rod-shaped microorganisms, 0.5 μm to 1 μm in width, and 5 μm to 7.5 μm in length (the microorganisms, hereafter referred to as methylotrophic microorganisms, were capable of growth with methanol as a sole substrate). A more diversified microbial community was observed when the real condensate feed was used (approximately 25% to 30% of the total organic carbon consisted of other [i.e. non-methanolic] compounds). In addition to the rod-shaped methylotrophic microorganisms, larger rod-shaped (2 μm to 3 μm in width, 10 μm to 15 μm in length) and filamentous (0.5 μm to 1 μm in width, 50 μm to 100 μm in length) microorganisms (i.e. non-methylotrophic microorganisms) were noted with real condensate as feed. In the presence of both methanol and non-methanolic substrates, non-methylotrophic microorganisms compete with methylotrophic microorganisms for the available methanol. This is consistent with results reported by Bitzi et al. (1991) which indicated that although some microorganisms are not capable of growth on methanol as a sole substrate, they can use methanol as an energy source, while using non-methanolic substrates for cell synthesis. Non-methylotrophic microorganisms exhibited a lower specific methanol utilization rate (0.45 $day^{-1}$) than methylotrophic microorganisms (0.81

day$^{-1}$). Bérubé and Hall (1999b) suggested that if methanol removal is the main treatment objective, the evaporator condensate should be segregated and treated separately form other wastewater streams in a Kraft pulp mill. Treatment of the segregated evaporator condensate could result in a higher specific methanol utilization rate as opposed to treating combined mill effluent, since combined mill effluent contains a larger number of non-methanolic compounds, which could reduce the overall specific methanol utilization rate. It was also suggested that since the composition of the condensate matrix can significantly affect the methanol removal kinetics, it is not possible to confirm whether the lower observed specific methanol utilization rate reported by Barton et al. (1996) at a lower temperature is due to the effect of the operating temperature, or to matrix effects associated with a different evaporator condensates. Nevertheless, their study confirms that it is possible to achieve relatively high methanol removal rates when operating a biological treatment system at an elevated temperature (60°C). The major benefit of operation at high temperature is a reduction in condensate cooling required prior to treatment and retention of heat in the treated condensate for reuse.

At increased operating temperatures, a larger fraction of the methanol is biologically oxidized to $CO_2$, reducing the observed growth yield (Bérubé and Hall, 2000). The reduction in the observed growth yield at higher temperatures indicated that less excess sludge is likely to be produced in a biological treatment system operated at high temperatures. Snedecore and Cooney (1974) observed a similar decline when investigating the effect of temperature on the observed growth yield for a mixed culture of methanol-consuming microorganisms at temperatures ranging from 45°C to 65°C. They suggested that, at higher temperatures, microorganisms require more energy to maintain metabolic activities. However, the result of Bérubé and Hall (2000) could not confirm the hypothesis of whether the microorganisms used the additional energy produced at higher temperatures. Kim et al. (1981) suggested that the decrease in the observed growth yield was not due to a decline in the true growth yield, but to an increase in the rate of microbial decay. This increase in the rate of microbial decay would likely result in an increase in the amount of non-biodegradable microbial products formed (Rittmann et al., 1987). Yet, in the previous studies by Bérubé and Hall (2000), the

concentrations of non-biodegradable compounds in the MBR, measured as soluble total organic carbon (TOC), were similar for the different operating temperatures investigated. This suggested that the operating temperature did not significantly affect the extent of microbial decay over the range of temperatures investigated. Further research is required to confirm the mechanism responsible for the decline in the observed growth yield at elevated temperatures.

Generally, the advantages of thermophilic aerobic biological technology include rapid biodegradation rates, low sludge yields, and excellent process stability (Lapara and Alleman, 1999). Substrate utilization rates reported in the technical literature are 3-10 times greater than that observed with analogous mesophilic processes, and sludge production rates are generally similar to anaerobic treatment processes. Thermophilic aerobic processes are particularly advantageous for the treatment of high-strength wastewaters that can fully benefit from the rapid biodegradation rates and low sludge yields. High-strength wastewaters also contain the necessary energy content to facilitate auto-thermal operation, such that exogenous heat input is not required. Most researchers have reported that thermophilic bacteria fail to aggregate, making biomass separation from the treated effluent a key design criterion. Two options are to simply operate biological reactors without cell recycle or to design a membrane-coupled biological system.

### 1.2.2 Anaerobic Treatment Processes

An anaerobic process is considered more suitable to treat high strength organic effluents. Before the 1980s, the treatment of pulp mill effluents by anaerobic means was limited, as most of the pulp mill effluents at that time were less concentrated (300–2000 mg/L BOD) (Bajpai, 2000) and were not suitable for anaerobic treatment. Anaerobic filter, upflow sludge blanket (UASB), fluidized bed, anaerobic lagoon, and anaerobic contact reactors are anaerobic processes that are commonly used to treat pulp and paper mill effluents. Pretreatment of the Kraft mill black liquor was investigated by Poggi-Varaldo et al. (1996) and they reported that continuous anaerobic treatment of wastewater contaminated with black liquor was feasible at low to medium loading rates, with a total

COD removal of 48–80% and biodegradable COD reduction of 87–96%. Jahren et al. (1999) compared anaerobic and aerobic treatment for thermo-mechanical pulp (TMP) mill effluent and found that 84% and 86% removal of COD from anaerobic and aerobic treatment systems, respectively, was achieved. Rajeshwari et al. (2000) reported that chlorine bleaching effluents were not suitable for anaerobic treatment due to their low biodegradability and presence of toxic substances that affects methanogens. Sandquist and Sandstrom (2000) developed a new treatment technology to treat foul condensate (sulfide) from the black liquor, which consisted of three steps: (1) stripping of sulfides and other volatile components from condensate; (2) regenerative thermal oxidation of stripper off-gases; (3) adsorption of sulfur oxide. Removal efficiency for foul condensate was reported to be more than 99% at a pH of 4 and removal of methanol was 90% at a low liquid/gas ratio. Jackson-Moss et al. (1992) found that 50% removal of COD and colour could be achieved by anaerobic biological granular activated carbon. Dufresne et al. (2001) observed that undiluted foul condensates at Windsor mill were toxic to anaerobic biomass. Chen and Horan (1998) stated that COD and sulfate removals of 66% and 73%, respectively, were obtained using a UASB reactor with a hydraulic retention time of 6 hr. Peerbhoi (2000) investigated anaerobic treatability of black liquor by a UASB reactor in the study at the University of Roorkee, India. The author concluded that anaerobic biological treatment of black liquor was not feasible, as the pollutants were not readily degradable. Perez et al. (1998) evaluated two anaerobic systems (anaerobic filters and fluidized bed) in laboratory-scale reactors and reported that an organic removal efficiency of 81% was obtained in the case of fluidized bed with porous packing and 50% removal was obtained in the case of anaerobic filters on corrugated plastic tubes. Rajeswori et al. (2000) reported a 50% reduction of BOD of debarking wastewater by a fluidized bed reactor. Thompson et al. (2001) reported that a COD removal efficiency of 80% was achievable, but the residual COD was around 800 mg/L, meaning that additional treatment was essential. Schnell et al. (1992) concluded that anaerobic treatment systems were less suitable for treatment of sulfite-spent liquor compared to an aerobic system.

In anaerobic environments, methanol can either be directly converted to methane by methylotrophic methanogens or be converted to acetate by acetogens. The COD removal efficiency and stability of anaerobic reactors treating methanolic wastewaters are dependent on which route methanol is degraded (Florencio et al., 1996). Zhou et al (2007) found that applying limited aeration in the regular up-flow anaerobic sludge blanket (UASB) reactor to alleviate the sulfide inhibition is feasible. Since the limited aeration causes no oxygen inhibition to the anaerobic microorganisms, sulfide oxidization and $H_2S$ removal were observed, which was beneficial to the methanogens. The COD removal rate increased from 40% to 80%. Furthermore, a reduction in total cost is achieved through energy recovery using the evolved methane gas, reduced production of excess sludge, and less electric power consumption, which is a major energy cost due to aeration in aerobic treatment (Minami, K., 1994; Kleerebezem and Macarie, 2003).

### 1.2.3 Operational Parameters in Anaerobic Treatment

**Temperature** — The three common temperature ranges at which anaerobic digestion operates are thermophilic (50°C - 65°C), mesophilic (20°C - 45°C) and psychrophillic (<20°C). In all microbial systems, temperature increase leads to increased microbial activity and thus enzyme activity. However, changes in overall process efficiency due to increased metabolic activity are balanced by a corresponding increase in microbial inactivation, i.e. above the optimum temperature efficiency of the process decreases (Henze and Mladenovski, 1991). The thermophilic digestion process offers a number of advantages, namely rapid metabolic activity which leads to shorter retention times, higher loading rates, and smaller digester volumes. Operation of the bioreactors at thermophilic temperatures prevents accumulation of bacterial pathogens. The disadvantages of thermophilic operations are that they require higher energy inputs for heating and maintenance costs are also high (Henze and Mladenovski, 1991).

**pH** — The optimum pH range is between 6.5 and 8.0. Maintenance of this neutral pH is due to the conversion of acid end-products to methane in the methanogenic anaerobic digestion and $H_2S$ production coupled with precipitation of heavy metals in the sulfate reduction process. The major controlling buffer is the carbonate-bicarbonate system, with

orthophosphoric acid, hydrosulfuric acid, volatile acids, and ammonia contributing to pH stabilization. At lower pH values, volatile fatty acids (VFA) regulate buffer capacity. Anaerobic digestion is sensitive to pH changes and microbial activities can be altered. Changes in microbial activities imply changes in enzyme activities. Florencio et al (1996) developed a mathematical model to estimate the optimum alkalinity dosage for good pH stability in reactors treating methanol. Continuous experiments were performed in five UASB reactors and methanol (5 g COD/L) was the only substrate used. $NaHCO_3$ and $K_2HPO_4$ were the sources of added alkalinity. The amount of added alkalinity varied from 0 to 50 meq/L.

**Retention times** — Mesophilic and thermophilic digesters can operate at mean sludge retention times typically in the range of 25 - 35 days and sometimes as low as 12 - 15 days (Henze and Mladenovski, 1991).

**Substrate loading** — Chemical oxygen demand (COD) parameters can be used to calculate substrate loading. The COD is a measure of the organic content of a sample (sludge/substrate) that is susceptible to oxidation by a strong chemical oxidant. Volatile solids can also be used as a measure of organic content of the sludge, and loadings are normally expressed in terms of $kg/m^3/day$. If a feed containing a lower concentration of biodegradable organics is added at a rate sufficient to maintain the normal organic load, higher volumetric loading is required to reduce the retention times (Henze and Mladenovski, 1991).

**Volatile acids** — Instability in anaerobic digestion occurs when the series of microbiological reactions become uncoupled. Uncoupling may be a result of inhibition of methane-forming organisms or organic overload, which allows faster growing acidogens to outproduce the methanogens. When acid-forming bacteria out-produce acid-consuming bacteria, a sharp rise in volatile acids follows.

### 1.2.4 Anaerobic Mesophilic Treatment

Anaerobic treatment of condensates relies on anaerobic microorganisms to convert methanol into biogas. Kleerebezem and Stam (2000) suggest that for anaerobic fermentation, where two or three hydrogen molecules have to be released per molecule of substrate, small changes in the hydrogen partial pressure may have a large impact on substrate conversion rates. Also, bicarbonate plays an important role in the anaerobic conversion of methanol, since it is a required co-substrate in the acetogenesis of methanol (Ljungdahl, 1986). The effects of bicarbonate on the competition between methanogens and homoacetogens for methanol under mesophilic conditions have been studied by Florencio et al. (1993, 1995). They found that homoacetogenesis occurred when bicarbonate was added, when unionized volatile fatty acids (VFA) accumulated, and when high methanol concentrations were present. The same authors found that, under mesophilic conditions, conversion of methanol to $CH_4$ without addition of bicarbonate can be successfully achieved under both acidic conditions (pH of 4.2) and at neutral pH using a phosphate buffer. Under these conditions, no accumulation of VFA was detected (Florencio et al., 1993 and 1995). When methanolic wastewater was treated in an UASB reactor at 40°C, the consortia could hold a pH of approximately 6.0-6.3 without any addition of external buffer for 40 days, while the pH dropped to 5.5 over the next three days. The pH was further restored by the addition of 2.52 g/L $NaHCO_3$, without build up of VFA in the effluent (Bhatti et al., 1993). For efficient COD removal, the production of $CH_4$ is a prerequisite in the anaerobic treatment of a methanolic wastewater, whereas only little COD removal is achieved when VFA are formed.

Aquino and Stuckey (2007) investigated the effect of some chelating agents commonly found in industrial wastewaters (ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and citrate) on methanogenesis at 35°C using continuously stirred tank reactors (CSTRs). Later, they also discussed the role of soluble microbial products (SMP) in metal bioavailability and toxicity mitigation. They found that the reduced methane production rate may be caused by free EDTA (1mM) because of the unavailability of metals caused by the complexation of metal nutrients with EDTA. Addition of SMP did not change the metal distribution in anaerobic systems, despite

increasing the rate of methane production, and it seems that the degradation of SMP via hydrogenotrophic methanogenesis was not responsible for this increase. The metal distribution in systems inoculated with SMP suggested that specific microbial compounds might have been excreted to play a role in metal uptake, likely delivering nutrient metals to specific binding sites located on the cell surface and/or increasing Cu bioavailability through direct uptake of Cu-SMP complexes. However, addition of SMP did not reduce Cu toxicity, and the best protection was offered when stoichiometric amounts of NTA, which should complex and solubilize most of the Cu, were added.

The biogas produced through anaerobic digestion is primarily methane (> 85%) and is also a useful fuel. Sulfides from the condensates are partly stripped with the biogas, while some stay in the liquid phase, and the rest precipitate as metallic sulfides or elemental sulfur (Endo and Tohya, 1985). Anaerobic treatment can remove methanol with approximately 100% efficiency. Anaerobic wastewater treatment is typically used in different industries such as chemical, dairy, and pulp and paper mills. Existing anaerobic wastewater treatment facilities for pulp and paper typically treat total mill effluent. Some pilot trials have been conducted with the National Council on Air and Stream Improvement (NCASI) on segregated condensate streams (Barton et al., 1998; and Wiseman et al., 1998).

Dufresne et al. (2001) investigated the potential for anaerobic treatment of contaminated Kraft mill condensates at mesophilic temperatures (38°C). It was found that undiluted foul condensates (digester and evaporator) were toxic to the anaerobic biomass because of the high concentration of sulfides. This is especially true of foul evaporator condensates and does not apply to foul digester condensates, which have low sulfide and much higher methanol concentrations. Treatment of combined condensates is possible at an approximate volumetric loading of 10 to 12 g COD/L/day with good production of biogas (0.35 L/g of COD removed, close to the theoretical value), excellent methanol removal efficiency (better than 95%) and a COD removal efficiency of 70 to 75%. Treating condensates in this manner would allow the mill to meet the requirements of the U.S. EPA Cluster Rules with respect to methanol removal. The MACT component

of EPA's 1997 Cluster Rule offers several alternatives for the control of Kraft mill condensates, including: (a) recycle to a controlled pulping system component, (b) treat by steam stripping followed by incineration to destroy 'hazardous air pollutants' (HAPs), or (c) discharge by way of an enclosed pipe to a properly monitored biological treatment system (Barton and Matthews, 1998). The loading was primarily limited by the sulfide concentration in the inlet and in the biogas. The biogas produced is of excellent fuel quality with close to 90% methane, but with high sulfide content (close to 4%). This type of fuel is, however, easy to handle in the context of a Kraft pulp mill. Further work would also be required to gain a better understanding of the various factors affecting treatment performance.

The treated condensates effluent contained sulfides (primarily $H_2S$ and methyl mercaptan with some DMS and DMDS) and fine suspended solids (approximately 100 mg/L of suspended solids (90% volatile solids)) and was strongly coloured (Dufresne et al., 2001). Some polishing treatment had been explored, including the use of polymers to remove the suspended solids and the sulfides. Alum and an anionic, high-molecular-weight polymer were studied, while some aeration trials were also performed. It was found that alum and the polymer had to be used simultaneously to be efficient, and aeration was effective at removing the sulfides (Dufresne et al., 2001).

These results from Dufresne et al. (2001) demonstrate that a significant portion of the sulfides in the influent (more than 50%) remain after treatment. Most of the sulfides removed are evacuated in the biogas and a small portion is converted to elemental sulfur and iron sulfide (as iron was added in the micronutrients). The iron sulfide was a significant contributor to the dark colour of the effluent.

The anaerobic treatment of evaporator condensates system can support some toxic shocks and pH changes and recovers rapidly, but the faulty performance also existed and remained unexplained. Nevertheless, two hypotheses can be offered (Dufresne et al., 2001). First, the repeated toxic shocks may have gradually killed part of the biomass without sufficient recovery time allowed. Second, there may have been a slow

accumulation of an undetermined toxic substance in the biomass granules. Adequate subsequent testing has not been done to verify these hypotheses; nonetheless, the first hypothesis is believed to be more likely because it is known that methanol is a good food source. The growth rate for anaerobic biomass was less than 5% of the loading. There was not sufficient time to replace any damaged biomass after the system upsets. This may also have been compounded a by nutrient imbalance by the analysis of biomass before and after the trial, showing a significant difference in metals (Dufresne et al., 2001).

The manner of the start-up of an anaerobic system was studied as well. A faster and more reliable start-up in the most delicate phase of the operation of anaerobic digesters was achieved by pulsing feed to an upflow anaerobic filter (UAF) at 37°C, because pulsation allowed the useful volume and mass transfer rate to be increased, as well as a higher densification of occluded biomass between the packed bed (Franco et al., 2007). The UAF later became the prototype of the upflow anaerobic sludge blanket (UASB). Franco et al. (2002, 2003, 2006) found that when pulsation is applied to UASB reactors, granulation is also promoted when the inoculums are in the flocculent form, greatly improving the characteristics of granules when employing granular biomass as inoculums.

### 1.2.5 Anaerobic Thermophilic Treatment

The anaerobic treatment of methanolic wastewater under mesophilic conditions has been investigated by many researchers (Lettinga et al., 1979; Minami et al., 1991; Nishio et al., 1993; Florencio et al., 1994; Bhatti et al., 1996; Fukuzaki and Nichio, 1997) but so far, very little is known about methanol conversion under thermophilic conditions (Paulo et al., 2001).

Although anaerobically treating high-strength evaporator condensates at elevated temperatures is a considerably new concept, thermophilic processes have been in operation for decades. Thermophilic anaerobic digestion of primary and secondary wastewater sludge have been studied since 1930 (Rudolfs and Heukelekian, 1930), with full-scale studies beginning as early as 1931 (Fischer and Greene, 1945). Excellent reviews of thermophilic anaerobic digestion and thermophilic anaerobic wastewater

treatment are available by Buhr and Andrews (1977), Zinder (1986), Parkin and Owen (1986), and Van Lier (1996). Composting, commonly used to treat moist organic solids (e.g., yard refuse, sewage sludge, etc.), also represents a thermophilic waste treatment technology. With this process, an ancillary effect of microbial metabolism of the organic substrate is the release of significant quantities of energy, thereby maintaining autothermal thermophilic conditions.

High rate anaerobic digestion of evaporate condensate with methanol concentrations ranging from 1.5 to 24.5 g/L was studied (Minami et al., 1991; Minami et al., 1986; Minami et al., 1988; Yamaguchi et al., 1991). Lee et al. (2001) proposed a thermophilic, UASB reactor to treat acid condensate waste streams by high-rate anaerobic digestion. Besides the lower capital cost and short payback period compared to an existing fermentor, the thermophilic UASB reduced the total BOD discharge by 15%, and reduced the operating costs of their overall wastewater treatment facility.

Paulo et al. (2003) assessed the feasibility of thermophilic anaerobic conversion of methanol under acidic conditions, and the effects of the bicarbonate addition on the performance, stability, and on the pathway of conversion of methanol were determined. In their reported the thermophilic (55°C) anaerobic conversion of methanol was studied in an un-buffered medium (pH of 4 ± 0.2) and in a phosphate buffered medium (pH of 6.4 ± 0.1). In both cases, bicarbonate was not added, and methanol was used as the sole organic carbon source. The cultivated sludge consortium was unable to degrade methanol under acidic conditions. During the 160 days of continuous operation of an upflow anaerobic sludge blanket (UASB) reactor at an organic loading rate (OLR) of 6 g COD/L/day and pH of approximately 4, only 5% of the applied methanol load was consumed, and no methane ($CH_4$) was detected. However, Paulo et al. (2003) found that hydrogenotrphic methanogens were resistant to exposure to such conditions. At the end of the trial, the hydrogenotrophic methanogenic activity of the sludge was 1.23 ± 0.16 g COD/g VSS/day at a neutral pH. With methanol as the test substrate, the addition of bicarbonate led to acetate accumulation. When assessing the conversion of methanol at neutral pH (phosphate buffered) in a bicarbonate deprived medium, the reactor

performance was poor with a methanol-COD removal capacity limited to about 9.5 g COD/L/day. The system appeared to be quite susceptible to any type of disturbance, even at low organic loading rate (OLR). The fraction of methanol-COD converted to $CH_4$ and acetate was found to be unaffected by the OLR applied (Paulo et al., 2003).

Paulo et al. (2001, 2002) found that the conversion of methanol to $CH_4$ under thermophilic (55°C) conditions could be successfully achieved using sodium bicarbonate as a buffer. Even when exposing the system to some environmental disturbances (temperature drop, overloading, and no seeding), the performance remained almost unaffected and recovered quickly when normal operational conditions were restored.

### 1.3 Membrane Bioreactors for Pulp and Paper Mill Wastewater Treatment

Membrane separation techniques were reported to be suitable for removing adsorbable organic halides (AOX), COD, and colour from pulp and paper mills (Zaidi et al., 1992; Afonso and Pinho, 1991, Falth, 2000). De Pinho et al. (2000) compared the efficiency of ultrafiltration and ultrafiltration plus dissolved air flotation. The results showed 54%, 88%, 100% removal of TOC, colour, and SS, respectively by ultrafiltration alone. Ultrafiltration plus dissolved air flotation resulted in 65%, 90% and 100% removal of TOC, colour, and suspended solids (SS), respectively. Merrill et al. (2001) stated that membrane filtration (MF) and granular membrane filtration (GMF) were suitable for removing heavy metals from the pulp and paper mill wastewaters (Pokhrel and Viraraghavan, 2004).

One of the major problems in biological thermophilic treatment is related to the solid/liquid separation of the activated sludge by conventional gravity clarifiers. The bio-flocs formed in thermophilic processes are normally very small (pin-pointed flocs) and are difficult to separate by gravity (Dias et al., 2005). Therefore, a membrane ultrafiltration separation unit would have a clear advantage over gravity settling tanks. Moreover, MBR treatment of foul condensates at different temperatures showed to be feasible, reaching high COD, BOD, methanol, and TRS reduction. It is also important to

mention that membrane fluxes generally increase with the increase of temperature, which makes this option more attractive (Dias et al., 2005).

A cost comparison to steam stripping confirmed that the membrane bioreactor options could be significantly less expensive than the major alternative technology for this duty. The combined capital and operational costs for a high temperature MBR are significantly less than for a steam stripping system for both the treatment of the fouler fraction of the evaporator condensate only and the treatment of the fouler fraction and approximately 50% of the cleaner fraction of the evaporator condensates (i.e. all of the condensates which are typically discharged to the environment following combined mill effluent treatment). If polymeric membranes can be used, the capital cost of an MBR system may be significantly less than the cost of a steam stripping system for both operating scenarios. The operating cost of an MBR system is significantly less than the operating cost of a steam stripping system, particularly for treating the combined evaporator condensates (Bérubé and Hall, 1999a). This is similar to Vora (1995), who published cost estimates which indicate that the operating cost associated with generating steam can be prohibitively expensive with large steam stripping flows. The cost estimate for the MBR indicates that cost is most sensitive to the volume of wastewater to be treated and not the amount of methanol to remove.

### 1.3.1 Types of Membrane Processes

A membrane is defined as a selective barrier that permits the separation of certain species in a fluid by a combination of sieving and sorption diffusion mechanisms (Tansel et al., 2000; Mulder, 1991). Membranes are available in several different configurations such as tubular, hollow-fibre, plate and frame, and spiral wound. This technology simultaneously concentrates, fractionates and purifies the products via microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), dialysis and pervaporation (PV) (Beerlange et al., 2001). Characteristics of several typical membrane processes are listed in Table 1.1.

Table 1.1 Characteristics of Typical Membrane Processes (Melamane, 2003)

| Parameters | MF | UF | NF | RO |
|---|---|---|---|---|
| **Operating Pressure (bar)** | 1 - 4 | 2 - 7 | 10 - 40 | 15 – 100 |
| **Pore Size (μm)** | 0.1 – 1.5 | 0.01 – 0.05 | 0.001 – 0.01 | < 0.0002 |
| **MWCO Range (μm)** | > 300 000 | 300 000 – 100 000 | 200 000 – 20 000 | < 500 |
| **Size-cut-off Range (μm)** | 0.1 - 20 | 0.005 – 0.1 | 0.001 – 0.01 | < 0.001 |

Microfiltration (MF) is a membrane process that separates micron-size or sub-micron particles from the liquid or gaseous feed stream. The pore sizes of MF membranes are in the range of 0.1 to 1.5 μm. Thus, MF typically operates at low transmembrane pressures to minimize build-up of the suspended solids at the membrane surface. Pressures of 0.3 - 3.3 bar and cross flow velocities of up to 3 - 6 m/s in tubular modules are common. On an industrial scale, MF is usually carried out as a multistage (stages in series) operation in a feed and bleed mode of operation. Typical materials removed by MF are starch, bacteria, moulds, yeast, and emulsified oils (Kuberkar et al., 1998). The MF membrane with a pore size of 0.1 μm resulted in a minimal fouling tendency as anaerobic digestion (AD) broth filtrated through microfiltration (MF) and ultrafiltration (UF) membranes, suggesting that an optimal pore size exists due to the relationship between the sizes of membrane pore and broth constituents (Choo and Lee, 1996).

Ultrafiltration (UF) is also a low-pressure fractionation process (2 - 7 bar), selecting components by size. It separates dissolved solutes of 0.005 - 0.1 microns. This corresponds to a molecular weight cut-off (MWCO) of about 100,000 to 300,000. Depending on the MWCO selected, the membrane will concentrate high molecular weight species while allowing dissolved salts and lower molecular weight materials to pass through the membrane (Parmar et al., 2001; Jönsson and Trägårdh, 1990).

### 1.3.2 Types of Membranes

Membranes are classified as symmetric or asymmetric. Asymmetric membranes have tapering pores with a larger pore diameter in the top layer as compared with the diameter

of the pores in the bottom layer. Membranes have been further classified by their chemical properties into hydrophilic, hydrophobic, and inorganic membranes. Cellulose acetate, polyacryonitrile, polyvinylchloride, polyimide, and polyvinylideneflouride are examples of hydrophilic membranes, while polysulphone, polyethersulphone, and nylon membranes are hydrophobic (Melamane, 2003).

### 1.3.3 Membrane Operations

Combining membrane technology with biological reactors for the treatment of municipal and industrial wastewaters has led to the development of three generic membrane processes within bioreactors: for separation and recycle of solids, for bubbleless aeration of the bioreactor, and for extraction of priority organic pollutants from hostile industrial wastewaters (Brindle and Stephenson, 1996). In anaerobic digestion, there are two main types of membrane operations. When the membrane is operated under pressure, it is commonly called an external cross-flow membrane operation, whereas when a membrane is operated under vacuum, it is called submerged or immerged membrane operation (Liao et al., 2006). Until now, membranes operate predominantly in the cross-flow mode, where the membrane splits the feed stream into two streams known as permeate and retentate, as shown in Figure 1.1. In the cross-flow model, transmembrane pressure and cross-flow velocity are important parameters that are controlled throughout the membrane modules. Cross-flow velocity is the average rate at which the process fluid flows parallel to the membrane. Velocity has a major effect on the permeate flux, which depends on the applied pressure ($\Delta P$) for a given surface area up to a threshold $\Delta P$ (Tansel et al., 2000). Above this threshold pressure, which has to be experimentally determined for each application, higher pressures have little or no effect on permeates. In fact, higher pressure may aggravate fouling of the membrane (Tansel et al., 2000). Cho and Fane (2002) observed a characteristic two-stage transmembrane pressure (TMP) profile with an initially extended period of slow TMP rise followed by a sudden transition to a rapid TMP rise in a cross-flow microfilter coupled to an anaerobic bioreactor.

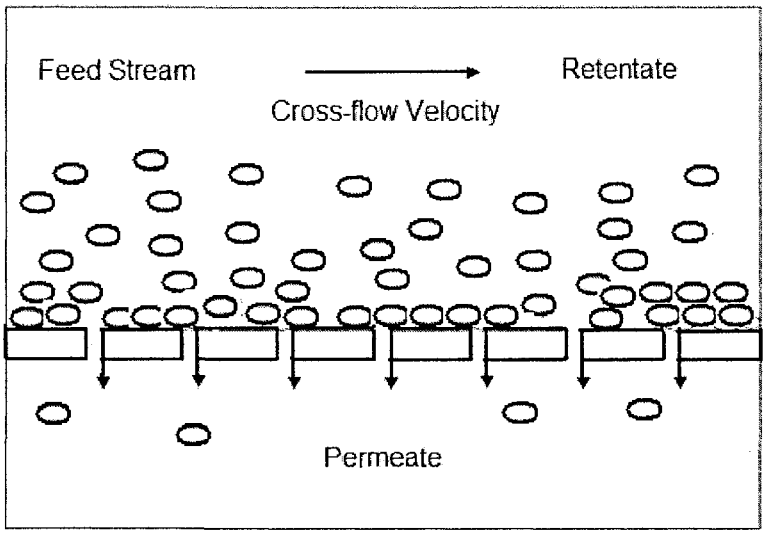



Fig. 1.1 Schematic diagram of a feed stream broken into permeate and retentate streams and fouling of the membrane depending on cross-flow velocity (Tansel et al., 2000)

### 1.3.4 Membrane System Performance

Membrane fouling, which is the process in which particles deposit onto the membrane surface or into membrane pores such that membrane performance is deteriorated, is one of the major operational concerns of membrane processes (Houghton and Stephenson, 2002). The overall performance of a membrane system is determined by the following characteristics: (i) membrane selectivity, including the characteristics of the membrane material such as its pore size etc. and (ii) permeate flux ($L/m^2/hr$) which is dependent upon the operating pressure, temperature, pH, pore sizes of the membrane, feed composition, and flow rate. Typical values may lie within the range of 20 - 2000 $L/m^2/hr$ (Beerlange et al., 2001; Houghton and Stephenson, 2002). Particles with effective diameters 2-3 times smaller than the membrane pore size may be retained, although the efficiency of this sub-pore size rejection depends upon: (i) the loading rate on the membrane and the membrane thickness, (ii) the pore size of the membrane compared to the dimensions of the particles, (iii) the trans-membrane pressure and flux rate, and (iv) the chemical characteristics of the membrane or any charge that is placed on the membrane together with the chemical and physical characteristics of the particles (Houghton and Stephenson, 2002).

### 1.3.5 Membrane Fouling and Management

Membrane fouling occurs due to the deposition of suspended or dissolved substances on the external surfaces at or within the pores (Madaeni et al., 2001). Depending on the membrane type, feed composition, and process conditions, the membrane performance will decrease due to fouling. Fouling can be quantified by the resistance appearing during the filtration, and cleaning can be specified by the removal of this resistance (Güell and Davis, 1996; Kim et al., 1992). Fouling results in (i) loss of membrane performance, (ii) lower than expected flux, (iii) reduced productivity, (iv) need for the use of harsh chemicals as cleaning agents, and (v) high cleaning costs.

Reduction of fouling and cleaning of fouled membranes has been approached in a number of ways (Maartens et al., 1998; Flemming, 1990) which included optimization of flow conditions, pre-treatment of the effluent, production of membranes with reduced absorptive conditions by modification of membrane surface, backflushing, and harsh chemical cleaning agents which result in high cleaning costs and industrial pollution (Kim et al., 1993; Trägårdh, 1989). Kang et al (2002) compared filtration characteristics of organic and inorganic membranes in terms of physicochemical properties of the membrane materials, cake layer formation, backflushing, and backfeeding effects in a membrane coupled anaerobic bioreactor. For the inorganic membrane, struvite ($MgNH_4PO_4 \cdot 6H_2O$) was found to have accumulated inside the membrane pore and plays a key role in flux decline. However, for the organic membrane, a thick cake layer composed of biomass and struvite formed on the membrane surface, thus causing a major hydraulic resistance. They recommended a backfeeding mode combined with the periodic alkaline backflushing operation method to reduce the membrane fouling, especially for the inorganic membrane in the system.

Challenges of membrane fouling and cleaning regimes experienced in membrane technology have led to a need for an environmental friendly, abundant, and cost effective source of enzymes. Enzymes, as biocatalysts, can be used effectively in combination with detergents to reduce fouling and restore permeate flux on previously fouled membranes (Maartens et al., 1996). Melamane (2003) found that enzymes from a sulphidogenic

bioreactor can clean or defoul membranes (UF process) that have been fouled by organic foulants from abattoir effluent.

On the other hand, sulfate reducing submerged anaerobic membrane bioreactors can be operated over extended periods of time without chemical cleaning of the membranes at a certain fixed flux if this flux is substantially below the nominal critical flux determined experimentally (18–21 $L/m^2/hr$). Intermittent operation as well as backflushing of the membranes was shown to slow the fouling in the membranes. Frequent backflushing (e.g. 1 min each 10 min) is the suggested operational strategy to minimize fouling in anaerobic MBRs (Vallero et al., 2005).

### 1.3.6 Membrane-coupled Anaerobic Bioreactors

As a membrane cooperates with the anaerobic biotreatment process, it keeps the merits from aerobic membrane bioreactors: complete biomass retention and elimination of suspended solids in the effluents, decoupled SRT and HRT, higher biomass concentration, and allowing higher organic loading rate. It presents, however, certain challenges too. Membrane fouling in anaerobic MBRs, for instance, is classified as composite fouling, including biofouling, organic, and inorganic fouling. Choo and Lee (1998) theoretically evaluated the flux decline in a membrane-coupled (external cross-flow) ultrafiltration anaerobic bioreactor (MCAB) in terms of size distribution of biosolids and reversibility of biofouling in order to predict the critical flux with the hydrodynamic models for particle transport. During ultrafiltration, due to irreversible biofouling, they suggested the biosolids movement toward the membrane surface should be controlled at the beginning of the MCAB operation. The optimal operating condition which prevents biosolids deposition onto the membrane surface could be predicted by the evaluation of the critical flux. Elmaleh and Abdelmoumni (1998) reported the filtration of an anaerobic suspension fed with acetic acid as sole carbon source at 2 g/L TOC. The effluent quality was excellent without sludge production. The tested filtration elements were tubular carbosep membranes. They found the main fouling mechanism appeared to be the particle deposition on the membrane surface, as no flux decline was observed at higher crossflow velocities. In order to investigate membrane fouling and to characterize

the foulants, Aquino et al. (2006) investigated membrane fouling and the foulant characteristics from two submerged anaerobic membrane bioreactors (SAnMBRs). One was added in powdered activated carbon addition (PAC 1.7 g/L) and one without. They were continuously fed with a low-strength feed (450 mg COD/L). The SAMBR which did not receive PAC experienced more fouling. They believe that high-MW protein and carbohydrate material originating mainly from cell lysis and extracellular polymeric substances (EPS) seemed to be the main organics that contributed to the internal fouling of the membrane.

### 1.3.7 Applications of AnMBRs in Treating Industrial Wastewaters

Non-food-processing industrial wastewaters include effluents from the pulp and paper, chemical, pharmaceutical, petroleum, and textile industries. The characteristics of industrial wastewaters are sector specific, although, in general, they have the potential to have a high organic strength and contain synthetic and natural chemicals that may be slowly degradable or non-biodegradable anaerobically and/or toxic.

Anaerobic treatment of pulp and paper wastewaters has become common, as approximately 9% of all anaerobic installations are for the pulp and paper industry (Liao et al., 2006). Usually, the pretreatment of the condensate (characterized by high soluble CODs of 10–42 g/L, due mainly to methanol, low suspended solids (<3 mg/L), plus inhibitory turpene oils and sulfur compounds) by microfiltration and biogas stripping was used to remove the inhibitory turpene oils and sulfur compounds, while the pH was adjusted to neutral. Minami (1994) investigated the treatment of pretreated condensate in a thermophilic attached-growth ultrafiltration AnMBR (cross-flow membrane) that provided a biochemical oxygen demand (BOD) removal efficiency of >93%. Bérubé and Hall (1999b) investigated the removal of methanol from Kraft pulp mill condensate using a high temperature aerobic membrane bioreactor (MBR). The effects of the complex matrix associated with real condensate, on methanol metabolism and removal kinetics were examined. Additionally, Bérubé and Hall (2000) used synthetic condensate to investigate the feasibility of biologically removing methanol from Kraft pulp mill evaporator condensate. They found the optimum temperature of 60°C with 99% methanol

removal. Since EC have no alkalinity, whereas methanogenesis is known to work best at neutral pH, additional alkalinity is needed to prevent the pH from dropping, and consequently, causing reactor instability.

Recently, Hu and Stuckey (2006, 2007) used a submerged anaerobic membrane bioreactor (SAnMBRs), with in-situ membrane cleaning (due to the bubbling of recycled biogas underneath them) to treat dilute municipal wastewaters (synthetic substrate, 460 mg COD/L) at a mesophilic temperature (35°C). It was found that more than 90% soluble COD removal efficiency was achieved. The membrane fouling appeared to be due to both fine particles (0.15-0.4 μm) found in the reactor, and a gel layer which acted like a dynamic secondary membrane, but also enhanced the effluent quality substantially. VFAs did not contribute much to the effluent COD because the SMPs produced at low HRTs were the primary constituent of the effluent COD. They, later on, continue their work through the addition of powdered activated carbon (AC) to the SAnMBRs. Enhanced COD removal, improved membrane flux, and reduced pressure drop across the membrane were observed. The results showed that activated carbon played an important role in reducing cake layer formation, resulting in lower TMPs. Activated carbon can adsorb fine colloids from the bulk solution so that the overall particle distribution shifts to a larger size range. In addition, the carbon seemed to have adsorbed high molecular weight organics form the solution, and this also helped in improving COD removal, lowering TMP, and enhancing the flux. Last but not the least, AC actually provided a solid support for biomass growth, thus reducing floc breakage. Powdered activated carbon particularly has a better performance than Granular activated carbon mainly due to PAC having a larger surface area per unit mass (1,300 $m^2/g$) for biomass growth than GAC (775 $m^2/g$), resulting a more active biomass in the SAMBR.

Jeison (2007) conducted a long-term laboratory scale study of two thermophilic anaerobic submerged membrane bioreactors (AnSMBR) for treating acidified and partially acidified synthetic wastewaters with tubular membranes. In both reactors, cake formation was identified as the key factor governing critical flux. Even though cake formation was observed to be mostly reversible, particle deposition proceeds quickly

once the critical flux is exceeded. Very little irreversible fouling was observed during long term operation, irrespective of the substrate. Critical flux values at the end of reactors operation were 7 and 3 $L/m^2/hr$ for the AnSMBRs fed with acidified and partially acidified wastewater, respectively, at a gas superficial velocity of 70 m/h. Small particle size was identified as the responsible parameter for the low observed flux values. The degree of wastewater acidification significantly affected the physical properties of the sludge and the determination of the attainable flux. Based on the fluxes observed in this research, the membrane costs would be in the range of 0.33 ¢ per $m^3$ of treated wastewater. Gas sparging was ineffective in increasing the critical flux values. However, preliminary tests showed that side-stream cross-flow operation may be a feasible alternative to reduce particle deposition.

A series of works have been done by Bérubé and Hall to aerobically remove methanol from Kraft condensates. They found that high temperature operation is actually more efficient at treating the evaporator condensate for reuse than conventional, lower temperature, biological treatment in an aerobic environment; and the system cost compared with the conventional air stripping system is less. However, their membrane bioreactor worked as an external membrane and needed the use of oxygen. There is actually a lack of information on the role of submerged membrane modules in an anaerobic bioreactor at treating evaporator condensates. In other words, the feasibility of submerged membrane bioreactors treating evaporator condensates from a Kraft pulp mill for reuse as process water at mesophilic and thermophilic temperature have not been investigated.

Only in the last few years, the concept of submerged AnMBRs has been tested for synthetic municipal and industrial wastewater treatment by using produced biogas for membrane surface scouring in laboratory-scale AnMBRs (Hu and Stuckey, 2006 and 2007; Jeison and Van Lier, 2006 and 2008). Nevertheless, at present there is no information available for treating high strength wastewater, such as Kraft EC, by using submerged AnMBRs.

## 1.4 Objective of This Study

The primary goal of this study was to develop better treatment technologies for energy recovery from pulp and paper wastewater and subsequent reuse of treated effluent and ultimately system closure. Specific objectives include:

1) To study the feasibility of using submerged AnMBRs for Kraft evaporator condensate treatment under both thermophilic and mesophilic temperatures

2) To quantify the chemical oxygen demand (COD) removal efficiency and biogas production (chemical composition and rate)

3) To characterize sludge properties, including particle size and extracellular polymeric substances (EPS)

4) To understand and control membrane fouling in submerged AnMBRs

## 1.5 Outline of This Thesis

The motivation, primary goal, and specific objectives of this research are stated in Chapter 1, as well as a comprehensive literature review of previous studies on Kraft evaporator condensate treatment technologies. Chapter 2 presents the materials and methods used in this project. Chapter 3 discusses the performance of mesophilic and thermophilic anaerobic submerged membrane bioreactors (SAnMBR), including COD removal efficiency under various COD influent loadings, particle size distribution, trans-membrane pressure (TMP), biomass concentration, biogas composition, and methane yield. The characteristics of biomass from mesophilic and thermophilic SAnMBRs and their role in membrane fouling were also described in Chapter 3. The general conclusions from this study and recommendations for future research are summarized in Chapter 4.

# Chapter 2

# Experimental Materials and Methods

## 2.1 Reactor Setup and Experimental Operation

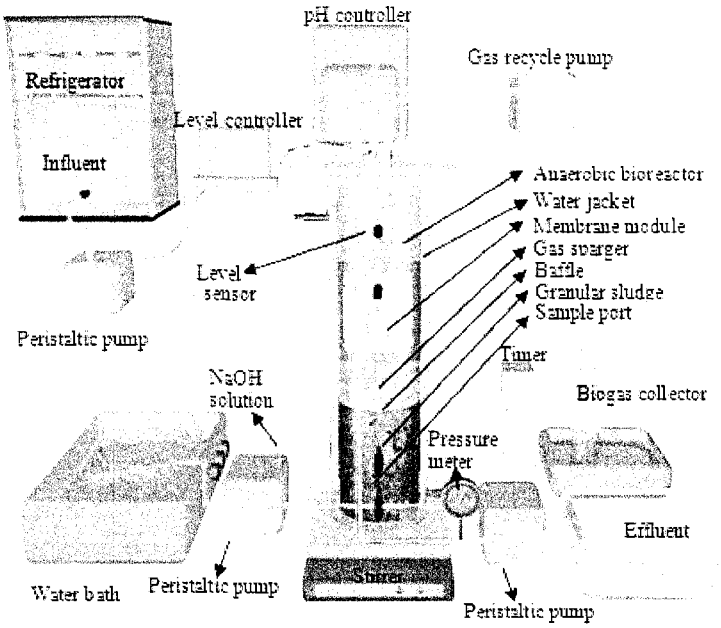



Fig. 2.1 Schematic of the anaerobic submerged membrane bioreactor and experimental setup

Two laboratory-scale submerged AnMBRs (shown in Figure 2.1) were constructed to treat Kraft evaporator condensate. The Kraft evaporator condensate used in the research was from Abitibi-Bowater Inc. (Thunder Bay, Ontario) and the anaerobic seed sludge was from an upflow anaerobic sludge blanket (UASB) reactor which treated acidic condensate wastewater at Tembec Industries Inc. (Temiscaming, Quebec). A baffle separated each bioreactor (diameter: 15 cm, height: 50 cm) into two parts: top zone (6.5 L) and bottom zone (3.5 L). The reactors had a working volume (bottom zone) of 3.5 L, where the sludge was seeded. A flat sheet microfiltration membrane module, with a membrane area of 0.03$m^2$ and a membrane pore size of 0.3 μm, was submerged in the top zone. All membranes used in this study were made of polyvinylidene fluoride (PVDF) materials using phase inversion method. The molecular weight cut off (MWCO) was characterized as 70000 Dalton. A vacuum driven peristaltic pump was employed to

acquire permeate from the membrane module. The pump was controlled by a timer, allowing the pump to extract permeate for four minutes, and then shutting the pump off for one minute. The purpose of the on/off cycle was to slow down the membrane fouling process. The permeate flux was controlled by adjusting the pump speed and two calibrations were conducted daily. A tubular, stainless steel gas sparging diffuser was located underneath the membrane module to provide biogas scouring to control solids deposition over the membrane surface. This was done by continuously recirculating the headspace biogas through a peristaltic pump at a biogas sparging rate 0.4-0.75 litres per minute (LPM). A magnetic stirrer was located at the bottom of each bioreactor, where the Kraft EC was fed in by another peristaltic pump, to provide necessary mixing of the sludge liquor. The feeding peristaltic pump was controlled by a liquid level sensor controller, such that the liquid level inside the reactor was maintained at a constant height. The temperature of the reactors were maintained constant at 37 ± 2°C for the mesophilic SAnMBR and 55 ± 2°C for the thermophilic SAnMBR throughout the course of this experiment. This was done by recirculating heated water from a temperature-controlled water bath to the water jacket of the reactor. The pH was monitored using a pH electrode (Dulcometer, Fa Prominent), and automatically adjusted to 7.0 using a pH regulation pump and a 0.1 N sodium hydroxide (NaOH) solution.

### 2.2 Reactor Start-up

The chemical composition and concentration of the real Kraft evaporator condensate (EC) were determined in terms of chemical oxygen demand (COD) and metal ion concentrations (ICP). The analytical results of EC discharges are listed in Table 2.1. Since the raw EC did not contain sufficient minerals or nutrients, some mineral salts and trace element nutrients, which can be seen in Table 2.2, were added to the raw EC as in the previous report (Welander et al., 1999). Macro-nutrients, nitrogen ($NH_4Cl$) and phosphorus ($KH_2PO_4$) were fed in a proportion of COD: N: P of 100: 2.6: 0.4 to sustain the nutrient concentrations required for biomass growth in an anaerobic environment (Vogelaar et al., 2002). Due to the fact that evaporator condensates used in the present study did not contain sufficient hardness to sustain biomass growth and granulation, additional $Na^+$ and $Mg^{2+}$ ions were added to the wastewater so that the $Na^+$ concentration

was maintained at 1.8 mM, and $Mg^{2+}$ concentration at 0.5 mM (Ahring et al., 1993). The feed had a COD of about 2600 mg/L. Additional methanol was added to the feed to increase the COD level to approximately 5600 mg/L and 10000 mg/L to increase the organic loading rate (OLR).

Table 2.1 Chemical Composition and Concentration of Kraft Evaporator Condensate

| Description | MDL | UNITS | Kraft EC |
|---|---|---|---|
| COD | 0.1 | mg/L | 2500.0 – 2700.0 |
| Total Aluminum | 0.005 | mg/L | 0.175 – 0.402 |
| Total Arsenic | 0.005 | mg/L | <DL |
| Total Barium | 0.003 | mg/L | 0.100 -0.276 |
| Total Beryllium | 0.002 | mg/L | <DL |
| Total Calcium | 0.005 | mg/L | 1.612 – 6.724 |
| Total Cadmium | 0.001 | mg/L | <DL |
| Total Cobalt | 0.010 | mg/L | <DL |
| Total Chromium | 0.002 | mg/L | <DL |
| Total Copper | 0.002 | mg/L | 0.010 -0.017 |
| Total Iron | 0.002 | mg/L | 0.002 – 0.181 |
| Total Potassium | 0.10 | mg/L | 0.40 – 7.26 |
| Total Magnesium | 0.01 | mg/L | 0.65 – 1.92 |
| Total Manganese | 0.0002 | mg/L | 0.0211 – 0.3722 |
| Total Molybdenum | 0.006 | mg/L | <DL |
| Total Sodium | 0.01 | mg/L | 2.41 – 16.81 |
| Total Nickel | 0.002 | mg/L | <DL |
| Total Lead | 0.005 | mg/L | <DL |
| Total Sulfur | 0.05 | mg/L | 16.08 - 17.31 |
| Total Strontium | 0.005 | mg/L | 0.007 – 0.037 |
| Total Titanium | 0.010 | mg/L | <DL |
| Total Vanadium | 0.010 | mg/L | <DL |
| Total Zinc | 0.001 | mg/L | 0.033 – 0.772 |
| Total K. Nitrogen | 0.015 | mg/L | 16.320 - 21.420 |
| Total Phosphorous | 0.005 | mg/L | 0.500 - 1.300 |

Table 2.2 List of Mineral Salts and Trace Element Nutrients

| Micro-Nutrients | |
|---|---|
| **Chemicals** | **Concentration in the Feed (M = mol/L)** |
| $MgCl_2$ | 0.1 mM |
| $FeCl_2$ | 5 μM |
| $CaCl_2$ | 5 μM |
| $MnCl_2$ | 0.1 μM |
| $CoCl_2$ | 0.1μM |
| $NiCl_2$ | 0.1 μM |
| $CuCl_2$ | 0.01 μM |
| $ZnCl_2$ | 0.01 μM |
| $NaSeO_3$ | 0.01 μM |

The anaerobic bioreactors were operated as batch reactors for the first 44 days. Effluent was manually discharged from the top taps of the reactors at a rate of 2 liters per day until day 30, then 3 liters per day until day 44. The anaerobic reactors were operated at a hydraulic retention time (HRT) of 42 hr for 30 days with a COD load of 1.42 g COD/L/day, then an HRT of 28 hr for another 13 days with a COD load of 2.14 g COD/L/day; for the first 43 days of the process, the reactors were manually discharged daily. After day 43, flat sheet membrane modules were installed with a timer operation. In the whole process, no sludge was discharged except for sludge samples and sludge cake formation on membrane surfaces. The operation was stopped and a physical cleaning procedure was carried out when the TMP reached 30 kPa, and resumed after washing of fouled membranes. This occurred because it was difficult to maintain the flux at a constant level at a TMP of over 30 kPa.

The mesophilic anaerobic sludge from a full-scale UASB (Tembec Inc.) was used as the seed to develop thermophilic anaerobic sludge. After the membrane module was incorporated to the anaerobic bioreactor, the thermophilic SAnMBR was operated at 37 ± 2°C for two weeks (day 1-14) to get used to the Kraft EC. After this time, the SAnMBR temperature was increased from 37°C in a stepwise manner (1-1.5°C/day) to 55 ± 2°C within 2 weeks (day 15-29).

## 2.3 Analytical Methods

### 2.3.1 Water Quality Measurements

All sludge samples collected from the top zone of the submerged AnMBRs were first centrifuged at 13,000 rpm. The supernatant was then analyzed for supernatant COD and/or soluble microbial products (SMP). Membrane permeate COD and SMP were analyzed without further treatment. COD and mixed liquor suspended solids (MLSS) were measured according to Standard Methods (APHA 1999). Particle size measurements were made using a Malvern Instruments particle size analyzer (Malvern Mastersizer 2000, U.K.). Biogas samples were taken from the headspace of the reactor, while the composition of the biogas (methane, nitrogen, and carbon dioxide) was

determined and quantified using a Shimadzu (Kyoto, GC-201) GC-TCD fitted with a silica gel packed column (5,486 × 3.18 mm). The amount of biogas produced was determined by a liquid displacement arrangement, as seen in Figure 2.1.

### 2.3.2 Calculation of the Total Membrane Resistance

According to Darcy law:

$$R_t = R_m + R_c + R_p = \frac{\Delta p_T}{\eta \times J} \quad (1)$$

where, $R_t$ is the total hydraulic resistance, $R_m$ is the membrane resistance, $R_p$ is the pore blocking resistance, $R_c$ is the cake layer resistance, $\Delta p_T$ is the transmembrane pressure, $\eta$ is the dynamic viscosity and $J$ is the membrane flux (Huang et al. 2000 and Wang et al. 2006). Each resistance value was determined using the same membrane module used in the lab-scale SAnMBR submerged in a mini-MBR with effective volume of 2.5 L. The experimental procedure to determine each resistance value was as follows: (1) $R_m$ was estimated by measuring the water flux of tap water; (2) $R_t$ was evaluated by the final flux of biomass microfiltration; (3) the membrane surface was then flushed with tap water and cleaned with a sponge to remove the cake layer. Following this step, the tap water flux was measured again to obtain the resistance of $R_m + R_p$. From steps (1)-(3), $R_t$, $R_m$, $R_p$ and $R_c$ could be calculated.

### 2.3.3 EPS Extraction and Measurement

The extraction of bound EPS was based on a cation exchange resin (CER) (Dowex® Marathon® C, Na+ form, Sigma-Aldrich, Bellefonte, PA) method (Frølund et al., 1996): 100 mL sludge suspension was taken and centrifuged at 13 000 rpm for 20 minutes at 4°C. The sludge pellets were resuspended to their original volume using a buffer consisting of 2 mM $Na_3PO_4$, 4 mM $NaH_2PO_4$, 9 mM NaCl and 1mM KCl at pH 7. Then, the sludge was transferred to an extraction beaker with baffles and the CER (80 g/g-MLSS) added. The suspension was stirred for the selected stirring intensity (600 rpm) and extraction time (1.5 hr) at 4°C. The selected EPS was harvested by centrifugation of a sample of the CER/sludge suspension for 20 minutes at 13 000 rpm at 4°C in order to remove the CER and MLSS. The EPS was normalized as the sum of polysaccharide and

protein, which were measured colourimetrically by the methods of Dubois et al. (1956) and Lowery et al. (1951), respectively. Bovine serum albumin (BSA) was used as a protein standard, and glucose was used as a polysaccharide standard.

### 2.3.4 Floc Size Distribution and Structure

The floc size distribution was determined by a Malvern Mastersizer 2000 instrument with a detection range of 0.02 - 2000μm. The scattered light is detected by means of a detector that converts the signal to a size distribution based on volume. Each sample was measured three times with a standard deviation of 0.1 – 4.5%.

The sludge flocs were examined by light microscopy and the images were captured on a Keyence VH-Z75 (Japan) microscope attached with a PC-based charge-coupled device.

## 2.4 Characterization of Cake Layer

### 2.4.1 Scanning Electron Microscopy

A 2% gluteraldehyde in phosphate buffer (pH of 7.0) was used to fix the samples by exposing the samples to the glutaraldehyde solution for 2 hours. Subsequently, the samples were washed with buffer three times with each 10 minute washing series. Samples were then fixed in 1% $OsO_4$ for 30 minutes and washed with the buffer twice and dehydrated in a series of graded ethanol with increasing concentrations of alcohol (50%, 70%, 80%, 90% and three rounds of 100%). Samples were then mounted on carbon tape and sputter coated in 20 nm gold with an Emitech K550 Sputter Coater. A Hitachi S-570 Scanning Electron Microscope (Tokyo, Japan) was used to capture micrographs. All images were acquired digitally using Quartz PCI software (Vancouver, BC, Canada), which was also used for the image analysis.

### 2.4.2 CLSM Analysis

The cake layer formed on the membrane surface was observed microscopically using the confocal laser scanning microscopy (CLSM). Samples were cut from the modules in the SAnMBR and examined by an upright CLSM (Leica DM RE microscope connected

to a Leica TCS SP2) system with 3 different visible light lasers, covering 6 excitation wavelengths. To observe EPS on the cake layer, two different probes were collectively applied: Concanavalin A, Alexa Flour 633 conjugate (5mg/L, Invitrogen) to target the polysaccharides with (α-Man, α-Glu (Polysaccharide) and SYPRO orange (Invitrogen) to target all the proteins. The membrane samples were placed and stained in 5 cm diameter Petri-plates and were then incubated in darkness at room temperature for 30 minutes. After staining, all the samples were washed gently three times with a phosphate buffer to remove any unbound probes. After washing, the treated samples were immediately observed in CLSM. Signals were recorded in the green channel (excitation 488 nm, emission 570 nm) for proteins and red channel (excitation 633 nm, emission 647 nm) for polysaccharides. For observation, three different lenses (i.e. 10x, 20x, and 40x water immersion lens) were used. The series of CLSM images were simultaneously taken from different random locations on the used specimen obtained from SAnMBR. Staining and obtaining confocal images were repeated to acquire a number of images. The confocal assistant software supplied by the manufacturer (Leica Confocal Software (LCS, version 2.61) was used to analyze the image.

### 2.4.3 Membrane AFM Analysis

Membrane surface roughness was determined by AFM imaging and analysis (Multi-Mode AFM, Agilent Technologies, Inc. Santa Clara CA, United States). Fouled membranes were taken from SAnMBRs following each experiment, and immediately rinsed in phosphate buffer (pH 7.0) to remove any macromolecules if attached on the surface. Imaging was performed in tapping mode on the membrane surface with a different scanning scale. Picoview 1.4 software was used to analyze AFM images and to calculate membrane roughness using height images. The surface roughness parameters calculated include the Z range (the difference between the height and lowest points within a scanned area), the mean (the average of all Z values), the root mean square (RMS: the standard deviation of the Z values), and the mean roughness (Ra; mean value of the surface relative to the center plane).

The sludge cake was placed in a dryer at 105°C for 24 hours to obtain dry foulants. A Bruker Ten 37 FTIR Spectrometer (Bruker Co., Ltd.) was used to characterize the major functional groups of biopolymers in membrane foulants. The elements of C, O, Na, Mg, Al, S, Si, P, K, Ca, and Fe were detected by SEM-EDX system.

# Chapter 3

# Results and Discussion

## 3.1 Feasibility of Kraft Evaporator Condensate Treatment Using a Submerged Mesophilic Anaerobic Membrane Bioreactor

### 3.1.1 HRT, OLR, and Soluble COD Removals

Figure 3.1 shows that the hydraulic retention time (HRT) varied from 16.9 to 39.4 hrs, with an average of 26 ± 5 hrs (day 1-130) and 21 ± 3 hrs (day 131-200), due to the change in membrane flux. An increase in the feed COD concentration was used to increase the organic loading rate (OLR) with time (Figure 3.2). Initially, the OLR was 2.1 ± 0.6 kg COD/$m^3$/day, and then increased gradually to a maximum of 12 ± 2 kg COD/$m^3$/day. The organic removal rate is quite close to the OLRs. Figure 3.3 shows the mesophilic submerged AnMBR soluble COD concentrations in the feed, supernatant and permeate over time at a biogas sparging rate of 0.4 or 0.75 LPM. During the course of this experiment, three levels of feed COD concentration were investigated: 2.6 ± 0.1 g/L, 5.6 ± 0.5 g/L, and 10.0 ± 0.7 g/L. Figure 3.3 shows that an average of 93-99% COD removal efficiency was achieved in the three stages of increasing feed COD, except from day 70 to day 90, when the system experienced a toxicity shock from the feed. The mesophilic SAnMBR showed an instant reaction to toxic influent, as effluent soluble COD increased from 100-200 to 760 mg/L right after the toxic influent was fed into the reactor. In these 20 days of reactor system upset, the soluble COD concentration in the permeate gradually decreased from 760 to 290 mg/L, and the COD removal efficiency increased from 86 to 95%. This still showed an average of 93% COD removal, indicating that the mesophilic SAnMBR can take on a certain level of influent toxicity shock and slowly recover from it. As shown in Figure 3.3, the mesophilic submerged AnMBR had a better and steadier performance at higher COD loading (level three) compared with the previous two COD loadings.

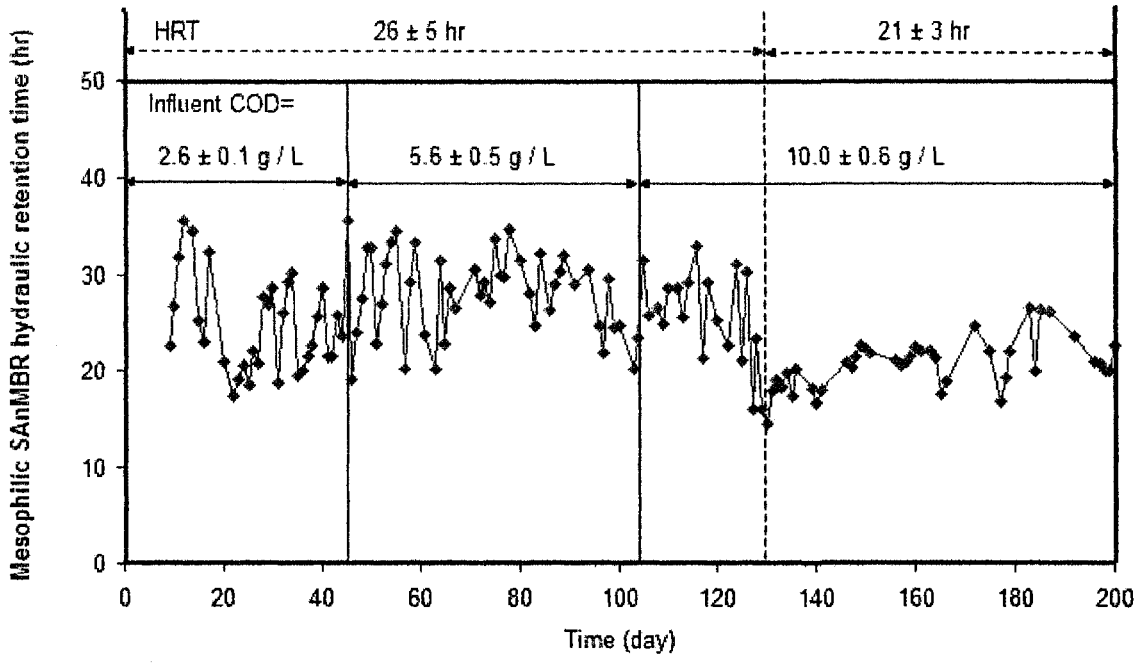



Fig. 3.1 Changes in hydraulic retention time with experimental time for mesophilic SAnMBR

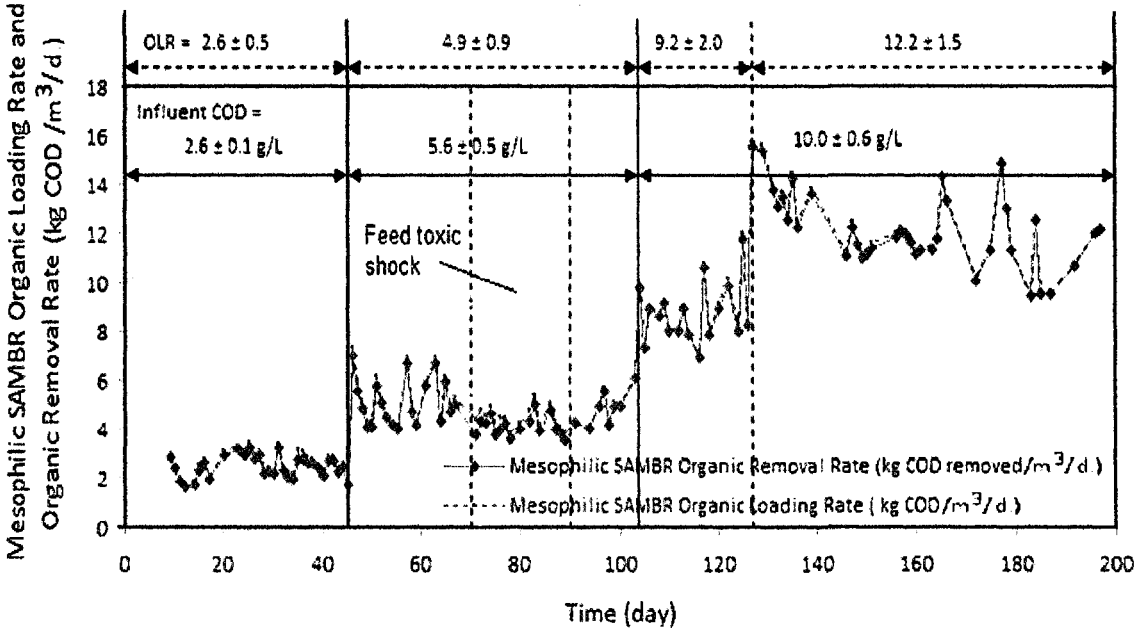



Fig. 3.2 Mesophilic SAnMBR organic loading rate and organic removal rate

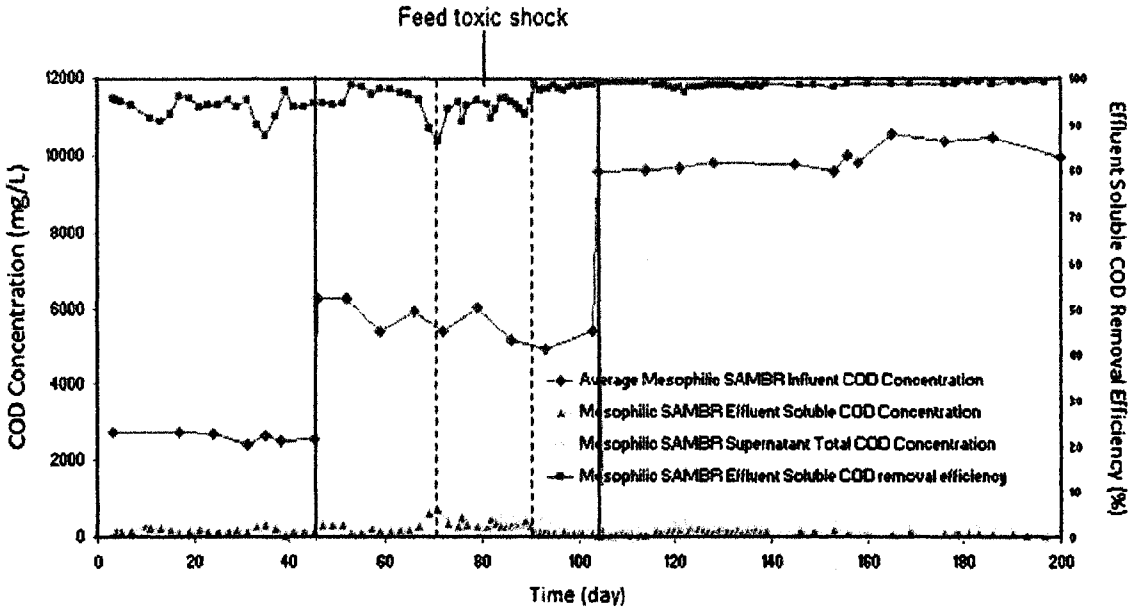



Fig. 3.3 Mesophilic SAnMBR soluble COD concentrations in the feed, effluent, reactor supernatant total COD concentrations, and effluent soluble COD removal efficiency vs. time

It is interesting to note that there was a difference between the supernatant soluble COD and permeate COD, as shown in Figure 3.3. This is consistent with the findings of previous studies (Goltara et al., 2003; Hu and Stuckey, 2006 and 2007). Previous researchers (Hu and Stuckey, 2006), however, found that the soluble COD concentrations inside a mesophilic submerged AnMBR treating synthetic municipal wastewater was more than three times higher than the permeate COD, attributed to the sieving effect (size exclusion) of the membrane to soluble microbial products (SMPs) (Huang et al., 2000; Shin and Kang, 2003). Similar results were observed in this study. However, three-fold differences or more have only been found during and after the influent toxicity shock. When the system fully recovered to its steady state, the soluble COD concentrations inside the SAnMBR were no more than two times higher than the permeate COD. It is in agreement with Aquino and Stuckey (2004) who show that more SMPs could be produced during unstable conditions. The decreased difference in the SMP production, as compared to that of previous studies (Goltara et al., 2003; Hu and Stuckey, 2006 and 2007) might be attributed to the effect of feed type since it is known that the type of feed substrate can make a significant difference to the SMP produced during anaerobic digestion (Barker and Stuckey, 2001; Hu and Stuckey, 2006). The analytical results of the supernatant soluble and permeate COD indicated that both proteins and carbohydrates

existed in the supernatant and permeate, implying that the supernatant and permeate contained SMPs.

A comparison of the water quality of the permeate from this study and the permeate or effluents from previous studies (Barton et al., 1998; Minami et al., 1991 and 1994; Welander et al., 1999; Dufresne et al., 2001) suggests that the permeate quality (clean and very low COD level, zero solids concentration) from this study is consistent with that of Minami et al. (1991 and 1994) using an external cross-flow AnMBR and is superior than that of conventional anaerobic digestion (Barton et al., 1998, Welander et al., 1999; Dufresne et al., 2001) in terms COD level, colour, and effluent solids. The permeate quality from this study is comparable to that of aerobic MBR treatment (Dias et al., 2005; Berube and Hall, 2001) in terms of COD level and permeate solids. This suggests that permeate from SAnMBR can be directly reused as process water without the need of further treatment, while a further polishing of the effluent, by physical, chemical or aerobic treatment, from conventional anaerobic digestion is usually needed (Barton et al., 1998; Welander et al., 1999; Dufresne et al., 2001).

### 3.1.2 Methane Production Rate and Biogas Composition

Methane production rate in the mesophilic SAnMBR under various OLRs and HRTs is shown in Figure 3.4. In the 210 days of operation, methane production rate ranged from 0.20 to 0.40 L $CH_4$ / g COD removed. The average methane production rate in the mesophilic submerged AnMBR, except from day 25 to day 40 and from day 67 to day 76, was 0.35 ± 0.08 L $CH_4$ / g COD; around 88 % of the theoretical yield (0.397 L $CH_4$ / g COD removed at 37°C). The occasionally higher methane production rate (0.4 - 0.58 L $CH_4$ / g COD removed) could be due to the contribution of sludge digestion. The average value is consistent with the finding (0.35 L $CH_4$ /g COD removal) of Dufresne et al. (2001). The low value of the methane production rate from day 25 to day 40 was due to system leaking. The decrease in biogas production rate from day 67 to 70 was caused by excessive sodium hydroxide in the reactor, due to the pH probe failure. The mesophilic SAnMBR recovered within 4 days from pH disruption; followed by the toxic influent shock from day 70 to day 76, where again the mesophilic SAnMBR system recovered

within 6 days, indicating a strong ability as handling unexpected system upset and shocks. The average methane yields are 0.31 ± 0.05, 0.33 ± 0.06 and 0.37 ± 0.09 L $CH_4$ / g COD removed for stages 1, 2 and 3, respectively. Although these values were moderate among the reported values in the literature, there was a gap of approximately 12 % in the mass balance. Based on a redox balance, the actual methane yield should reach 100 % of the theoretical value if the system is at steady state (Rittmann and McCarty, 2001). The effect of methane solubility in water on methane yield should also be taken into account. According to the Chemical Engineers' Handbook (Perry and Green 1984), methane solubility in water is 15 mL / 1,000 mL at 1 atm and 35°C. This would increase the actual methane yield (up to 30 % at very low HRTs), but a decline in methane yield with decreasing HRT (Hu and Stuckey, 2006 and 2007) was not observed in this study. This shows that the actual methane yield is close to the theoretical value of methane yield at 37°C, indicating Kraft evaporator condensate provides great food sources for anaerobic methanogens to further convert to methane.

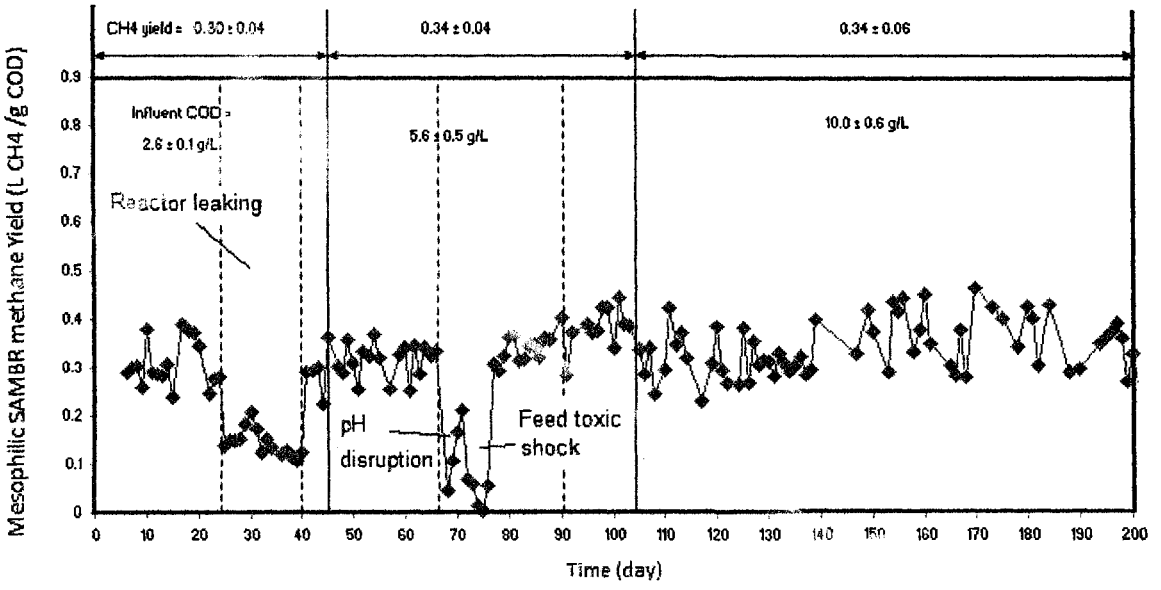



Fig. 3.4 Mesophilic SAnMBR methane yield

Figure 3.5 shows the biogas composition ($N_2$, $CH_4$, and $CO_2$) in the headspace of the mesophilic submerged AnMBR. The figure shows three distinct curves, namely methane, carbon dioxide, and nitrogen. When biogas started to be produced from day 1 to day 45

(feed COD = 2.6 ± 0.1 g/L), the average percentage of methane in the gas was approximately 84%, with the remaining biogas being composed of roughly 13% nitrogen and 3% carbon dioxide. As the feed COD increased to 5.6 ± 0.5 g/L from day 46 to day 103, the average percentage of methane in the biogas was approximately 87%, with an average of 7% nitrogen and 6% carbon dioxide. In the last stage from day 104 to day 210 (feed COD = 10.0 ± 0.7 g/L), the average percentage of methane was 85%, with 3% nitrogen and 12% carbon dioxide. It can be seen in Figure 3.5 that during the course of this experiment, the percentage of methane in the biogas remained constant around 85%, whereas the percentage of nitrogen decreased from 13% to 3% as carbon dioxide increased from 3% to 12%. The changes in nitrogen and carbon dioxide composition might have been caused by changes in the COD: N: P ratio. A COD: N: P ratio of 100: 9.6: 2.4 (as suggested by Schmidt and Ahring, 1995) was used in the first 45 days to facilitate granulation in the mesophilic SAnMBR. From day 46 until the end of this experiment, a COD: N: P ratio of 100: 2.6: 0.4 was carried out which was the minimum amount of macronutrients required for anaerobic bacteria to grow. This indicates that the N: P ratio does not have a direct impact on methane production, but it does affect nitrogen and carbon dioxide composition distribution in the biogas. In normal anaerobic systems, denitrification does not occur unless $NO_3^-$ or $NO_2^-$ are present in significant quantities. Low concentrations of $CO_2$ were observed because $CO_2$ quickly reached equilibrium in the bulk solution in the reactors forming bicarbonate, and were then removed in the effluent. This result is consistent with the findings of Dufresne et al. (2001).

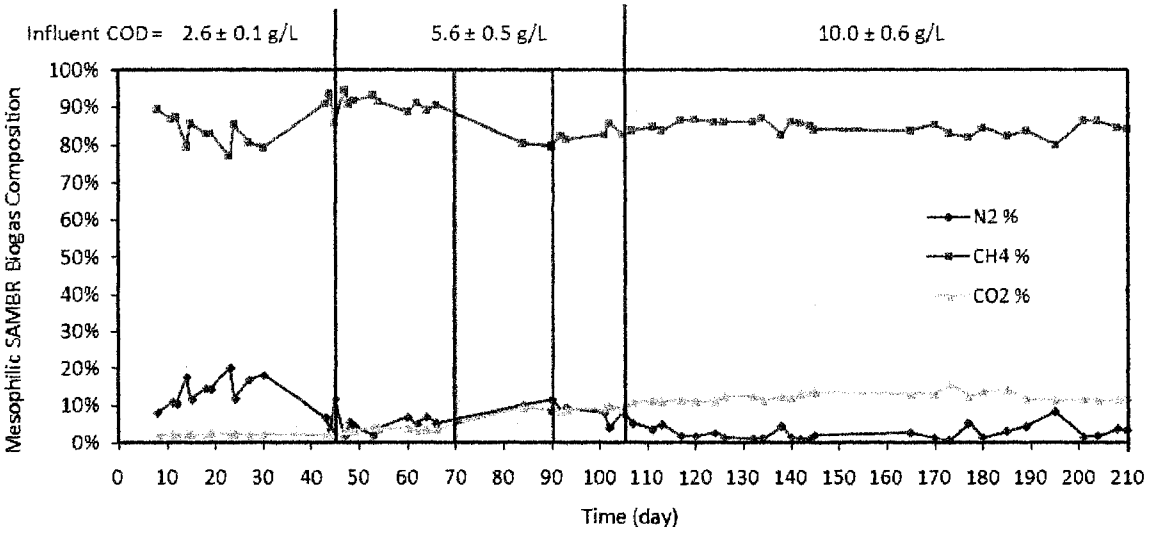



Fig. 3.5 Biogas composition and concentration with experimental time for mesophilic SAnMBR

### 3.1.3 Biomass

Figure 3.6 shows the mixed liquor suspended solids (MLSS) concentrations with experimental time. The initial inoculum mass of anaerobic sludge in the mesophilic SAnMBR was 80 ± 5 g TSS, which corresponded to a MLSS of about 18 g/L in the bottom zone and a MLSS of 2-3 g/L in the top zone. It is interesting to note that the top zone sludge concentration increased from the initial 2 g/L to approximately 4-5 g/L in stage 2 and then 6-10 g/L in stage 3. This was mainly caused by the magnetic mixing in the bottom zone and biogas sparging in the top zone, which resulted in the transfer of the bottom zone sludge to the top zone. A stoppage of the magnetic stirrer in the bottom zone, due to a mechanical error, resulted in a poor performance of the pH probe (poor mixing). When biogas sparing was off, the MLSS in the top zone did decrease as can be seen in Figure 3.6. Ideally, for an upflow anaerobic sludge blanket (UASB) reactor with good performance, the top zone should have a very low biomass concentration. The relative high biomass concentration in the top zone of this study is similar to the situation of sludge deflocculation. Therefore, the results of membrane performance (flux and membrane fouling) as discussed in the following sections stimulated the worst scenario - sludge deflocculation in a UASB with submerged membrane module. In full-scale design, a larger membrane filtration zone can be designed to minimize the impact of biogas sparging on the bottom sludge zone. After startup from day 1 to day 45, total biomass in

the mesophilic SAnMBR decreased rapidly to a level of about 50-60 g. There are three possible explanations: a) biomass loss during sampling and membrane cleaning process, because of the membrane cake layer formation and sludge sampling, and b) the pore size difference between the membrane used in the SAnMBR and the filter paper used for MLSS test (due to the fact that the membrane used this experiment had a pore size of 0.3 μm, whereas the filter paper used to conduct MLSS test has a pore size of 0.45 μm, in the case where particles that are smaller than 0.45 μm but bigger than 0.3 μm will not be able to be tested but still will be trapped in the reactor), and c) the loss of biomass as a result of biomass decay. Leenen et al. (1997) reported that if decay of biomass occurs, the biomass concentration decreases. Explanation (b) however seems unlikely as the main cause as no particles that had sizes smaller than 1 μm were found throughout the entire run of the mesophilic SAnMBR (see Figure 3.7). Despite the decrease in the initial concentration of sludge at first stage, no significant accumulation of effluent COD was found in the reactor during that time (see Figure 3.3). When the MLSS concentrations decreased over time to a steady state (stage 2) from day 46 to day 103, mesophilic SAnMBR total mass of biomass had an average of 52 g, indicating that OLR of around 4.0 ± 1.7 kg COD/$m^3$/day is the limiting OLR for maintaining steady total mass of biomass in the mesophilic SAnMBR. The biomass growth was facilitated when the OLR was increased to 12 ± 2 kg COD/$m^3$/day (stage 3), and it is clear from Figure 8 that total biomass increased over this period of time.

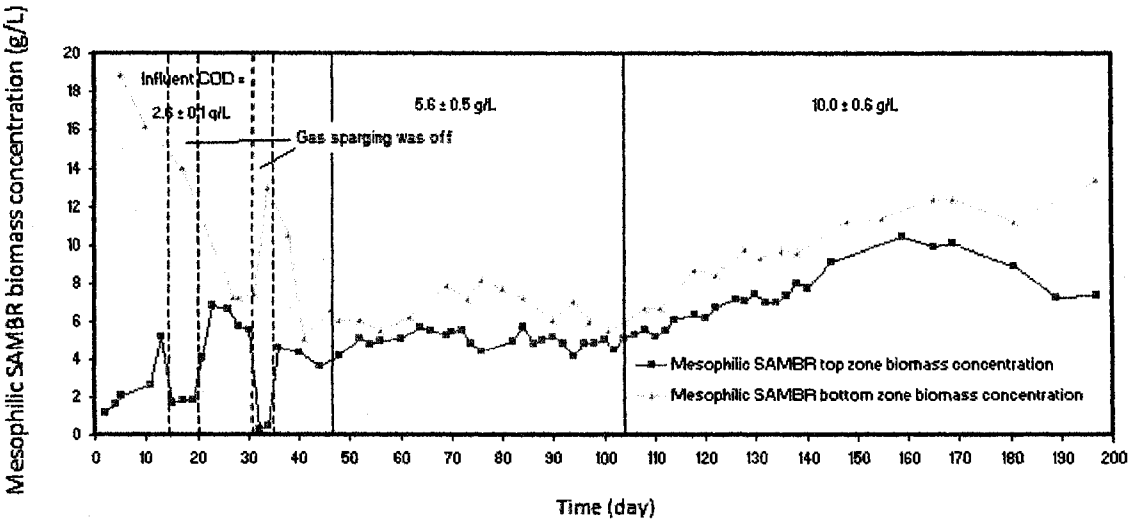



Fig. 3.6 Mesophilic SAnMBR total mass of biomass, top zone and bottom zone biomass concentrations vs. time

### 3.1.4 Particle Size Distribution

Figure 3.7 shows the particle size distribution of mixed liquor in the top zone, where the mixed liquor was in direct contact with membrane model, taken on day 63, day 70 and day 77. The results show three distinct patterns of particle size distribution. Feed toxic shocking and pH disruption resulted in a shift of particle size distribution to the left (more smaller particles), indicating sludge deflocculation. But the sludge recovered to normal size distribution after 3-5 days. This indicates that the mesophilic SAnMBR can handle a certain level of feed toxic shocking and pH disruption. Throughout the entire experiment, fine particles below 1 μm were not significant in the mixed liquor. Chang and Lee (1998) found that particles below membrane pore size have a tendency to block the membrane pore, causing irreversible fouling. Since no fine particles were found during the run, which provide an opportunity in industrial application for an in-situ mechanical membrane cleaning methods to extend the life time of a membrane in operation and a subsequent lower operational cost.

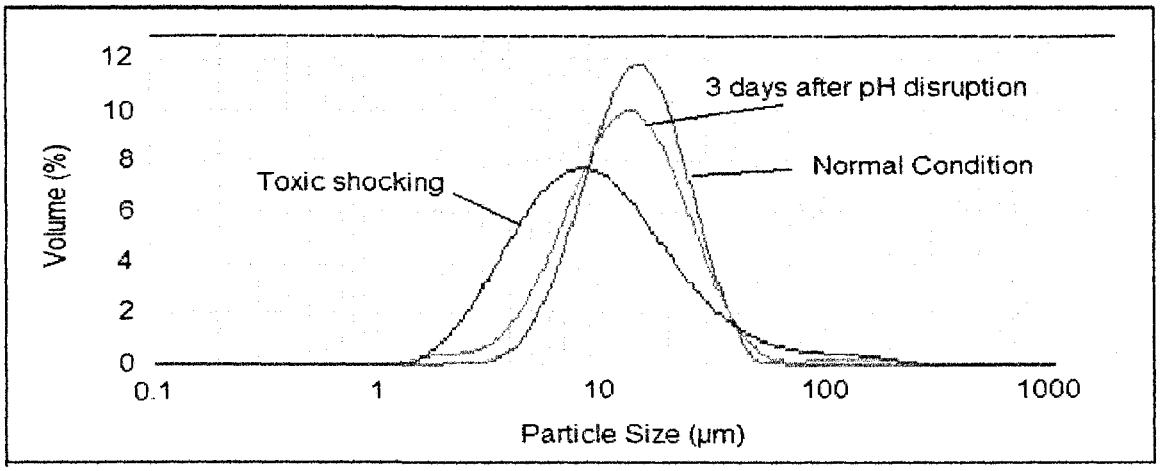



Fig. 3.7 Particle size distribution of the top zone mixed liquor in mesophilic SAnMBR

Figure 3.8 shows the particle size distribution of mixed liquor from the bottom and top zones. The results show that there is no significant difference in particle size distribution of mixed liquor between the bottom and top zones, implying no significant floc breakage was found at a biogas sparging rate of 0.75 LPM. This is consistent with the finding of Hu and Stuckey (2006) in that shear stress from biogas sparging is more gentle than that of mixed liquor recirculation pump used the external cross-flow AnMBR and results in

much less floc breakage. This is one of the advantages of using SAnMBR for wastewater treatment, as compared to the external cross-flow AnMBR.

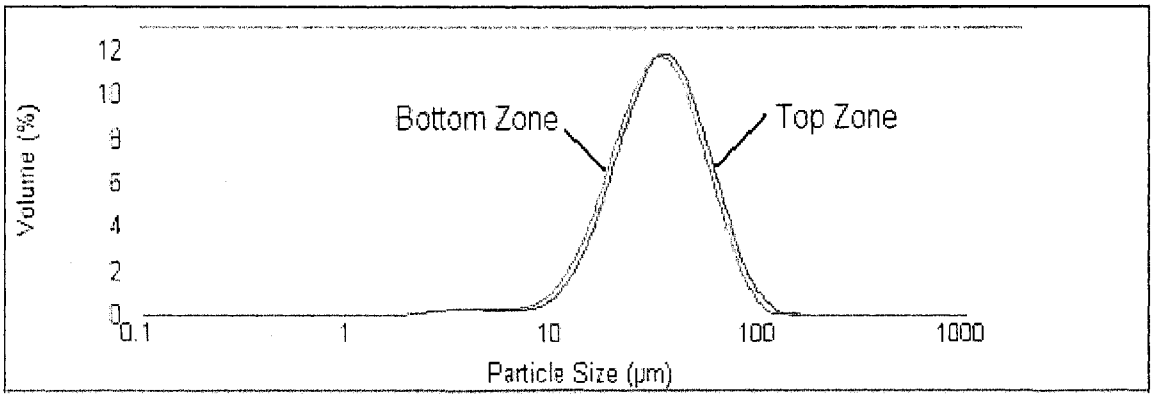



Fig. 3.8 Particle size distribution of the sludge bed in mesophilic SAnMBR

### 3.1.5 Transmembrane Pressure and Flux

Figure 3.9 shows the transmembrane total resistance vs. time in the mesophilic SAnMBR. The impact of biogas sparging on membrane fouling was studied from day 15 to day 20 and from day 30 to day 34 by shutting off the biogas sparging. A noticeable increase in the membrane resistance was observed for these periods of time, indicating the positive impact of biogas sparging in membrane fouling control. The membrane fouling rate can be calculated from the total resistance divided by time, which are the slopes of the lines in Figure 3.9. It is clear that the membrane resistance or membrane fouling rate was smaller in normal operation (before day 60), as compared to when pH disruption and feed toxic shocking were experienced (days 65-80). This could be the result of changes in particle size distribution. As shown in Figure 3.7, before the toxic influent shock supernatant mixed liquor had a mean particle size of 15 -17 μm; during the toxic influent shock, the supernatant mixed liquor had one peak with a mean particle size of 6 – 6.5 μm. Even though these particles are much bigger than the membrane pore size of 0.3 μm, the hypothesis is that as the anaerobic sludge formed a thin sludge cake layer attached to the surface of the membrane, the supernatant mixed liquor particle had to pass through the sludge cake layer first before they reached to the membrane. The sludge cake layer may have had a looser pore size than membrane, such that those particles will block the channel in the sludge cake layer even though they are not blocked in the membrane.

This sludge cake layer happens immediately after the membrane model is in operation. The longer the membrane service time, the thicker the sludge cake layer will grow and the harder for particles that are smaller than 20 μm to pass through, resulting in an increased transmembrane total resistance peak value during each membrane service time, as mechanical cleaning can not thoroughly clean the sludge cake formation on the membrane. This may also be the reason why frequent mechanical cleaning still can not help to decrease the total transmembrane resistance (day 70 to day 80). As the anaerobic system recovered from the previous shock, the particles grew large enough so that they will not be easily trapped on sludge cake layer. The membrane service time had been largely increased, but no increasing trend was observed in the peak value of transmembrane total resistance.

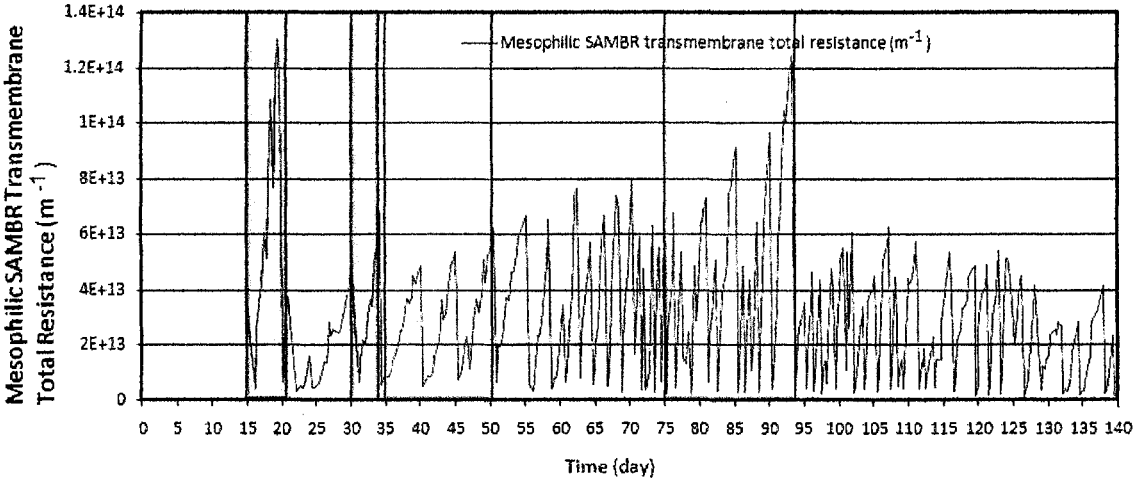



Fig. 3.9 Mesophilic SAnMBR transmembrane total resistance vs. time

Figure 3.10 shows the correlation between the diameter of less than or equal to 10 % volume of the measured biomass particles, D(0.1), and membrane fouling rate. A smaller D(0.1) is related to a higher membrane fouling rate. This indicates that the portion of fine (smaller) particles plays an important role in membrane fouling. The fine (smaller) particles have a higher tendency to deposit on membrane surfaces to form a sludge cake layer and block membrane pores. This is consistent with the findings of previous studies (Meng et al., 2007).

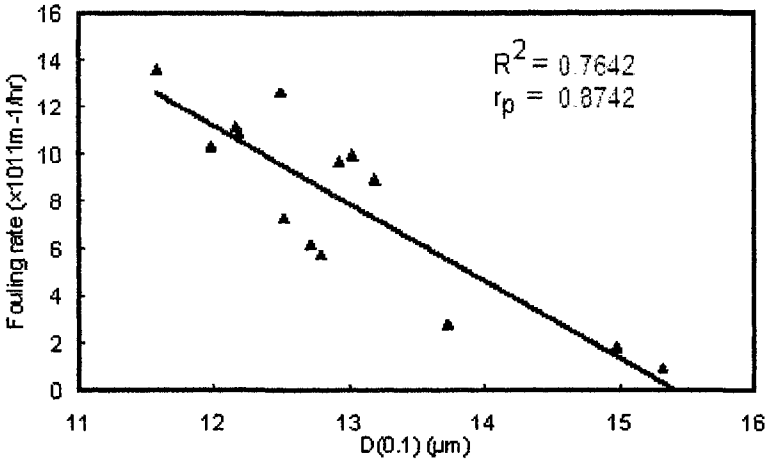



Fig. 3.10 Correlation between membrane fouling rate and particle size D(0.1) of supernatant

Figure 3.11 shows the change in membrane flux with experimental time. An average membrane flux value of 5.6 ± 1.0 L/m$^2$/hr was maintained at a biogas sparging rate of 0.4 LPM (before day 128). When the biogas sparging rate was increased to 0.75 LPM, a higher membrane flux of 7.1 ± 0.8 L/m$^2$/hr was achieved. This indicates the impact of biogas sparging rate on membrane fouling. It is anticipated that a further increase in the biogas sparing rate will lead to a further increase in membrane flux. The results from this study suggest that in-situ membrane cleaning by biogas sparging is effective, depending on the biogas sparging rate.

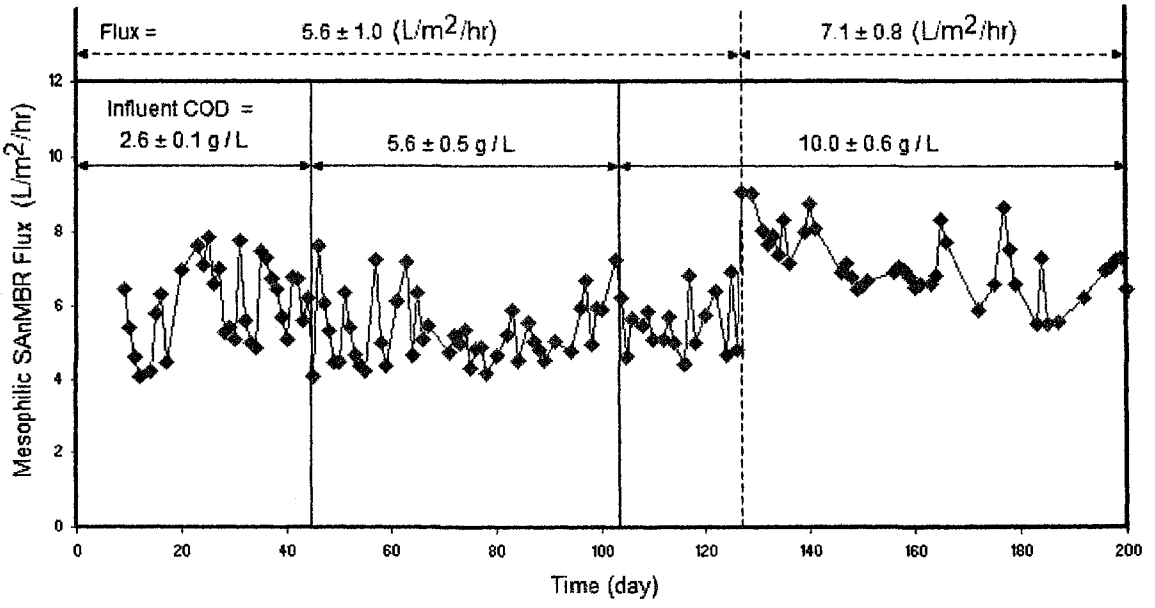



Fig. 3.11 Profile of the mesophilic SAnMBR flux changes

## 3.2 Feasibility of Kraft Evaporator Condensate Treatment Using a Submerged Thermophilic Anaerobic Membrane Bioreactor

### 3.2.1 Soluble COD Removal under Various Influent COD Loadings

Figure 3.12 shows the change in HRT with experimental time. In the first run (day 10-95), the HRT was maintained in the range of 20-35 hrs. The first run was terminated, due to feed toxic shocking. In the second run (day 96-210), the HRT was significant higher than the first run. Even the use of a higher biogas sparging rate could not bring the HRT down too much. The main cause of the difference in HRT was due to the presence of a large portion of fine colloidal particles in the second run as discussed in the later sections. Figure 3.13 shows the change in organic loading rate (OLR) and removal rate with experimental time. A higher HRT corresponds to a lower OLR. The tested OLR range was from 1 to 7 kg COD/$m^3$/day. The lower organic removal rate from day 85 to 95 was caused by feed toxic shocking from the feed and finally the anaerobic stopped function (no biogas production).

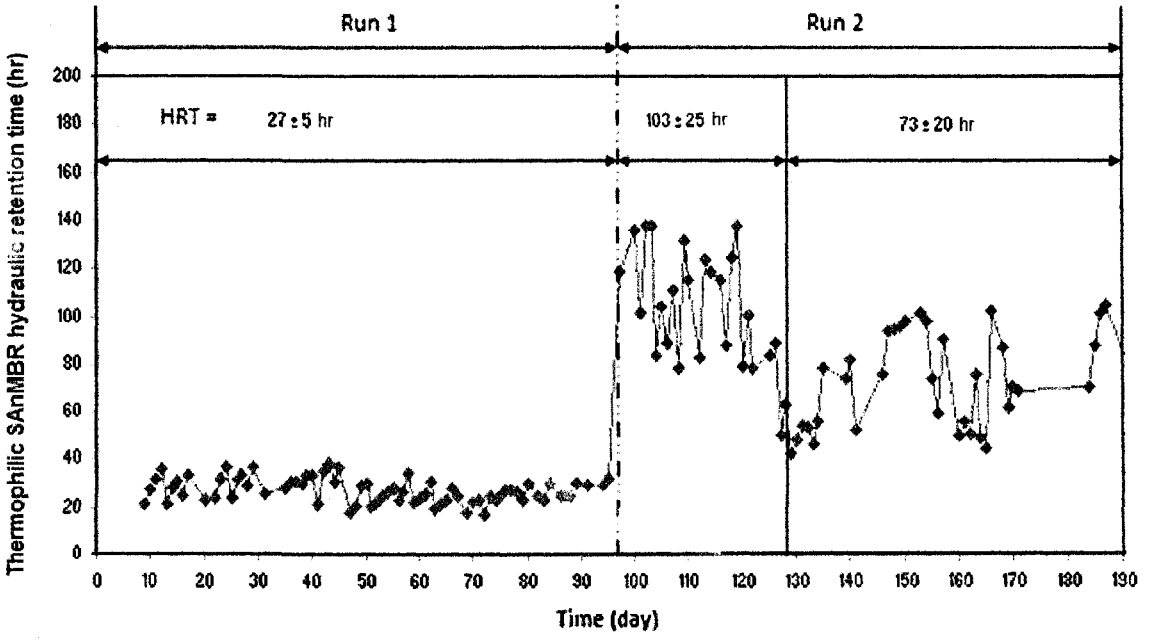



Fig. 3.12 Changes in hydraulic retention time with experimental time for thermophilic SAnMBR

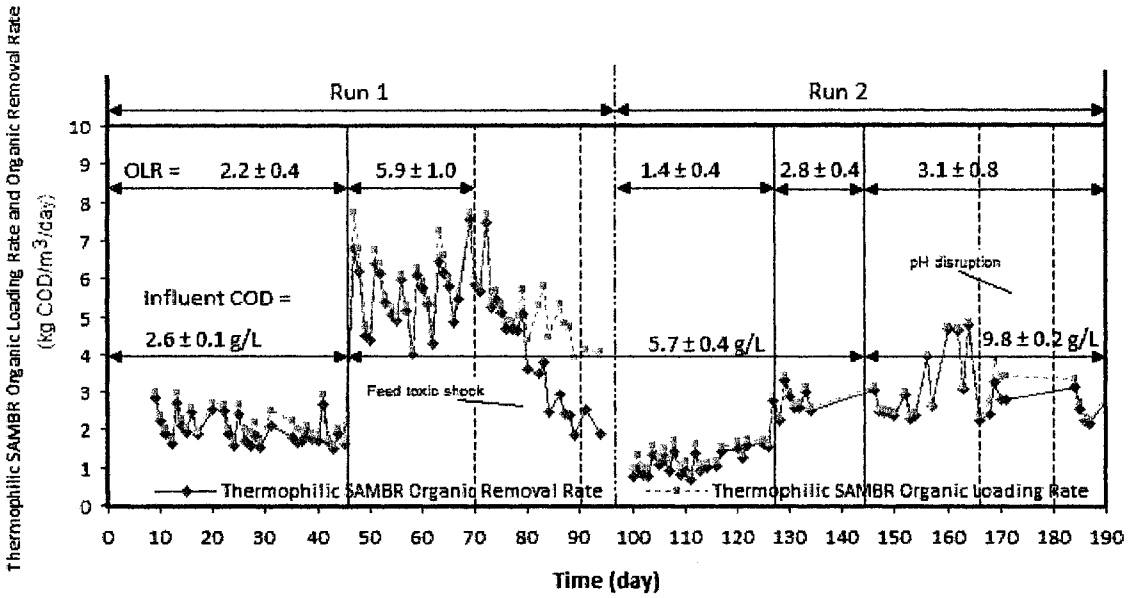



Fig. 3.13 Thermophilic SAnMBR organic loading rate and organic removal rate

Figure 3.14 shows the thermophilic SAnMBR soluble COD concentrations in the feed, reactor, and permeate over time. It is clear that the COD removal efficiency deteriorated slightly from 95% to 85% during the transition from mesophilic (37°C) to thermophilic temperature (55°C) (day 15-29). But after this time, the COD removal efficiency recovered back to 95% within one week. This removal efficiency was maintained until day 75, when a feed toxic shocking occurred. The feed toxic shocking resulted in a significant loss of biological activity, with no biogas production and significant low COD removal efficiency. The thermophilic SAnMBR was not able to recover within 3 weeks and thus this run was terminated at day 95. Therefore, the thermophilic SAnMBR was re-inoculated with 3.5 L seed sludge on day 96. Also, the temperature of the thermophilic SAnMBR went from 37°C to 55°C within the eight-day duration after re-inoculation. It took 16 days (after the thermophilic SAMBR attained a temperature of 55 ± 2°C) for the system to reach a steady-state, which occurred on day 122. The overall average effluent soluble COD concentration was 187 mg/L and a 96.8% COD removal was attained at this COD load. However, the OLR was much lower than that used in the first run, due to the limited membrane flux caused by membrane fouling. The OLR ranged from 1 to 4 kg COD/$m^3$/day in the second run.

It is interesting to note that there are significant differences between the supernatant COD in the bioreactor and the permeate COD. This is consistent with the findings of previous studies (Hu and Stuckey, 2006) indicating the sieving effect of the membrane and sludge cake on membrane surfaces. The significantly higher supernatant COD and the lower COD removal efficiency from day 100 to day 130 was probably caused by sludge digestion at a lower OLR (1 $kg/m^3/day$), as indicated by the decrease in mixed liquor concentration (as shown in Figure 3.17 in a later section). An increase in the supernatant COD was also observed during the period of pH disruption (day 165-178). This is consistent with the findings of Aquino and Stuckey (2004) in that more SMPs could be produced during unstable conditions. Previous researchers (Hu and Stuckey, 2006), however, found that the COD concentrations inside a mesophilic SAnMBR treating municipal wastewater were more than three times higher than the effluent COD, attributed to the sieving effect (size exclusion) of the membrane to soluble microbial products (SMPs) (Huang et al., 2000; Shin and Kang, 2003). Similar results have also been observed for the thermophilic SAnMBR in treating Kraft evaporator condensate. After the thermophilic SAnMBR was re-inoculated with seed sludge, a three to six times higher COD concentration inside the SAnMBR was observed as compared to the permeate COD. This difference (3-6 times) is much larger than that (2 times) found in the mesophilic SAnMBR treating Kraft evaporator condensate. The large difference was probably caused by the lower OLR in the thermophilic SAnMBR, which could result in more sludge digestion and the thermal extraction of extracellular polymers (EPS) from the surface of thermophilic sludge.

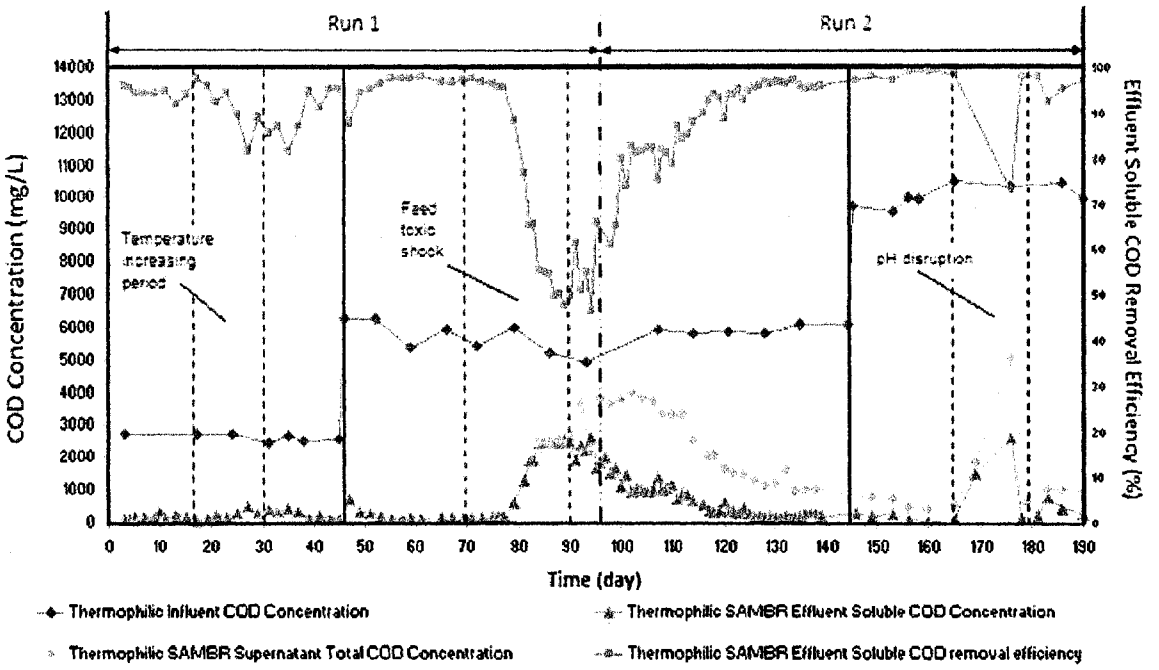



Fig. 3.14 Thermophilic SAnMBR soluble COD concentrations in the feed, effluent, reactor supernatant total COD concentrations, and effluent soluble COD removal efficiency vs. time

### 3.2.2 Biogas Composition and Production

Figure 3.15 shows the gas composition ($N_2$, $CH_4$, and $CO_2$) in the headspace of the thermophilic SAnMBR. The results show three distinct curves, namely, methane, carbon dioxide, and nitrogen. When biogas started to be produced from day 1 to day 45 (OLR = 2-3 kg COD/$m^3$/day), the average percentage of methane in the gas was approximately 90%, with the remaining gas being composed of roughly 7% nitrogen and 3% carbon dioxide. As the OLR was increased to 6 ± 1 kg/$m^3$/day from day 46 to day 75, the average percentage of methane in the biogas was about 87%, with an average of 7% nitrogen and 6% carbon dioxide. After the starting of the second run from day 104 to day 130 (OLR = 1 kg COD/$m^3$/day), the average percentage of methane was 85%, nitrogen 6%, and carbon dioxide 9%. It is shown clearly in Figure 3.15 that during the course of this experiment, the percentage of methane in the biogas slightly decreased from 90% to 85%, the percentage of nitrogen remained at same level about 6% to 7%, and carbon dioxide increased from 3% to 9% in the biogas. The changes in nitrogen and carbon dioxide compositions may have been caused by changes in COD: N: P ratio in the feed. A COD: N: P ratio of 100: 9.6: 2.4 was used in the first 65 days to facilitate granulation

in thermophilic SAMBR (Schmidt and Ahring, 1995). From day 66 until the end of this experiment, a COD: N: P ratio of 100: 2.6: 0.4 was carried out, which was the minimum amount of macronutrients required for anaerobic bacteria to grow (Vogelaar et al., 2002). In normal anaerobic systems, denitrification does not occur unless $NO_3^-$ or $NO_2^-$ are present in significant quantities. Since the $NO_3^-$-N and/or $NO_2^-$-N source was not present in the system in significant quantities, the percentage of nitrogen did not greatly vary as the N: P ratio changed.

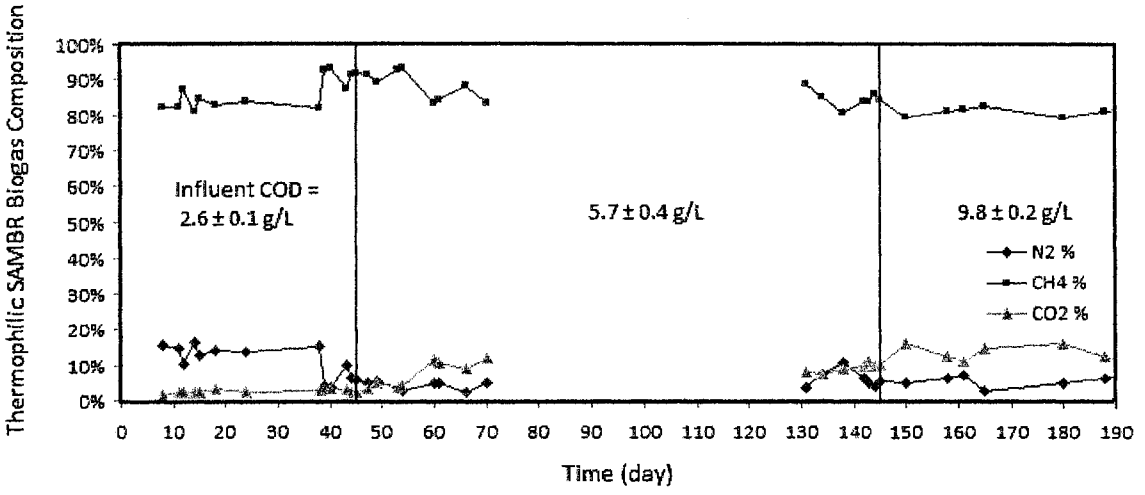



Fig. 3.15 Biogas composition and concentration with experimental time for thermophilic SAnMBR

Methane yield in the thermophilic SAnMBR under various OLRs is shown in Figure 3.16. The average methane production rate in the thermophilic SAnMBR during an OLR of 2-3 kg COD/$m^3$/day, from day 38 to day 45, was 0.3 L $CH_4$ / g COD, around 71% of the theoretical yield (0.421 L $CH_4$ / g COD removed at 55°C). When the OLR was increased to 6 ± 1 kg COD/$m^3$/day from day 46 to 75, the same methane yield (0.3 L $CH_4$ / g COD) was obtained. The decrease in methane yield from day 70 to 90 was caused by toxic influent, and the thermophilic SAnMBR system was not able to recover from it, even when the toxic influent was replaced by a non-toxic one after day 90. This demonstrates the poor ability of the thermophilic SAnMBR to handle unexpected system upsets and shocks. At the beginning of the second run, a relatively higher methane yield (0.4-0.5 L $CH_4$ / g COD removed) was observed (day 100-128). This was caused by the additional contribution of significant sludge digestion under the lower OLR (1.5 ± 0.5 kg

COD/$m^3$/day). When the OLR was increased to 4 ± 1 kg COD/$m^3$/day after day 130, the methane yield was reduced to 0.35 ± 0.1 L $CH_4$ / g COD removed. This is more consistent with the results obtained in the first run. Although the results from previous studies suggest a higher methane yield under the thermophilic conditions, the results from this study suggest that methane yield is comparable between thermophilic and mesophilic treatment. The higher methane yield could be caused by a larger contribution of the higher sludge digestion rate under thermophilic temperatures.

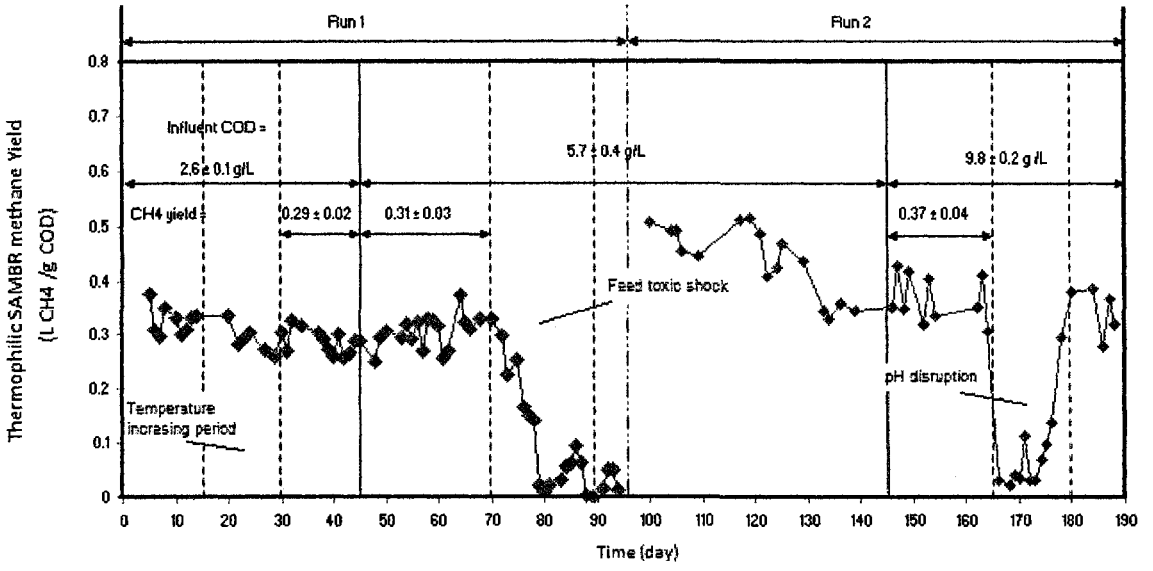



Fig. 3.16 Thermophilic SAnMBR methane yield

### 3.2.3 Biomass

In Figure 3.17, the initial inoculum of sludge in the thermophilic SAnMBR was 80 ± 5 g TSS in the first run. After start-up from day 1 to day 45 (first run) and from day 96 to day 140 (second run), biomass concentrations in the thermophilic SAnMBR decreased rapidly. There are three possible explanations. First, biomass may have been reduced due to sludge sampling and membrane cake formation and characterization. Second, there was a pore size difference between the membrane used in the SAMBR and the filter paper used for TSS test. Due to the fact that the membrane used this experiment had a pore size of 0.3 μm, whereas the filter paper used to conduct TSS test had a pore size of 0.45 μm, particles that were smaller than 0.45 μm but bigger than 0.3 μm would not be

able to be tested but would still be trapped in the reactor. Third, the loss of biomass could be a result of biomass decay. A higher temperature results in a higher biomass decay rate. Leenen et al. (1997) reported that if decay of biomass occurs, the biomass concentration decreases. This explanation was true for the first 45 days of operation, but was not responsible for the biomass lost after day 96. The second explanation seems to be a reasonable hypothesis after the seed sludge was re-inoculated in the thermophilic SAnMBR from day 96 to day 140, because a great deal of particles that were smaller than 1 μm were found in the reactor; whereas in the first 96 days of operation, no particles had sizes smaller than 1 μm were found (see Figures 3.18 and 3.19). Despite the decrease in the initial concentration of inactive substances in first 45 days, no significant accumulation of effluent COD was found in the reactor during that time (see Figure 3.14). When the TSS concentrations decreased over time to a steady state (stage two) from day 46 to day 96, the thermophilic SAnMBR total mass of biomass had an average of 47 g.

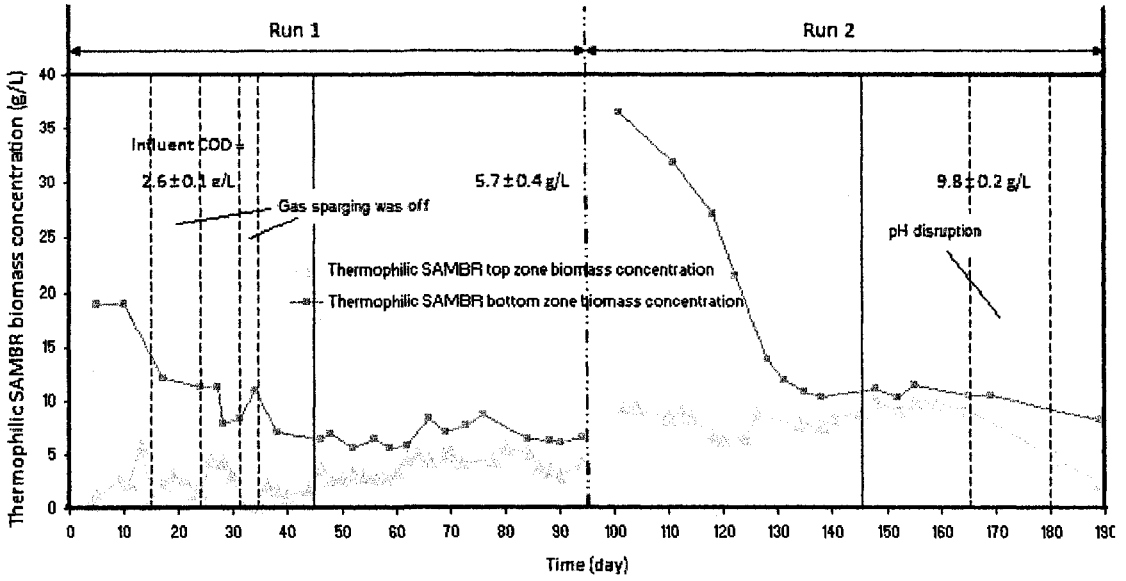



Fig. 3.17 Thermophilic SAnMBR total mass of biomass, top zone and bottom zone biomass concentrations vs. time

### 3.2.4 Particle Size Distribution

Figure 3.18 shows the particle size distribution of the top zone mixed liquor, which was in direct contact with membrane model, taken on day 63 (first run) and 138 (second run). The results show one single peak of the particle size distribution of top zone mixed liquor, ranging from 2 to 50 μm with a mean size of 9.5-10 μm in the first run. During the

first 96 days operation of the first run, no fine particles below 1 μm were found. Chang and Lee (1998) found that particles below the membrane pore size have a tendency to block the membrane pore, causing irreversible fouling. Since no fine particles were found during the run, irreversible fouling would not occur. This provides an opportunity in industry for in-situ mechanical membrane cleaning methods, which extend the lifetime of a membrane in operation and represents lower operational costs. The image taken on day 138 (shown in Figure 3.18) shows the particle size distribution of the thermophilic SAnMBR mixed liquor after the thermophilic SAMBR was re-inoculated with seed sludge after day 96. It shows two distinct peaks, one in the range of 0.1 to 1 μm with a mean size of 0.25 – 0.27 μm, and the other in the range of 1 to 40 μm with a mean size of 7 – 8 μm. The fine particles were already present in the seed sludge. The fine particles in the thermophilic SAnMBR contribute to the high transmembrane resistance that occurred after day 96. Similar results were obtained by Kwon et al. (2000) who suggested that particle sizes close to the membrane pore size region increase the transmembrane pressure (TMP). For membranes that have a pore size of 0.3 μm, particles below this size have a tendency to block the membrane pores (Chang and Lee 1998). Once the pores of the membrane are blocked, the sparging gas will not be able to remove the particles, resulting in irreversible fouling.

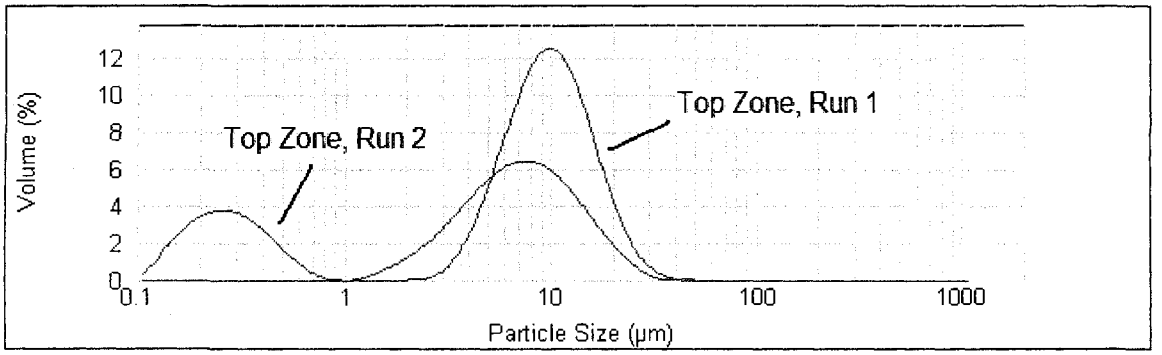
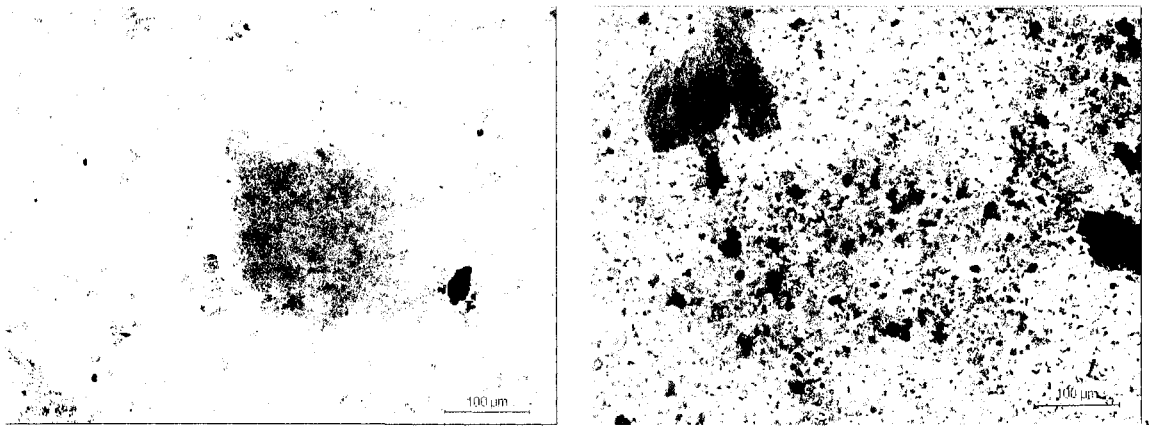



Fig. 3.18 Particle size distribution of the supernatant mixed liquor in thermophilic SAnMBR




(a) (b)

Fig. 3.19 Images of thermophilic anaerobic sludge flocs on (a) day 65 (1st run) and (b) day 140 (2nd run)

### 3.2.5 Transmembrane Pressure and Flux

Figure 3.20 shows the transmembrane total resistance (TMR) vs. time in the thermophilic SAnMBR. From day 15 to day 20 and from day 30 to day 34, the biogas sparger was shut off in the reactor, so that the gas sparging effect on membrane surface could be analyzed. It is shown in Figure 3.20 that during the period when gas sparging was shut off, the transmembrane total resistance was significantly higher when compared with the period when gas sparging was in operation (e.g. from day 21 to day 29) at a sparging rate of 0.25 LPM. This indicated that gas sparging had a positive effect on decreasing the membrane fouling rate. Figure 3.20 shows an increase in the peak value of transmembrane total resistance in the membrane operation from day 75 to day 94, but was not the case for the last membrane, as the TMR values were consistently higher than any of the other three regions. This may occur as a result of changes in particle size distribution. As shown in Figure 3.18, before the toxic influent shock, supernatant mixed liquor had a mean particle size of 9.5 -10 µm; however during the toxic influent shock, the supernatant mixed liquor had one peak with a mean particle size of 6 – 6.5 µm. Even though these particles are much bigger than the membrane pore size of 0.3 µm, the hypothesis is that as the anaerobic sludge formed a thin layer of biofilm attached to the surface of the membranes, the supernatant mixed liquor particle had to pass through the biofilm first before they reached the membrane. The biofilm may have a much looser pore size than membrane (up to 20 µm), such that those particles would block the channel on the biofilm, even though they do not block the membrane pores. This biofilm

formation happens immediately after the membrane model is in operation. The longer the membrane service time, the thicker the biofilm will grow and the harder for particles that are smaller than 20 μm to pass through, resulting in an increased transmembrane total resistance peak value during each membrane service time. The biofilm formation also occurred despite the mechanical cleaning, which did not wash off the biofilm on the membrane surface. Also, from day 38 to day 96, the high operational temperature (55°C) should also be taken into account in increasing membrane flux and lower TMR. Water viscosity was taken into consideration when calculating the transmembrane resistance and it is known that the viscosity of water decreases as temperature increases. After seed sludge was re-inoculated on day 96 until day 140, the thermophilic SAnMBR experienced a period of high transmembrane total resistance, due to the irreversible membrane fouling caused by fine particle (smaller than 1 μm) found in the reactor mixed liquor.

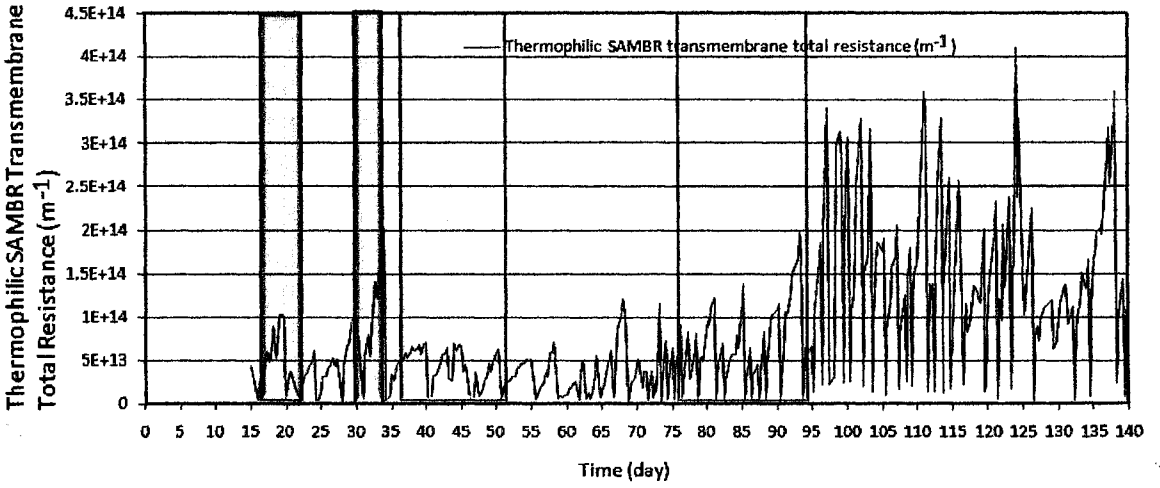



Fig. 3.20 Thermophilic SAnMBR transmembrane total resistance

Figure 3.21 shows changes in membrane flux with experimental time. Clearly, the membrane flux in the first run (day 1 - 95) was significantly higher than that in the second run (day 96 - 210). This is caused by the difference in particle size distribution in these two runs, as shown in Figures 3.18 and 3.19. The presence of a large portion of fine particles (1 – 10 μm) caused serious membrane fouling in the second run, making it

difficult to maintain the same flux as used in the first run. To improve the membrane flux, the portion of fine particles (1 – 10 μm) has to be minimized. One way is to settle the large particles and dump the supernatant with the fine particles. Practically, the thermophilic anaerobic bioreactor can be operated as a conventional anaerobic bioreactor at the beginning for a couple of weeks. The fine particles will stay in the supernatant and thus be wasted. Membrane modules can then be added to the bioreactor after a major portion of fine particles is wasted. This strategy was approved in the first run, in which the bioreactor was operated for 43 days as batch reactor before the membrane module was added. In future studies, the strategies for minimizing the portion of fine particles have to be investigated.

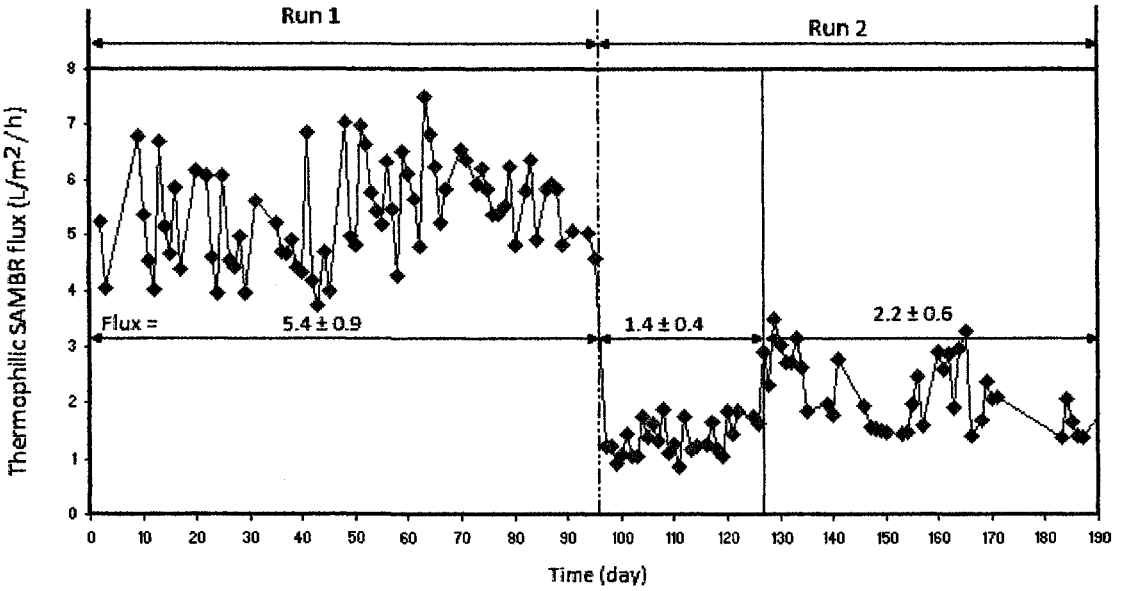



Fig. 3.21 Profile of the thermophilic SAnMBR flux changes

## 3.3 Sludge Properties and their Effects on Membrane Fouling in Submerged Anaerobic Membrane Bioreactors (SAnMBR)

### 3.3.1 Comparison of Filtration Characteristics

The increasing rate of transmembrane pressure (TMP) is an important factor to evaluate the system performance in submerged MBR because it is directly related to the rate of membrane fouling. Continuous experiments were operated initially at a fixed flux of

of approximately 7.4 L/m$^2$/hr without any cleaning or additional fouling control measures with the exception of the imposed gas sparging and intermittent filtration operation. Evolutions of TMP and flux were monitored, as shown in Figure 3.22. It can be seen from Figure 3.22 that the two SAnMBRs showed different filtration characteristics. For the thermophilic SAnMBR, an abrupt flux decline and TMP increase occurred simultaneously at the initial stage, with the duration of this stage being approximately 1.25 hr. Following this stage was the second stage, characterized by a slow TMP increase with a stable flux of 1.8 L/m$^2$/hr, which lasted approximately 240 hr. In this stage, the filtration resistance was as high as $5.3\times10^{13}$ m$^{-1}$. Thereafter, an abrupt TMP jump of over 27 kPa was observed in a short period of time. This stage lasted about 38 hr. For the mesophilic SAnMBR, a three distinct-stage TMP profile can also be observed. The three stages lasted approximately 90 hr, 370 hr, and 60 hr, respectively, and the stable flux was about 7.4 L/m$^2$/hr. A difference in the filtration resistance was found, as the second stage resistance was $0.51\times10^{13}$ m$^{-1}$, which was only about one tenth of that observed in the thermophilic SAnMBR.

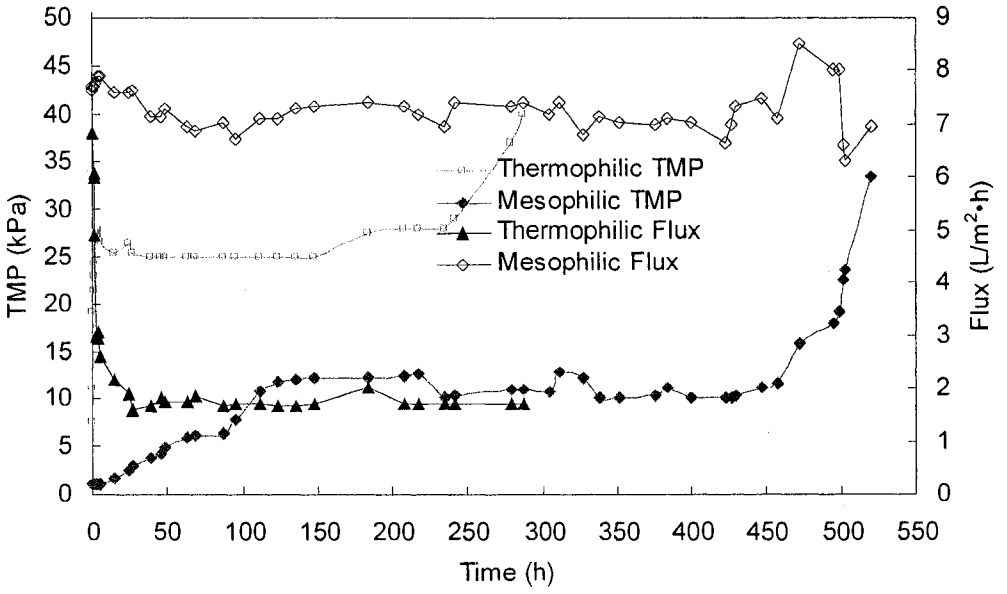



Fig. 3.22 Variations of the TMP and flux for both thermophilic and mesophilic SAnMBRs

The filtration operations were terminated when the TMP for the thermophilic SAnMBR reached 40 kPa and when the mesophilic SAnMBR TMP reached 35 kPa. The membrane modules were taken out from the reactors at this point. The cake sludge was

carefully scraped off from the membrane surface using a spatula, after then, a procedure as described in section 2.3.2 was conducted to measure filtration resistances for the both systems. The results are summarized in Table 3.1.

Table 3.1 Resistances for the Thermophilic and Mesophilic SAnMBRs

| | $R_m$ ($\times 10^{13} m^{-1}$) | $R_f$ ($\times 10^{13} m^{-1}$) | $R_c$ ($\times 10^{13} m^{-1}$) | $R_t$ ($\times 10^{13} m^{-1}$) |
|---|---|---|---|---|
| Thermophilic SAnMBR | 0.057(0.7%)* | 0.304(3.6%) | 8.110(95.7%) | 8.47(100) |
| Mesophilic SAnMBR | 0.059(3.4%) | 0.127(7.4%) | 1.534(89.2%) | 1.72(100) |

*Percentage of the total resistance $R_t$ shown in parentheses.

As shown in Table 3.1, the total hydraulic resistance for the mesophilic SAnMBR was much lower than that of thermophilic system. For both systems, the resistances caused by cake formation accounted for a large portion of the total resistance, while the fouling resistance caused by adsorption or pore plugging was marginal. These results indicate that cake layer played a key role in filtration behavior.

The main cause of the difference in the filtration behaviors of the thermophilic and mesophilic SAnMBRs is unclear, and has not previously been investigated. Generally, membrane fouling occurred due to imposed working conditions (i.e. suction force, sparging rate, for example) as well as membrane biological reactor response (i.e. accumulation of reaction co-products, such as soluble microbial products). Since the two SAnMBRs were operated in parallel under the same suction force and biogas sparging rate, the possible reasons should largely reside in sludge properties and cake layers on the membrane surface. To obtain a comprehensive insight into membrane fouling mechanisms in the SAnMBRs, the sludge characteristics and cake layers structure were thus compared, and their influences on the membrane fouling were also examined.

### 3.3.2 Comparison of Sludge Concentration and Supernatant Properties

Figure 3.23 shows the changes in top zone MLSS, COD in the effluent, and COD in the supernatant of the two SAnMBRs over a period of 40 days. It can be seen from Figure 3.23a that MLSS concentration increased with operation time for the both SAnMBRs,

however a slight decrease in membrane fouling in terms of TMP was observed. This result indicates that the membrane permeability was not significantly affected by the gradual increase in biomass concentration, and there was no correlation between membrane fouling and MLSS concentration. Similar observations have been published previously (Rosenberger et al., 2005; Hong et al., 2002; Le-Clech et al., 2003). This can be mainly attributed to the complexity and variability of the biomass components, as changing MLSS concentration can impact upon biomass characteristics. Nevertheless, the analysis of variance (ANOVA) shows no statistical difference in MLSS concentration between the two SAnMBRs, with 95% confidence. This suggests that MLSS concentration was not the cause of the different filtration performance between the two systems.

Given the easy biodegradability of the feeding substrate (mainly methanol) in this study, the organic matter in the supernatant is believed to consist of SMP. SMP by definition are soluble organic matter in the supernatant, and ideally should be able to go through membrane of 0.3 μm pore size used in this study with the effluent. Therefore, COD in the effluent can represent SMP content. Analyses of the effluent indicate that proteins and carbohydrates, which are the components of SMPs, were present in the effluents. Figures 3.23b and 3.23c show that COD in the effluent for the thermophilic SAnMBR ranged from 74.3 to 276.4 mg/L, with an average of 196.9 ± 53.9 mg/L, while the mesophilic SAnMBR had an effluent COD that ranged from 96.7 to 204.0 mg/L, with an average of 151.3 ± 28.2 mg/L. ANOVA reveals that there are significantly difference ($p<0.05$) in the effluent COD between the two systems. A similar observation has been made by Visvanathan et al. (Visvanathan et al., 2007) who found that the amount of SMP produced under thermophilic condition is almost 2.5 times higher than that under mesophilic condition when treating landfill leachate with aerobic MBRs. It seems that high temperature would induce high SMP production. On the other hand, in this study, a low F/M ratio was found, due to the lower filtration flux that can be maintained under thermophilic condition, resulting in a part of the biomass in an endogenous metabolism state. In general, larger amounts of SMP would be produced as endogenous metabolism

predominates at high solids retention times (SRTs) or low F/M ratios (Sheintuch, 1987). This mechanism could partly explain the higher SMP under the thermophilic condition.

In previous studies (Meng et al., 2006; Huang et al., 2000; Liang et al., 2007), it was found that SMP demonstrated considerable influence on membrane fouling, and SMP was always considered as a foulant affecting the membrane permeability of the mixed liquor, as well as reducing the cake porosity by filling the void spaces between the cell particles in the cake layer. Nevertheless, for the thermophilic SAnMBR, COD in the effluent in average was only 30.1% higher than that for mesophilic SAnMBR, while filtration resistance was over ten times of that for mesophilic SAnMBR, In general, a higher SMP content corresponded to a higher filtration resistance. Meng et al (2006) found that filtration resistance increased linearly with SMP content. These results suggest that the difference in SMP was a contributor, but may not be the main contributor to the big difference in filtration behaviors between the two systems.

It can be seen from Figures 3.23b and 3.23c that, in all cases, COD in the supernatant was consistently higher than that in the effluent, indicating the significant retention of organic matter by the membrane filtration and cake layer. Similar phenomenon was previously observed by Wang et al. (2008) in works performed with aerobic submerged MBRs. They suggested there existed a group of organic substances classified as biopolymer clusters (BPC) in supernatant, which might exert a significant influence on filtration resistance. In this study, BPC content was estimated by calculating the difference in COD concentration between the supernatant and the effluent. During the whole test period, the BPC concentration ranged from 300.1 to 1430.8 mg/L in terms of the COD, with an average of 676.9 ± 289.9mg/L for the thermophilic SAnMBR, and from 34.0 to 214.3 mg/L with an average of 108.2 ± 48.6mg/L for the mesophilic SAnMBR, showing a large difference between them. It has been reported that BPC in the sludge cake was much higher than that in the bulk sludge (Wang et al., 2007), suggesting that the accumulation of BPC in the sludge liquor would facilitate the formation of the sludge cake layer on the membrane surface. According to above, it can be expected that an increase in the BPC concentration tends to form a dense cake layer, and thus cause

serous fouling problems. Therefore, BPC should be at least partially responsible for the differences in membrane fouling between the two systems.

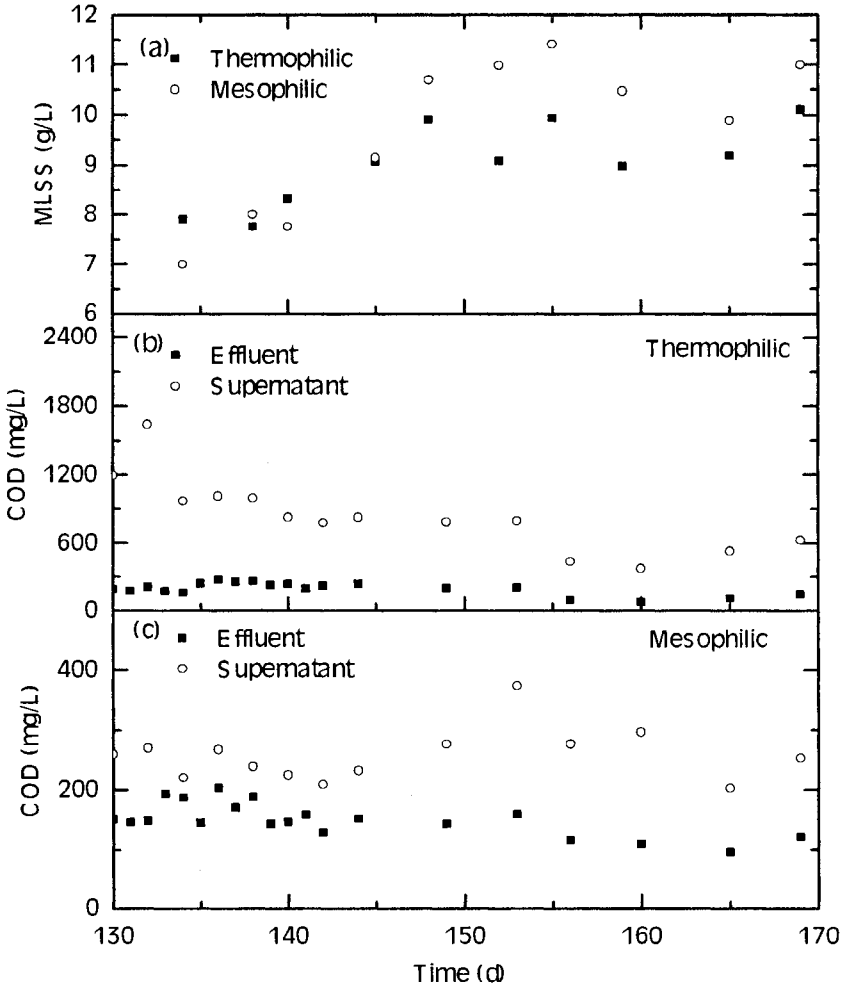



Fig. 3.23 Evolution of parameters over the operation time: (a) MLSS concentration, (b) COD in effluent and supernatant for thermophilic SAnMBR, and (c) COD in effluent and supernatant for mesophilic SAnMBR

### 3.3.3 Comparison of Bound EPS

In this work, the sum of total proteins and polysaccharides was considered to represent the total amount of EPS because these are the dominant components typically found in extracted EPS (Lee et al., 2003; Bura et al., 1998). Figure 3.24 presents the comparison of bound EPS values measured for the two SAnMBRs. Thermophilic sludge had a relatively high protein concentration but a low polysaccharide concentration. Thus, the

protein (PN) to polysaccharide (PS) ratio in the bound EPS was 1.33 for the thermophilic sludge and 0.84 for the mesophilic sludge.

The content of EPS or PN/PS ratio would depend on the respective rates of production and degradation of each molecule category. Polysaccharides are synthesized extracellularly for a specific function, while proteins can exist in the extracellular polymer network due to the excretion of intracellular polymers or cell lysis (Lee et al., 2003; Bura et al., 1998). It has been reported that, at lower food to microorganism (F/M) ratios, the polysaccharide in microbial flocs declined, which reflected the available carbon. On the other hand, the amount of protein on the cell surface increased, likely due to cell lysis (Lee et al., 2003). Therefore, a relatively lower F/M in the thermophilic SAnMBR would partially contribute to the higher PN/PS ratio in the thermophilic SAnMBR. Another contributor would reside in the adsorption equilibrium between bound and soluble biopolymers. In relation with their hydrophobicity and surface charge, affinity between proteins and flocs could be higher than that between polysaccharide and flocs. A higher temperature would be expected to reduce these affinities, and more polysaccharides would be released to the bulk phase, which could partially explain why higher PN/PS ratios are observed in bound polymers in thermophilic SAnMBR.

It has been reported that the decreasing PN/PS ratio could induce a decrease in floc hydrophobicity, estimated by contact angle measurement (Sponza, 2003). Thus, a higher PN/PS ratio in the thermophilic SAnMBR could favor the formation of sludge cake layers. It was shown that the PN/PS ratio rather than the quantity of total EPS play a key role in the fouling resistance (Lee et al., 2003). Therefore, this parameter could be an indicator of fouling propensity of bulk sludge. From the comparison of bound EPS, it is clear that the higher PN/PS ratio of bulk sludge in the thermophilic SAnMBR would contribute to the differences in membrane fouling between the two systems.

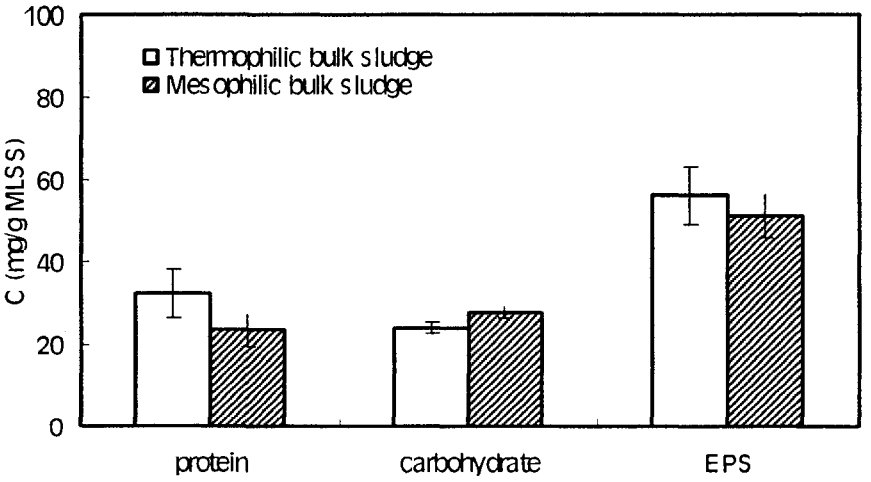



Fig. 3.24 Comparison of bound EPS of the bulk sludge in thermophilic and mesophilic SAnMBRs

### 3.3.4 Comparison of Sludge Morphology

Sludge morphology has been analyzed by means of particle size analyzer and microscopic observation. Figure 3.25 shows the typical particle size distribution of sludge from the thermophilic and mesophilic SAnMBRs. A bimodal curve was observed in the flocs distribution of sludge from the thermophilic SAnMBR, whereas mesophilic flocs always showed a unimodal distribution. This indicated that two populations of aggregates are maintained in the thermophilic SAnMBR, a dispersed one whose size was around 1-10 μm and a macroflocs population whose mean size was between 50 and 200 μm. The two-peak distribution of thermophilic flocs was clearly demonstrated by microscopic observations of sludge liquor, as shown in Figure 3.26. A larger quantity of fine particles can be found in the thermophilic SAnMBR. Higgins and Novak (1997) reported that the "supercolloidal" particles in the range 1 – 10 μm had the greatest effect on the dewaterability of sludge, and thus affected filtration ability of sludge. Wisniewski (1998) found that the suspension produced after the flocs breakup consists mainly of particles having a size of around 2 μm responsible for flux decline. Earlier work also showed that fine particles in the range 1 – 10 μm have a stronger tendency to deposit on the membrane surface. Moreover, Massé et al. (2006) reported that the reduction in the diameter size may be associated with a more compact floc structure. It could be explained by the fact that the small particles, i.e. dispersed bacteria and small colonies, have a higher density than the large flocs with more bridging between biopolymers. The smaller

aggregates population with size range of 1 – 10 μm were expected to have a denser structure, and thus cause more severe membrane fouling as suggested by Li et al. (2008).

According to the current investigation, together with previous work in the literature, it can be concluded that the large amount of aggregates with size range of 1 – 10 μm in the thermophilic SAnMBR played a key role in cake formation process, as well as cake layer structure, and are most likely responsible for the big difference in membrane fouling between the two systems.

The bimodal curve pattern of floc size distribution in the thermophilic SAnMBR can also correlate to the increasing amount of non-flocculating flocs in the thermophilic SAnMBR. This can be clearly demonstrated by the microscopic observations in Figure 6. This phenomenon could possibly be due to several reasons: (1) high temperature reduced affinity between EPS and flocs, and favored small size flocs, (2) as F/M decreased due to severe membrane fouling in the thermophilic SAnMBR, less polysaccharide or EPS were produced as energy is probably used for cell maintenance, and hence biodeflocculation due to EPS decreased, or (3) as substrate became less available at low F/M, non-flocculating organism growth was enhanced because dispersed bacteria were exposed to a higher substrate concentration than that developed in macro-flocs.

Although a higher temperature affected sludge or permeate rheology and was expected to improve permeate ability, the notorious lower filtration performance was observed in the thermophilic SAnMBR. This suggested that physiological effects of temperature on the properties and composition of the sludge are much more important for membrane filtration than the physical effect of temperature on sludge or permeate rheology.

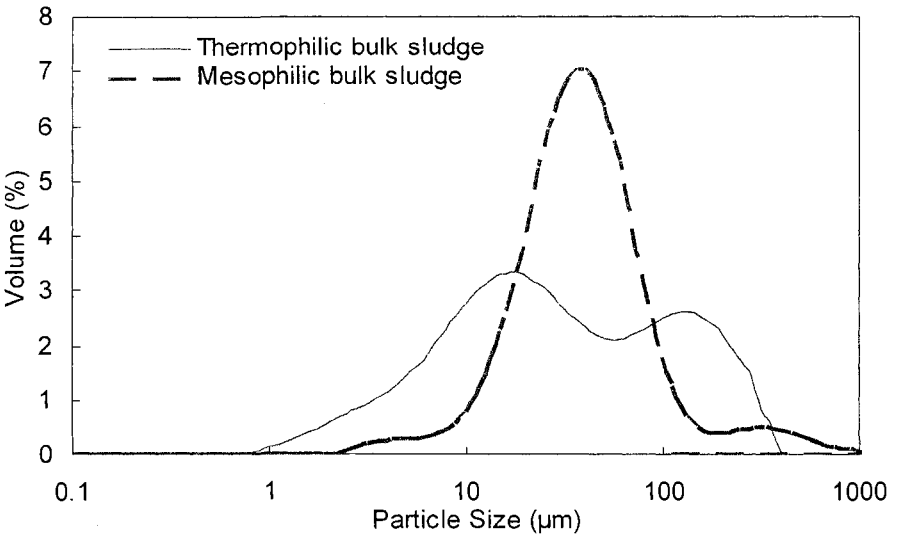



Fig. 3.25 Particle size distribution of bulk sludge liquor for the thermophilic and mesophilic SAnMBRs

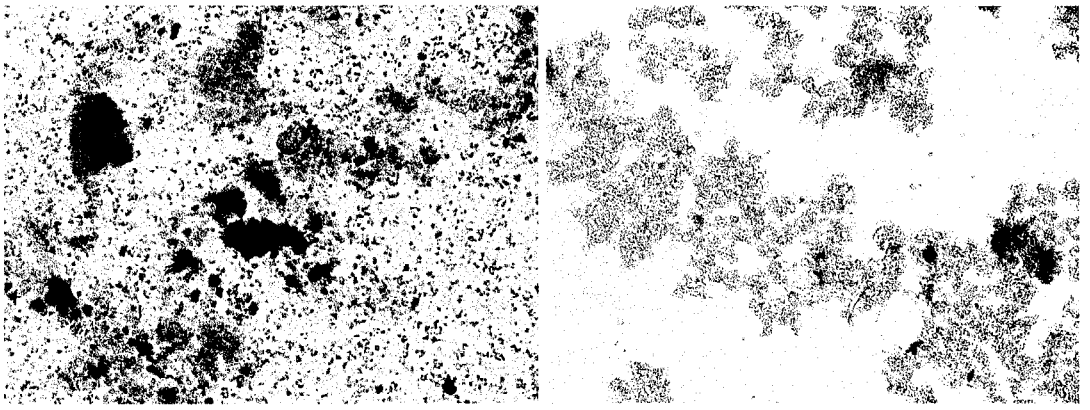


Fig. 3.26 Microscopic observation of sludge from (a) thermophilic SAnMBR, and (b) mesophilic SAnMBR

### 3.3.5 Comparison of Cake Layer

It seems that the differences in filtration characteristics are due to the differences in the formation of the cake layer on the membrane surface between two systems. Therefore, it is necessary to characterize the cake layer.

The FTIR was used to detect the biomass functional groups in the cake layer. As shown in Figure 3.27, there are two peaks at 1652 $cm^{-1}$ and 1544 $cm^{-1}$ in the spectrum unique to the protein secondary structure, called amides I and II (Maruyama et al., 2001). The peaks at 1385 $cm^{-1}$ and 1235 $cm^{-1}$ imply the presence of amide III. This result indicates that there were proteins in the membrane foulants. The broad peak at 1065 $cm^{-1}$

is due to polysaccharide or polysaccharide-like substances (Kimura et al., 2005). By the FTIR spectra in Figure 3.27, the major components of the foulants were identified as proteins and polysaccharides materials. The presence of EPS in the cake layer was also proved by CLSM observation as seen in Figure 3.28. From Figure 3.28, it can be seen that both proteins (green channel) and polysaccharides (red channel) were present on the membrane surface. Both the protein and polysaccharides were found to coexist (yellow) or overlap on many regions of the membrane surface.

It also can be seen from Figure 3.29 that the intensity of membrane foulants formed with the thermophilic sludge was stronger than that of the mesophilic sludge. The absorption intensity reflected the relative amount of biopolymers in the total foulants, indicating that quantity of foulants like EPS for the thermophilic SAnMBR was higher than that for the mesophilic SAnMBR.

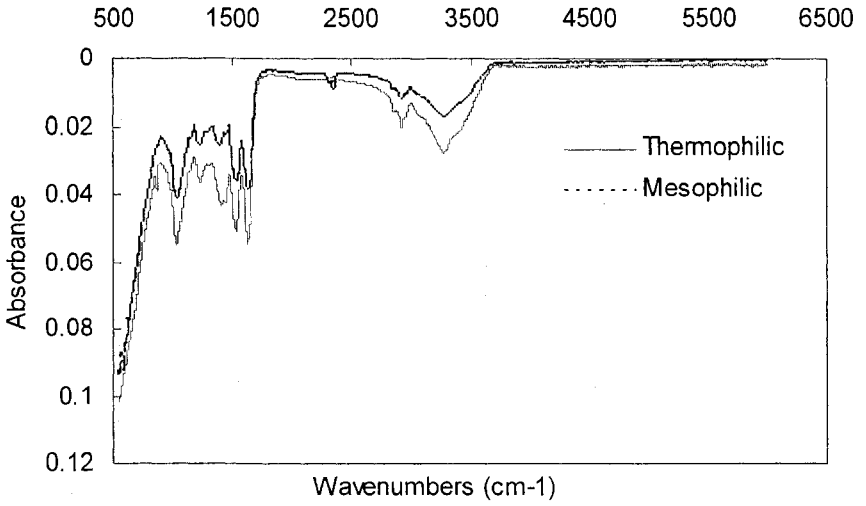



Fig. 3.27 FTIR spectra of cake layers for the thermophilic and mesophilic SAnMBRs

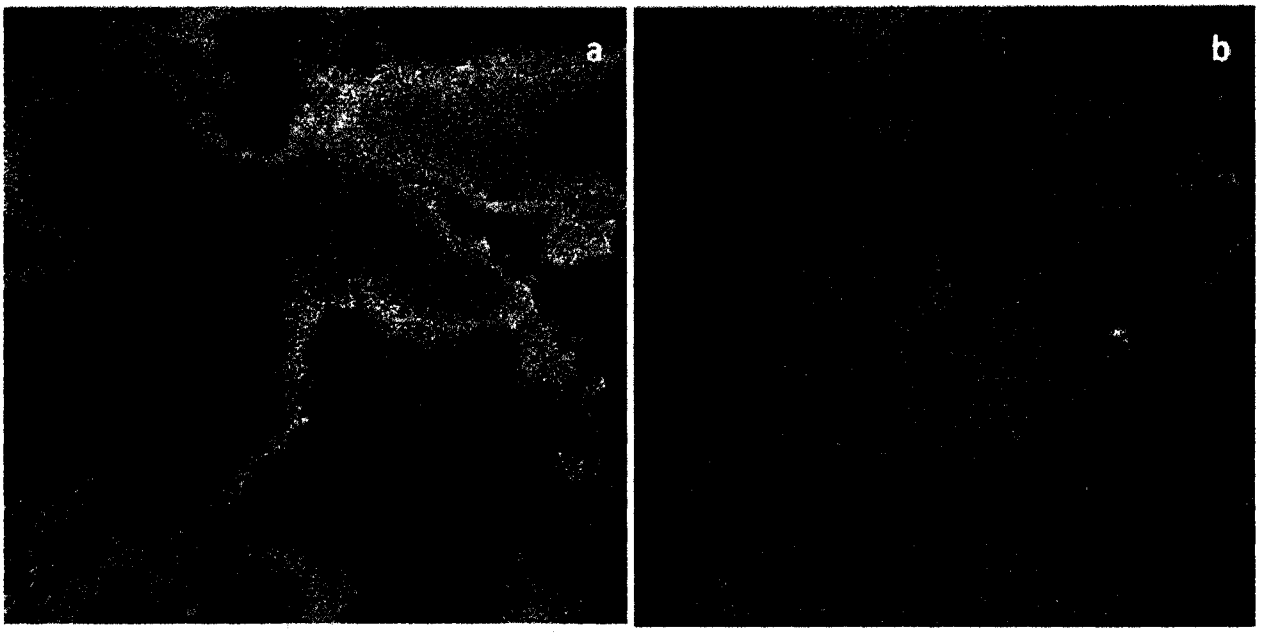



Fig. 3.28 CSLM image of cake layer on SAnMBR membrane: (a) mesophilic membrane; (b) thermophilic membrane. Green and red signals indicate the presence of proteins and carbohydrates respectively. The images correspond to a z-projection of series of stack along the axis perpendicular to image plane, inside the cake

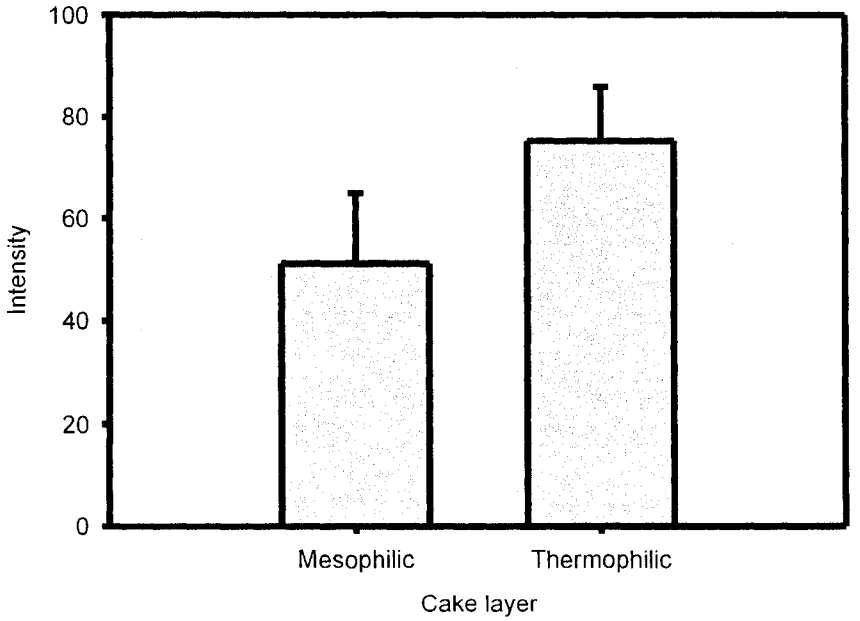



Fig. 3.29 Intensity of membrane foulants: the intensity corresponds to a z-projection of 50 image stack along the axis perpendicular to image plane, inside the cake

The EPS concentrations in the sludge cake layer are shown in Figure 3.30. A higher level of protein and carbohydrate in EPS was always observed in the sludge cake layer than that in the bulk sludge, as described in Figure 3.24. This is probably caused by the adsorption and interception of SMP and other organic macromolecules by the sludge cake layer and membrane. For the comparison of sludge cake layer EPS between the two systems, thermophilic sludge cake showed a slightly higher EPS content. This result is consistent with data from FTIR spectra and supernatant COD measurements. EPS would play a significant role in sludge or bacterial adhesion onto membrane surface by altering the physicochemical characteristics such as charge, hydrophobicity, and the polymeric properties (Gómez-Suárez et al., 2002; Tansel et al., 2006). Moreover, EPS provides a highly hydrated gel matrix in which microorganisms are embedded. They are considered to reduce the cake porosity by filling the void spaces between the cell particles in the cake layer (Liang et al., 2007). Therefore, the cake sludge layer formed under thermophilic condition would have more filtration resistance than that under the mesophilic condition.

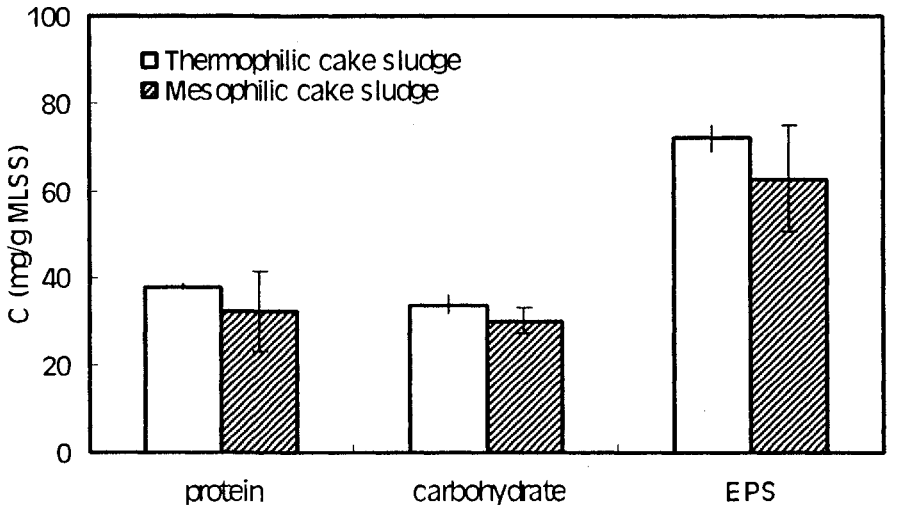



Fig. 3.30 Comparison of EPS of the cake sludge in thermophilic and mesophilic SAnMBRs

Typical energy dispersive spectrum analysis, which can be seen in Figure 3.31, of the sludge cake layer shows the existence of Mg, P, S, Ca, Fe and Zn, with Ca and Fe detected in greater abundance in the cake layer for the thermophilic SAnMBR. Although the relative contents of these metal ions were lower, these components presented the

origin of inorganic fouling, and may have significant impacts on the formation of the cake layer. It has been shown that $CaCO_3$, $SiO_2$, and $Fe_2(SO_4)_3$ present a challenge for desalination systems (Demadis et al., 2005). The biopolymers contain ionizable groups such as $SO_4^{2-}$,$CO_3^{2-}$, $PO_4^{3-}$, and $OH^-$. The cations, such as $Ca^{2+}$, $Mg^{2+}$, $Al^{3+}$, and $Fe^{3+}$ could be easily precipitated by these negative ions. Through charge neutralization, metal clusters and metal ions were caught by the flocs or biopolymers, which enhanced membrane fouling (Seidel and Elimelech, 2002). Bridging between deposited biopolymers and metal ions further enhanced the compactness of the fouling layer (Hong and Elimelech, 1997). The synergistic interactions between different kinds of foulants (e.g., bacterial clusters, colloids, macromolecules, and inorganic elements) could result in faster and more substantial foulant deposition on the membrane surface (Murthy et al., 1998). The results from Figure 3.31 suggested that thermophilic sludge cake layer had a higher ability to intercept metal ions since the same feed was used in both systems. Nevertheless, sludge cake layer containing more Ca and Fe would have a more compact and dense structure, and would certainly play a role and may partially explain the differences observed in Figure 3.22.

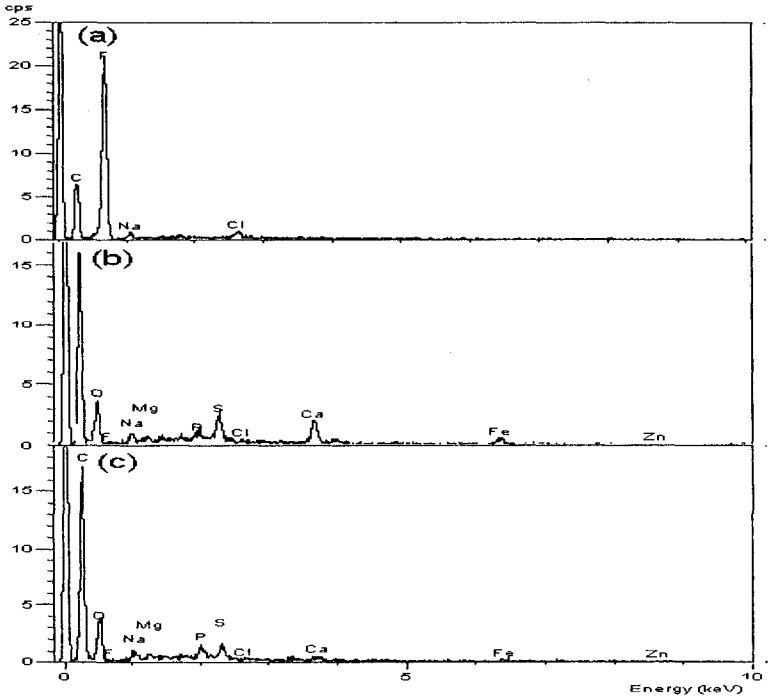



Fig. 3.31 Typical energy dispersive spectrum of (a) new membrane; (b) thermophilic cake layer, and (c) mesophilic cake layer

It had been proved that AFM was an effective method to analyze microstructure at the nano-meter (Cortalezzi et al., 2002). AFM images can provide information on the roughness of the cake layer. The result of analysis of the cake layers is presented in Figure 3.32. Average roughness parameter was calculated from AFM tapping mode height images on the fouled membrane layer. The root-mean-square was about 58 nm and 28 nm for the thermophilic and mesophilic sludge cake layer, respectively. Clearly, roughness of the thermophilic cake layer was higher than that of the mesophilic, suggesting the thermophilic cake layer had a more compact structure.

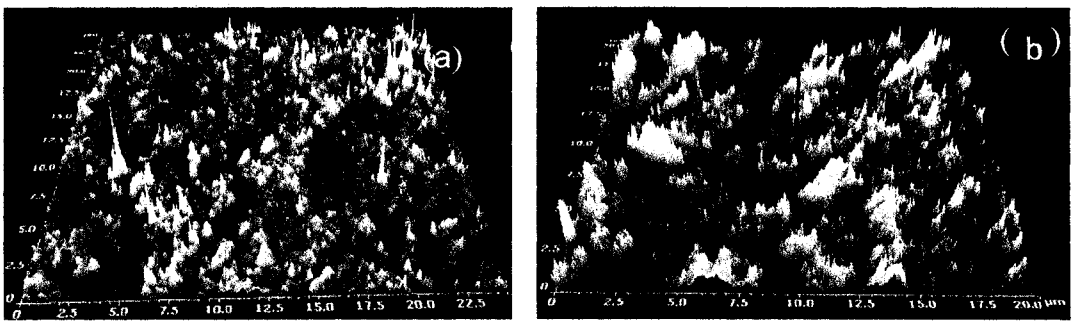



Fig. 3.32 Atomic force microscope images of cake layer surfaces: tapping mode 3D height images of (a) thermophilic, and (b) mesophilic cake layers (average roughness parameters calculated were 52.37 nm and 28.75 nm on thermophilic and mesophilic membranes, respectively)

Figure 3.33 shows the SEM images of cake layer over the membrane surface. The cake layer seemed to be denser and nonporous for the thermophilic SAnMBR. This conclusion can be confirmed by comparison of moisture content in the cake layer. Typical values were 87% for the sludge cake layer from the thermophilic SAnMBR and 94% for the sludge cake layer from the mesophilic SAnMBR, indicating cake layer in the mesophilic SAnMBR was more porous and less compressed.

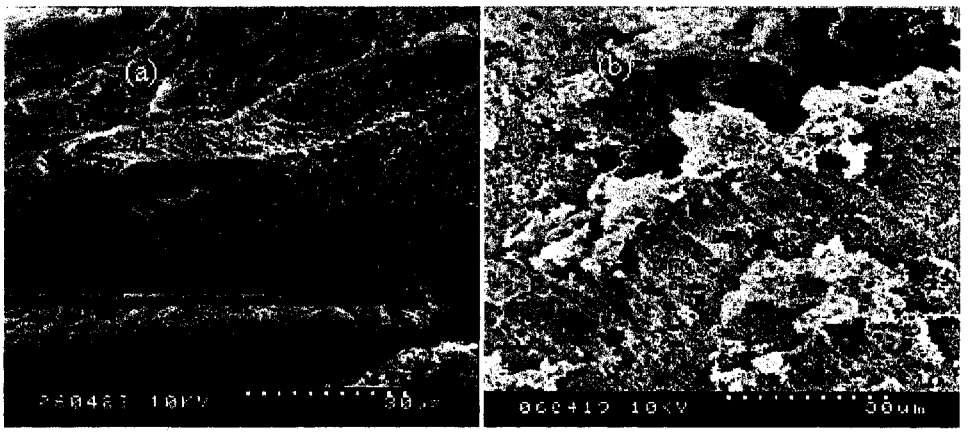



Fig. 3.33 Scanning electron microscope images of sludge cake layers for (a) thermophilic, and (b) mesophilic SAnMBRs

Figure 3.34 shows a comparison of the typical particle size distribution of cake sludge liquors. The cake sludge liquor was prepared by gently resuspending fresh cake sludge (accumulated in 24 hr) using permeate. For both systems, as compared to that in bulk sludge liquor (from Figure 3.25), much smaller flocs were detected in the cake sludge liquors, showing smaller flocs have a stronger tendency to deposit on membrane surface. From Figure 3.34, it also can be seen that the thermophilic cake sludge liquor was comprised of an increased number of smaller flocs. The Carman-Kozeny equation provides an important implication that the smaller particles deposited on the membrane surface would form a denser cake layer and generate greater specific resistance (Bai and Leow, 2002). Therefore, a denser cake layer formed by smaller flocs under thermophilic conditions was evident.

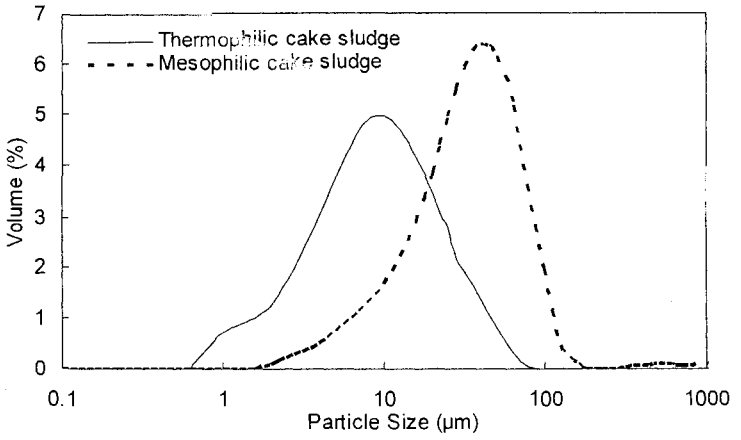



Fig. 3.34 Particle size distribution of cake layer liquor for the thermophilic and mesophilic SAnMBRs

From these results, it is clear that the major organic foulants in cake layer are proteins and polysaccharide materials, and the major inorganic elements in cake layer are Ca, Fe, Mg, and Zn. The differences in these components should partially be responsible for the differences of filtration behaviors between the thermophilic and mesophilic systems. Floc sizes also affected the morphology of the sludge cake layer, and higher contents of these foulants and fine flocs tended to form a denser and nonporous cake layer, giving rise to filtration resistance.

# Chapter 4

# Conclusions and Recommendations for Further Research on Submerged Anaerobic Membrane Bioreactors

## 4.1 Conclusions for Feasibility of Mesophilic and Thermophilic SAnMBRs

The feasibility of using mesophilic (37 ± 2°C) and thermophilic (55 ± 2°C) SAnMBRs for treating Kraft evaporator condensate was tested for a period of 200 and 190 days, respectively. The following main conclusions can be drawn based on the experimental results:

### Conclusions for Mesophilic SAnMBR

1.) An overall soluble COD removal efficiency of greater than 95 % was achieved with a feed COD concentration varying from 2600 – 10,000 mg/L. The permeate was clean (colourless), had a very low soluble COD (100-200 mg/L) and zero solids concentration. An average of 85 % methane was found in the biogas, with an overall methane yield of approximately 0.35 L $CH_4$ / g COD removed. This indicates treatment of Kraft evaporator condensate using a mesophilic SAnMBR can achieve a good quality of fuel, which can be added to the boiler for heat generation or used for power generation. The results from this study show the promise of using this novel reactor design for energy recovery from pulp and paper wastewater and for subsequent reuse of permeate for system closure

2.) Membrane fouling appeared to be an issue, due to sludge cake formation. Biogas sparging rate has a significant impact on sludge cake formation, as an increase in sparging rate decreases the cake formation rate. A stable membrane flux could be achieved only under a relatively high sparging rate. Effective membrane fouling control can be achieved by using a biogas sparging rate of at least 0.75 LPM. This suggests that in-situ membrane cleaning by using biogas bubbling is feasible. Membrane fouling can be controlled to the same extent as that in aerobic MBRs.

3.) The system performance (biological activity and membrane fouling) was affected by system upsets (toxic shocking and pH disruption). The biogas production rate decreased and membrane fouling rate increased during the periods of system upsets. The mesophilic SAnMBR recovered from modest toxic shocking and pH disruption within one week. The results suggest that the mesophilic SAnMBR can tolerate a certain level of toxic shocking and pH disruption.

**Conclusions for Thermophilic SAnMBR**

1.) The results show that Kraft evaporator condensate treatment using a SAnMBR is feasible under thermophilic conditions in terms of COD removal and biogas production. Under the tested OLR of 1-7 kg COD/$m^3$/day, a COD removal efficiency of 85-97% was achieved. The methane yield was 0.35 ± 0.1 L $CH_4$ / g COD removal with an excellent fuel quality close to 85% methane in the biogas.

2.) Membrane fouling may be a challenge for the operation of the thermophilic SAnMBR. A higher membrane fouling rate was observed when a larger portion of fine colloidal particles were present in the mixed liquor. Biogas sparging was ineffective in maintaining membrane flux when a larger portion of fine colloidal particles exists in the mixed liquor. Operation of the bioreactor as a conventional anaerobic bioreactor at the beginning was effective in wasting the fine colloidal particles in the effluent to minimize the impact of fine colloidal particle on membrane fouling.

3.) The thermophilic SAnMBR was sensitive to the toxic compounds in the feed. Pre-treatment of the feed may be required to remove toxic sulfur compounds to sustain thermophilic biological activity.

### 4.2 Conclusions on Sludge Properties and their Effects on Membrane Fouling

Comparison of the properties of sludge liquor and cake layer from the two systems was made to expose major factors governing the different filtration characteristics. Based on the results presented in this study, the following conclusions can be drawn as follows:

1.) The mesophilic SAnMBR had a better filtration performance than the thermophilic SAnMBR in terms of filtration resistance and stable operation period.

2.) A higher temperature and a relatively lower organic loading rate promoted EPS release, a higher content of SMP and BPC, increased PN/PS ratio in bound EPS, smaller size flocs, and thus gave rise to increased filtration resistance in the thermophilic SAnMBR. This also indicated the advantage of operating SAnMBRs at moderate temperatures and relative high organic loading rates.

3.) Sludge properties, including SMP, BPC, bound EPS, and flocs size, are the important parameters in governing sludge cake formation and membrane fouling in SAnMBR systems

4.) Physiological effects of temperature on the properties and composition of the sludge are much more important for membrane filtration than the physical effect of temperature on sludge or permeate rheology.

### 4.3 Recommendations for Future Work

A number of research areas should be examined for further studies on submerged anaerobic membrane bioreactors. An optimization of the reactor design at the laboratory scale should be conducted, such that operating conditions can be effectively controlled. Furthermore, membrane fouling studies can be further pursued in order to decrease the filtration resistance encountered in submerged anaerobic membrane bioreactors, specifically for the thermophilic condition. In this way, the membrane flux can be more easily maintained. A membrane fouling control strategy may be required, which can also be examined in future studies.

The maximum treatment capacity for SAnMBR technologies was not determined in this research, but can be further studied. In this way, the optimal loading rates and hydraulic retention times for mesophilic and thermophilic SAnMBRs can be found. In terms of optimization, a closed-loop pre-treatment process can also be developed in order

to eliminate components that are toxic to the anaerobic biomass. This can allow the SAnMBRs to operate efficiently, without the potential for process upsets.

At the industrial scale, a full capital and operating cost analysis can be conducted, comparing thermophilic and mesophilic SAnMBRs to current treatment technologies. Upon completion of these recommendations, a thorough, complete analysis of the potential and capacity for SAnMBR technologies can be achieved.

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## Appendix I Evaluation of Methodology for Mesophilic SAnMBR

| Date | Day | Hydraulic Retention Time (hr) | Mesophilic SAnMBR Flux ($L/m^2/hr$) | Organic Loading Rate (kg $COD/m^3/day$) | Organic Removal Rate (kg $COD/m^3/day$) |
|---|---|---|---|---|---|
| 17/01/08 | 8 | | | | |
| 18/01/08 | 9 | 22.63 | 6.44 | 2.83 | 2.63 |
| 19/01/08 | 10 | 26.84 | 5.43 | 2.38 | 2.20 |
| 20/01/08 | 11 | 31.70 | 4.60 | 2.02 | 1.84 |
| 21/01/08 | 12 | 35.59 | 4.10 | 1.80 | 1.64 |
| 23/01/08 | 14 | 34.43 | 4.24 | 1.86 | 1.70 |
| 24/01/08 | 15 | 25.23 | 5.78 | 2.54 | 2.34 |
| 25/01/08 | 16 | 23.08 | 6.32 | 2.77 | 2.61 |
| 26/01/08 | 17 | 32.43 | 4.50 | 1.97 | 1.90 |
| 29/01/08 | 20 | 21.00 | 6.94 | 3.05 | 2.89 |
| 30/01/08 | 21 | | | | |
| 01/02/08 | 23 | 19.18 | 7.60 | 3.34 | 3.15 |
| 02/02/08 | 24 | 20.59 | 7.08 | 3.11 | 2.93 |
| 03/02/08 | 25 | 18.54 | 7.86 | 3.45 | 3.25 |
| 04/02/08 | 26 | 22.11 | 6.60 | 2.90 | 2.74 |
| 05/02/08 | 27 | 20.84 | 7.00 | 3.07 | 2.92 |
| 06/02/08 | 28 | 27.63 | 5.28 | 2.32 | 2.19 |
| 07/02/08 | 29 | 27.01 | 5.40 | 2.37 | 2.22 |
| 08/02/08 | 30 | 28.57 | 5.10 | 2.24 | 2.12 |
| 09/02/08 | 31 | 18.83 | 7.74 | 3.40 | 3.24 |
| 10/02/08 | 32 | 26.01 | 5.61 | 2.46 | 2.28 |
| 11/02/08 | 33 | 29.17 | 5.00 | 2.19 | 1.97 |
| 12/02/08 | 34 | 30.11 | 4.84 | 2.13 | 1.89 |
| 13/02/08 | 35 | 19.58 | 7.45 | 3.18 | 2.78 |
| 14/02/08 | 36 | 20.00 | 7.29 | 3.11 | 2.79 |
| 15/02/08 | 37 | 21.65 | 6.74 | 2.88 | 2.64 |
| 16/02/08 | 38 | 22.64 | 6.44 | 2.75 | 2.60 |
| 17/02/08 | 39 | 25.61 | 5.69 | 2.43 | 2.37 |
| 18/02/08 | 40 | 28.67 | 5.09 | 2.17 | 2.08 |
| 19/02/08 | 41 | 21.59 | 6.75 | 2.88 | 2.71 |
| 20/02/08 | 42 | 21.65 | 6.74 | 2.88 | 2.70 |
| 21/02/08 | 43 | 25.93 | 5.63 | 2.40 | 2.25 |
| 22/02/08 | 44 | 23.53 | 6.20 | 2.65 | 2.49 |
| 23/02/08 | 45 | | 4.11 | 1.76 | 1.66 |
| 24/02/08 | 46 | 19.18 | 7.60 | 7.33 | 7.04 |
| 25/02/08 | 47 | 24.00 | 6.08 | 5.86 | 5.53 |
| 26/02/08 | 48 | 27.45 | 5.31 | 5.12 | 4.83 |
| 27/02/08 | 49 | 32.68 | 4.46 | 4.30 | 4.05 |
| 28/02/08 | 50 | 32.68 | 4.46 | 4.30 | 4.06 |
| 29/02/08 | 51 | 22.95 | 6.35 | 6.12 | 5.79 |
| 01/03/08 | 52 | 26.92 | 5.42 | 5.22 | 5.04 |
| 02/03/08 | 53 | 31.11 | 4.69 | 4.52 | 4.45 |

| Date | Day | Hydraulic Retention Time (hr) | Mesophilic SAnMBR Flux ($L/m^2/hr$) | Organic Loading Rate (kg $COD/m^3/day$) | Organic Removal Rate (kg $COD/m^3/day$) |
|---|---|---|---|---|---|
| 03/03/08 | 54 | 33.33 | 4.38 | 4.22 | 4.15 |
| 04/03/08 | 55 | 34.43 | 4.24 | 4.08 | 4.01 |
| 05/03/08 | 56 | | | | |
| 06/03/08 | 57 | 20.19 | 7.22 | 6.96 | 6.71 |
| 07/03/08 | 58 | 29.17 | 5.00 | 4.82 | 4.67 |
| 08/03/08 | 59 | 33.20 | 4.39 | 4.23 | 4.13 |
| 09/03/08 | 60 | | | | |
| 10/03/08 | 61 | 23.86 | 6.11 | 5.89 | 5.75 |
| 11/03/08 | 62 | | | | |
| 12/03/08 | 63 | 20.34 | 7.17 | 6.91 | 6.70 |
| 13/03/08 | 64 | 31.34 | 4.65 | 4.48 | 4.34 |
| 14/03/08 | 65 | 22.95 | 6.35 | 6.12 | 5.92 |
| 15/03/08 | 66 | 28.57 | 5.10 | 4.92 | 4.72 |
| 16/03/08 | 67 | 26.67 | 5.47 | 5.27 | 5.03 |
| 18/03/08 | 69 | | | | |
| 20/03/08 | 71 | 30.55 | 4.77 | 4.35 | 3.75 |
| 21/03/08 | 72 | 27.81 | 5.24 | 4.78 | 4.29 |
| 22/03/08 | 73 | 29.27 | 4.98 | 4.54 | 4.24 |
| 23/03/08 | 74 | 27.10 | 5.38 | 4.90 | 4.62 |
| 24/03/08 | 75 | 33.60 | 4.34 | 3.96 | 3.76 |
| 25/03/08 | 76 | 29.89 | 4.88 | 4.45 | 4.03 |
| 26/03/08 | 77 | 29.68 | 4.91 | 4.48 | 4.21 |
| 27/03/08 | 78 | 34.57 | 4.22 | 3.84 | 3.64 |
| 29/03/08 | 80 | 31.34 | 4.65 | 4.24 | 4.02 |
| 31/03/08 | 82 | 28.00 | 5.21 | 4.75 | 4.34 |
| 01/04/08 | 83 | 24.71 | 5.90 | 5.38 | 5.01 |
| 02/04/08 | 84 | 32.18 | 4.53 | 4.13 | 3.95 |
| 04/04/08 | 86 | 26.33 | 5.54 | 5.05 | 4.78 |
| 05/04/08 | 87 | 28.97 | 5.03 | 4.28 | 4.03 |
| 06/04/08 | 88 | 30.22 | 4.83 | 4.10 | 3.82 |
| 07/04/08 | 89 | 32.06 | 4.55 | 3.87 | 3.56 |
| 08/04/08 | 90 | | | | |
| 09/04/08 | 91 | 28.97 | 5.03 | 4.28 | 4.21 |
| 12/04/08 | 94 | 30.56 | 4.77 | 4.06 | 3.97 |
| 14/04/08 | 96 | 24.63 | 5.92 | 5.03 | 4.91 |
| 15/04/08 | 97 | 21.88 | 6.67 | 5.67 | 5.52 |
| 16/04/08 | 98 | 29.47 | 4.95 | 4.21 | 4.12 |
| 17/04/08 | 99 | 24.56 | 5.94 | 5.05 | 4.96 |
| 18/04/08 | 100 | 24.71 | 5.90 | 5.02 | 4.91 |
| 19/04/08 | 101 | | | | |
| 20/04/08 | 102 | | | | |
| 21/04/08 | 103 | 20.19 | 7.22 | 6.14 | 6.04 |
| 22/04/08 | 104 | 23.46 | 6.22 | 9.85 | 9.77 |
| 23/04/08 | 105 | 31.43 | 4.64 | 7.35 | 7.30 |
| 24/04/08 | 106 | 25.77 | 5.66 | 8.97 | 8.89 |

| Date | Day | Hydraulic Retention Time (hr) | Mesophilic SAnMBR Flux ($L/m^2/hr$) | Organic Loading Rate (kg $COD/m^3/day$) | Organic Removal Rate (kg $COD/m^3/day$) |
|---|---|---|---|---|---|
| 26/04/08 | 108 | 26.67 | 5.47 | 8.66 | 8.60 |
| 27/04/08 | 109 | 25.00 | 5.83 | 9.24 | 9.16 |
| 28/04/08 | 110 | 28.57 | 5.10 | 8.09 | 8.02 |
| 29/04/08 | 111 | | | | |
| 30/04/08 | 112 | 28.57 | 5.10 | 8.09 | 8.03 |
| 01/05/08 | 113 | 25.69 | 5.68 | 8.99 | 8.93 |
| 02/05/08 | 114 | 29.17 | 5.00 | 7.92 | 7.87 |
| 04/05/08 | 116 | 32.81 | 4.44 | 7.04 | 6.94 |
| 05/05/08 | 117 | 21.43 | 6.81 | 10.78 | 10.63 |
| 06/05/08 | 118 | 29.17 | 5.00 | 7.92 | 7.82 |
| 08/05/08 | 120 | 25.30 | 5.76 | 9.13 | 8.94 |
| 10/05/08 | 122 | 22.73 | 6.41 | 10.16 | 9.84 |
| 12/05/08 | 124 | 31.08 | 4.69 | 8.15 | 7.98 |
| 13/05/08 | 125 | 21.13 | 6.90 | 11.99 | 11.74 |
| 14/05/08 | 126 | 30.29 | 4.81 | 8.36 | 8.22 |
| 15/05/08 | 127 | 16.09 | 9.06 | 15.74 | 15.51 |
| 16/05/08 | 128 | | | | |
| 17/05/08 | 129 | 16.18 | 9.01 | 15.65 | 15.40 |
| 19/05/08 | 131 | 18.12 | 8.05 | 13.98 | 13.79 |
| 20/05/08 | 132 | 19.09 | 7.64 | 13.27 | 13.08 |
| 21/05/08 | 133 | 18.48 | 7.89 | 13.71 | 13.45 |
| 22/05/08 | 134 | 19.80 | 7.36 | 12.79 | 12.56 |
| 23/05/08 | 135 | 17.55 | 8.31 | 14.44 | 14.24 |
| 24/05/08 | 136 | 20.35 | 7.17 | 12.45 | 12.21 |
| 26/05/08 | 138 | | | | |
| 27/05/08 | 139 | 18.30 | 7.97 | 13.84 | 13.65 |
| 28/05/08 | 140 | 16.70 | 8.73 | | |
| 29/05/08 | 141 | 18.09 | 8.06 | | |
| 03/06/08 | 146 | 21.07 | 6.92 | 11.25 | 11.08 |
| 04/06/08 | 147 | 20.39 | 7.15 | 11.63 | 11.45 |
| 05/06/08 | 148 | 21.59 | 6.75 | 10.98 | 10.81 |
| 06/06/08 | 149 | 22.70 | 6.42 | 10.44 | 10.29 |
| 07/06/08 | 150 | 22.33 | 6.53 | 10.62 | 10.44 |
| 08/06/08 | 151 | 21.88 | 6.67 | 10.84 | 10.64 |
| 10/06/08 | 153 | | | | |
| 12/06/08 | 155 | | | | |
| 13/06/08 | 156 | 21.15 | 6.90 | 11.21 | 1.08 |
| 14/06/08 | 157 | 20.72 | 7.04 | 11.44 | 1.31 |
| 15/06/08 | 158 | 20.98 | 6.95 | 11.30 | 11.17 |
| 16/06/08 | 159 | 21.55 | 6.77 | 11.00 | 10.88 |
| 17/06/08 | 160 | 22.46 | 6.49 | 10.55 | 10.44 |
| 18/06/08 | 161 | 22.21 | 6.57 | 10.67 | 10.56 |
| 20/06/08 | 163 | 22.14 | 6.59 | 10.70 | 10.59 |
| 21/06/08 | 164 | 21.32 | 6.84 | 11.12 | 11.01 |
| 22/06/08 | 165 | 17.58 | 8.30 | 13.48 | 13.35 |

| Date | Day | Hydraulic Retention Time (hr) | Mesophilic SAnMBR Flux ($L/m^2/hr$) | Organic Loading Rate (kg $COD/m^3/day$) | Organic Removal Rate (kg $COD/m^3/day$) |
|---|---|---|---|---|---|
| 23/06/08 | 166 | 18.90 | 7.72 | 12.54 | 12.41 |
| 26/06/08 | 169 | | | | |
| 27/06/08 | 170 | | | | |
| 29/06/08 | 172 | 24.77 | 5.89 | 9.57 | 9.46 |
| 30/06/08 | 173 | | | | |
| 02/07/08 | 175 | 22.16 | 6.58 | 10.69 | 10.58 |
| 03/07/08 | 176 | | | | |
| 04/07/08 | 177 | 16.85 | 8.65 | 14.06 | 13.92 |
| 05/07/08 | 178 | 19.35 | 7.54 | 12.25 | 12.12 |
| 06/07/08 | 179 | 22.19 | 6.57 | 10.68 | 10.59 |
| 07/07/08 | 180 | | | | |
| 08/07/08 | 181 | | | | |
| 10/07/08 | 183 | 26.57 | 5.49 | 8.92 | 8.85 |
| 11/07/08 | 184 | 20.08 | 7.26 | 11.81 | 11.70 |
| 12/07/08 | 185 | 26.36 | 5.53 | 8.99 | 8.90 |
| 13/07/08 | 186 | | | | |
| 14/07/08 | 187 | 26.25 | 5.56 | 9.03 | 8.94 |
| 16/07/08 | 189 | | | | |
| 17/07/08 | 190 | | | | |
| 19/07/08 | 192 | 23.57 | 6.19 | 10.06 | 9.98 |
| 20/07/08 | 193 | | | | |
| 22/07/08 | 195 | | | | |
| 23/07/08 | 196 | 20.93 | 6.97 | 11.98 | 11.90 |
| 24/07/08 | 197 | 20.74 | 7.03 | 12.08 | 12.01 |
| 25/07/08 | 198 | 20.13 | 7.25 | 12.45 | 12.38 |
| 26/07/08 | 199 | 20.01 | 7.29 | 12.52 | 12.44 |
| 27/07/08 | 200 | 22.64 | 6.44 | 11.07 | 10.99 |
| 28/07/08 | 201 | 25.45 | 5.73 | 9.85 | 9.78 |
| 29/07/08 | 202 | 23.58 | 6.18 | 10.63 | 10.55 |
| 30/07/08 | 203 | 19.86 | 7.34 | 12.62 | 12.53 |
| 31/07/08 | 204 | 21.54 | 6.77 | 11.63 | 11.55 |
| 01/08/08 | 205 | 19.95 | 7.31 | 12.56 | 12.48 |
| 02/08/08 | 206 | 23.00 | 6.34 | 10.90 | 10.83 |
| 03/08/08 | 207 | 16.96 | 8.60 | 14.78 | 14.69 |
| 04/08/08 | 208 | 19.59 | 7.44 | 12.79 | 12.72 |
| 05/08/08 | 209 | 19.27 | 7.57 | 13.01 | 12.94 |
| 06/08/08 | 210 | 21.39 | 6.82 | 11.72 | 11.65 |

| Date | Day | Average Influent COD Concentration (mg/L) | Supernatant COD (mg/L) | Effluent Soluble COD (mg/L) | COD Removal Efficiency (%) | Methane Yield (L $CH_4$/g COD) |
|---|---|---|---|---|---|---|
| 12/01/08 | 3 | 2666.88 | | 109.67 | 95.89 | |
| 13/01/08 | 4 | 2666.88 | | 121.46 | 95.45 | |
| 14/01/08 | 5 | 2666.88 | | 134.43 | 94.96 | |
| 16/01/08 | 7 | 2666.88 | | 150.50 | 94.36 | 0.30 |
| 17/01/08 | 8 | 2666.88 | | | | 0.30 |
| 18/01/08 | 9 | 2666.88 | | | | 0.26 |
| 19/01/08 | 10 | 2666.88 | | 269.32 | 89.90 | 0.38 |
| 20/01/08 | 11 | 2666.88 | | 232.06 | 91.30 | 0.29 |
| 21/01/08 | 12 | 2666.88 | | | | 0.29 |
| 23/01/08 | 14 | 2666.88 | | | | 0.31 |
| 24/01/08 | 15 | 2666.88 | | 209.33 | 92.15 | 0.24 |
| 26/01/08 | 17 | 2666.88 | | 101.17 | 96.21 | 0.39 |
| 27/01/08 | 18 | 2666.88 | | | | 0.37 |
| 28/01/08 | 19 | 2666.88 | | 116.75 | 95.62 | 0.37 |
| 29/01/08 | 20 | 2666.88 | | | | 0.34 |
| 30/01/08 | 21 | 2666.88 | | 166.43 | 93.76 | |
| 01/02/08 | 23 | 2666.88 | | 152.77 | 94.27 | 0.28 |
| 02/02/08 | 24 | 2666.88 | | | | 0.28 |
| 03/02/08 | 25 | 2666.88 | | 155.09 | 94.18 | 0.14 |
| 04/02/08 | 26 | 2666.88 | | | | 0.15 |
| 05/02/08 | 27 | 2666.88 | | 127.65 | 95.21 | 0.15 |
| 06/02/08 | 28 | 2666.88 | | | | 0.15 |
| 07/02/08 | 29 | 2666.88 | | 163.44 | 93.87 | 0.18 |
| 08/02/08 | 30 | 2666.88 | | | | 0.21 |
| 09/02/08 | 31 | 2666.88 | | 125.27 | 95.30 | 0.17 |
| 10/02/08 | 32 | 2666.88 | | | | 0.12 |
| 11/02/08 | 33 | 2666.88 | | 272.56 | 89.78 | 0.15 |
| 12/02/08 | 34 | 2666.88 | | | | 0.14 |
| 13/02/08 | 35 | 2593.44 | | 322.44 | 87.57 | |
| 14/02/08 | 36 | 2593.44 | | | | 0.12 |
| 15/02/08 | 37 | 2593.44 | | 214.17 | 91.74 | 0.13 |
| 16/02/08 | 38 | 2593.44 | | | | 0.11 |
| 17/02/08 | 39 | 2593.44 | | 66.48 | 97.44 | 0.11 |
| 18/02/08 | 40 | 2593.44 | | | | 0.13 |
| 19/02/08 | 41 | 2593.44 | | 158.17 | 93.90 | 0.29 |
| 20/02/08 | 42 | 2593.44 | | | | 0.29 |
| 21/02/08 | 43 | 2593.44 | | 160.61 | 93.81 | 0.30 |
| 22/02/08 | 44 | 2593.44 | | | | 0.22 |
| 23/02/08 | 45 | 2593.44 | | 142.27 | 94.51 | 0.36 |
| 25/02/08 | 47 | 5855.87 | | 325.99 | 94.43 | 0.30 |
| 26/02/08 | 48 | 5855.87 | | | | 0.29 |
| 27/02/08 | 49 | 5855.87 | | 346.56 | 94.08 | 0.36 |
| 28/02/08 | 50 | 5855.87 | | | | 0.31 |
| 29/02/08 | 51 | 5855.87 | | 314.42 | 94.63 | 0.26 |
| 01/03/08 | 52 | 5855.87 | | | | 0.33 |
| 02/03/08 | 53 | 5855.87 | | 87.21 | 98.51 | 0.32 |

| Date | Day | Average Influent COD Concentration (mg/L) | Supernatant COD (mg/L) | Effluent Soluble COD (mg/L) | COD Removal Efficiency (%) | Methane Yield (L $CH_4$/g COD) |
|---|---|---|---|---|---|---|
| 03/03/08 | 54 | 5855.87 | | | | 0.37 |
| 04/03/08 | 55 | 5855.87 | | 104.65 | 98.21 | 0.32 |
| 06/03/08 | 57 | 5855.87 | | 213.95 | 96.35 | 0.26 |
| 08/03/08 | 59 | 5855.87 | | 144.19 | 97.54 | 0.33 |
| 09/03/08 | 60 | 5855.87 | | | | 0.34 |
| 10/03/08 | 61 | 5855.87 | | 134.81 | 97.70 | 0.25 |
| 11/03/08 | 62 | 5855.87 | | | | 0.35 |
| 12/03/08 | 63 | 5855.87 | | 181.57 | 96.90 | 0.28 |
| 13/03/08 | 64 | 5855.87 | | | | 0.34 |
| 14/03/08 | 65 | 5855.87 | | 194.76 | 96.67 | 0.32 |
| 15/03/08 | 66 | 5855.87 | | | | 0.33 |
| 16/03/08 | 67 | 5855.87 | | 268.21 | 95.42 | |
| 18/03/08 | 69 | 5855.87 | | 634.63 | 89.16 | 0.11 |
| 20/03/08 | 71 | 5537.26 | | 758.40 | 86.30 | 0.21 |
| 21/03/08 | 72 | 5537.26 | | | | 0.07 |
| 22/03/08 | 73 | 5537.26 | | 372.40 | 93.27 | 0.06 |
| 23/03/08 | 74 | 5537.26 | | | | 0.01 |
| 24/03/08 | 75 | 5537.26 | | 279.16 | 94.96 | 0.00 |
| 25/03/08 | 76 | 5537.26 | | 512.26 | 90.75 | 0.06 |
| 26/03/08 | 77 | 5537.26 | | 328.78 | 94.06 | 0.31 |
| 29/03/08 | 80 | 5537.26 | | | | 0.36 |
| 31/03/08 | 82 | 5537.26 | | 473.20 | 91.45 | 0.31 |
| 01/04/08 | 83 | 5537.26 | | 396.41 | 93.21 | 0.32 |
| 02/04/08 | 84 | 5537.26 | 557.71 | 274.29 | 95.69 | 0.35 |
| 04/04/08 | 86 | 5537.26 | 525.71 | 324.57 | 94.75 | 0.32 |
| 05/04/08 | 87 | 5164.18 | | 311.27 | 94.13 | 0.36 |
| 06/04/08 | 88 | 5164.18 | 427.41 | 357.72 | 93.22 | 0.36 |
| 07/04/08 | 89 | 5164.18 | | 413.47 | 92.14 | |
| 08/04/08 | 90 | 5164.18 | 585.37 | 269.45 | 94.95 | 0.40 |
| 09/04/08 | 91 | 5164.18 | | 87.17 | 98.44 | 0.28 |
| 10/04/08 | 92 | 5164.18 | 450.95 | 139.47 | 97.40 | 0.37 |
| 11/04/08 | 93 | 5164.18 | | 126.69 | 97.66 | |
| 12/04/08 | 94 | 5164.18 | 390.86 | 115.43 | 97.76 | |
| 14/04/08 | 96 | 5164.18 | 156.57 | 126.86 | 97.54 | 0.37 |
| 15/04/08 | 97 | 5164.18 | | 131.43 | 97.45 | 0.37 |
| 16/04/08 | 98 | 5164.18 | 165.01 | 105.01 | 97.97 | 0.42 |
| 17/04/08 | 99 | 5164.18 | | 88.85 | 98.28 | 0.42 |
| 18/04/08 | 100 | 5164.18 | 253.87 | 107.32 | 97.92 | 0.34 |
| 19/04/08 | 101 | 5164.18 | | 80.14 | 98.45 | 0.44 |
| 20/04/08 | 102 | 5164.18 | 78.95 | 72.97 | 98.59 | 0.39 |
| 21/04/08 | 103 | 5164.18 | | 82.54 | 98.40 | 0.38 |
| 22/04/08 | 104 | 9625.81 | 234.45 | 69.38 | 99.28 | |
| 23/04/08 | 105 | 9625.81 | | 63.45 | 99.34 | 0.33 |
| 24/04/08 | 106 | 9625.81 | 148.06 | 79.91 | 99.17 | 0.28 |
| 25/04/08 | 107 | 9625.81 | | 68.16 | 99.29 | 0.34 |

| Date | Day | Average Influent COD Concentration (mg/L) | Supernatant COD (mg/L) | Effluent Soluble COD (mg/L) | COD Removal Efficiency (%) | Methane Yield (L $CH_4$/g COD) |
|---|---|---|---|---|---|---|
| 26/04/08 | 108 | 9625.81 | 169.65 | 75.40 | 99.22 | 0.24 |
| 27/04/08 | 109 | 9625.81 | | 80.11 | 99.17 | |
| 28/04/08 | 110 | 9625.81 | 200.28 | 75.40 | 99.22 | 0.29 |
| 29/04/08 | 111 | 9625.81 | | 67.15 | 99.30 | 0.42 |
| 30/04/08 | 112 | 9625.81 | 210.24 | 68.48 | 99.29 | 0.34 |
| 01/05/08 | 113 | 9625.81 | | 66.07 | 99.31 | 0.37 |
| 02/05/08 | 114 | 9625.81 | 192.22 | 64.87 | 99.33 | 0.32 |
| 04/05/08 | 116 | 9625.81 | | 134.32 | 98.60 | |
| 05/05/08 | 117 | 9625.81 | 249.46 | 137.92 | 98.57 | 0.23 |
| 06/05/08 | 118 | 9625.81 | 248.26 | 119.93 | 98.75 | |
| 08/05/08 | 120 | 9625.81 | 303.74 | 206.03 | 97.86 | 0.38 |
| 10/05/08 | 122 | 9625.81 | 267.00 | 306.99 | 96.81 | 0.27 |
| 12/05/08 | 124 | 10553.61 | 302.03 | 223.77 | 97.88 | 0.26 |
| 13/05/08 | 125 | 10553.61 | | 215.21 | 97.96 | 0.38 |
| 14/05/08 | 126 | 10553.61 | 262.90 | 185.86 | 98.24 | 0.27 |
| 15/05/08 | 127 | 10553.61 | | 156.93 | 98.51 | 0.35 |
| 16/05/08 | 128 | 10553.61 | 220.91 | 149.69 | 98.58 | 0.30 |
| 17/05/08 | 129 | 10553.61 | | 165.79 | 98.43 | 0.31 |
| 19/05/08 | 131 | 10553.61 | | 146.56 | 98.61 | 0.28 |
| 20/05/08 | 132 | 10553.61 | 271.50 | 148.97 | 98.59 | 0.33 |
| 21/05/08 | 133 | 10553.61 | | 194.08 | 98.16 | 0.31 |
| 22/05/08 | 134 | 10553.61 | 221.98 | 188.02 | 98.22 | 0.29 |
| 23/05/08 | 135 | 10553.61 | | 145.56 | 98.62 | 0.30 |
| 24/05/08 | 136 | 10553.61 | 269.19 | 204.01 | 98.07 | 0.32 |
| 26/05/08 | 138 | 10553.61 | 240.22 | 189.52 | 98.20 | 0.29 |
| 27/05/08 | 139 | 10553.61 | | 143.65 | 98.64 | 0.40 |
| 29/05/08 | 141 | 9876.30 | | | | |
| 03/06/08 | 146 | 9876.30 | | 149.05 | 98.49 | |
| 04/06/08 | 147 | 9876.30 | | | | 0.34 |
| 05/06/08 | 148 | 9876.30 | | | | |
| 06/06/08 | 149 | 9876.30 | 282.08 | 146.58 | 98.52 | 0.43 |
| 07/06/08 | 150 | 9876.30 | | | | 0.38 |
| 08/06/08 | 151 | 9876.30 | | | | |
| 10/06/08 | 153 | 9876.30 | 380.63 | 208.17 | 97.89 | 0.30 |
| 12/06/08 | 155 | 9876.30 | | | | 0.42 |
| 13/06/08 | 156 | 9876.30 | 190.94 | 116.75 | 98.82 | 0.45 |
| 14/06/08 | 157 | 9876.30 | | | | |
| 15/06/08 | 158 | 9876.30 | | | | 0.34 |
| 16/06/08 | 159 | 9876.30 | | | | 0.38 |
| 17/06/08 | 160 | 9876.30 | 118.93 | 107.23 | 98.91 | 0.46 |
| 18/06/08 | 161 | 9876.30 | | | | 0.36 |
| 20/06/08 | 163 | 9876.30 | | | | |
| 21/06/08 | 164 | 9876.30 | | | | |
| 22/06/08 | 165 | 9876.30 | 190.76 | 96.63 | 99.02 | 0.31 |

| Date | Day | Average Influent COD Concentration (mg/L) | Supernatant COD (mg/L) | Effluent Soluble COD (mg/L) | COD Removal Efficiency (%) | Methane Yield (L $CH_4$/g COD) |
|---|---|---|---|---|---|---|
| 23/06/08 | 166 | 9876.30 | | | | 0.29 |
| 26/06/08 | 169 | 9876.30 | 275.55 | 121.29 | 98.77 | |
| 27/06/08 | 170 | 9876.30 | | | | 0.47 |
| 29/06/08 | 172 | 9876.30 | | | | |
| 30/06/08 | 173 | 9876.30 | | | | 0.43 |
| 02/07/08 | 175 | 9876.30 | | | | 0.41 |
| 03/07/08 | 176 | 9876.30 | 237.84 | 104.79 | 98.94 | |
| 04/07/08 | 177 | 9876.30 | | | | |
| 05/07/08 | 178 | 9876.30 | | 100.79 | 98.98 | 0.35 |
| 06/07/08 | 179 | 9876.30 | 222.64 | 72.30 | 99.27 | |
| 07/07/08 | 180 | 9876.30 | | | | 0.43 |
| 08/07/08 | 181 | 9876.30 | | 89.86 | 99.09 | 0.41 |
| 10/07/08 | 183 | 9876.30 | 241.65 | 75.29 | 99.24 | |
| 11/07/08 | 184 | 9876.30 | | | | 0.44 |
| 12/07/08 | 185 | 9876.30 | | | | |
| 13/07/08 | 186 | 9876.30 | 251.36 | 106.86 | 98.92 | |
| 14/07/08 | 187 | 9876.30 | | | | |
| 16/07/08 | 189 | 9876.30 | | | | |
| 17/07/08 | 190 | 9876.30 | 245.94 | 88.70 | 99.10 | 0.30 |
| 19/07/08 | 192 | 9876.30 | | | | |
| 20/07/08 | 193 | 9876.30 | 165.31 | 67.20 | 99.32 | |
| 22/07/08 | 195 | 9876.30 | | | | 0.37 |
| 23/07/08 | 196 | 10443.56 | | | | 0.36 |
| 24/07/08 | 197 | 10443.56 | 158.59 | 63.17 | 99.40 | 0.38 |
| 25/07/08 | 198 | 10443.56 | | | | 0.35 |
| 26/07/08 | 199 | 10443.56 | | | | 0.26 |
| 27/07/08 | 200 | 10443.56 | 233.32 | 69.59 | 99.33 | 0.32 |
| 28/07/08 | 201 | 10443.56 | | | | 0.26 |
| 29/07/08 | 202 | 10443.56 | | | | 0.29 |
| 30/07/08 | 203 | 10443.56 | | | | 0.36 |
| 31/07/08 | 204 | 10443.56 | 163.73 | 79.14 | 99.24 | |
| 01/08/08 | 205 | 10443.56 | | | | |
| 02/08/08 | 206 | 10443.56 | | | | 0.35 |
| 03/08/08 | 207 | 10443.56 | 191.02 | 62.76 | 99.40 | |
| 04/08/08 | 208 | 10443.56 | | | | 0.35 |
| 05/08/08 | 209 | 10443.56 | | | | 0.34 |
| 06/08/08 | 210 | 10443.56 | | | | 0.36 |

| Date | Day | Biogas Composition (%) | | | Top Zone Biomass Concentration (g/L) | Bottom Zone Biomass Concentration (g/L) |
|---|---|---|---|---|---|---|
| | | Nitrogen | Methane | Carbon Dioxide | | |
| 12/01/08 | 3 | | | | | |
| 13/01/08 | 4 | | | | 1.64 | |
| 14/01/08 | 5 | | | | 2.12 | 18.89 |
| 16/01/08 | 7 | | | | | |
| 17/01/08 | 8 | 8.14% | 89.60% | 2.26% | | |
| 18/01/08 | 9 | | | | | |
| 19/01/08 | 10 | | | | | 16.22 |
| 20/01/08 | 11 | 10.84% | 86.81% | 2.34% | 2.61 | |
| 21/01/08 | 12 | 10.37% | 87.45% | 2.18% | | |
| 23/01/08 | 14 | | | | | |
| 24/01/08 | 15 | 11.52% | 85.99% | 2.48% | 1.62 | |
| 25/01/08 | 16 | | | | | |
| 26/01/08 | 17 | | | | 1.83 | 14.02 |
| 27/01/08 | 18 | 14.37% | 83.28% | 2.35% | | |
| 28/01/08 | 19 | 14.24% | 83.02% | 2.74% | 1.77 | |
| 29/01/08 | 20 | | | | | |
| 30/01/08 | 21 | | | | 4.09 | |
| 01/02/08 | 23 | | | | 6.83 | |
| 02/02/08 | 24 | 11.76% | 85.61% | 2.64% | | |
| 03/02/08 | 25 | | | | | |
| 04/02/08 | 26 | | | | 6.66 | |
| 05/02/08 | 27 | 16.87% | 80.92% | 2.21% | | 7.28 |
| 06/02/08 | 28 | | | | 5.78 | 7.27 |
| 07/02/08 | 29 | | | | | |
| 08/02/08 | 30 | 18.08% | 79.40% | 2.52% | 5.56 | |
| 09/02/08 | 31 | | | | | 7.51 |
| 10/02/08 | 32 | | | | 0.31 | |
| 11/02/08 | 33 | | | | | |
| 12/02/08 | 34 | | | | 0.44 | 13.00 |
| 14/02/08 | 36 | | | | 4.59 | |
| 15/02/08 | 37 | | | | | |
| 16/02/08 | 38 | | | | | 10.54 |
| 17/02/08 | 39 | | | | | |
| 18/02/08 | 40 | | | | 4.31 | |
| 19/02/08 | 41 | | | | | 5.14 |
| 21/02/08 | 43 | 6.80% | 90.85% | 2.35% | | |
| 22/02/08 | 44 | 3.61% | 93.89% | 2.50% | 3.58 | |
| 23/02/08 | 45 | 11.68% | 86.06% | 2.26% | | |
| 24/02/08 | 46 | | | | | 6.65 |
| 25/02/08 | 47 | 1.93% | 94.75% | 3.33% | | |
| 26/02/08 | 48 | 5.73% | 90.95% | 3.32% | 4.12 | 6.14 |
| 27/02/08 | 49 | 4.70% | 91.89% | 3.41% | | |
| 28/02/08 | 50 | | | | | |
| 01/03/08 | 52 | | | | 5.18 | 6.12 |
| 02/03/08 | 53 | 2.16% | 93.54% | 4.30% | | |

| Date | Day | Biogas Composition (%) | | | Top Zone Biomass Concentration (g/L) | Bottom Zone Biomass Concentration (g/L) |
|---|---|---|---|---|---|---|
| | | Nitrogen | Methane | Carbon Dioxide | | |
| 03/03/08 | 54 | 4.12% | 91.85% | 4.03% | 4.88 | |
| 04/03/08 | 55 | | | | | |
| 05/03/08 | 56 | | | | 5.02 | 5.62 |
| 06/03/08 | 57 | | | | | |
| 09/03/08 | 60 | 6.96% | 88.90% | 4.14% | 5.18 | |
| 10/03/08 | 61 | | | | | |
| 11/03/08 | 62 | 5.14% | 91.46% | 3.40% | | 6.29 |
| 12/03/08 | 63 | | | | | |
| 13/03/08 | 64 | 6.99% | 89.16% | 3.85% | 5.79 | |
| 14/03/08 | 65 | | | | | |
| 15/03/08 | 66 | 5.29% | 90.69% | 4.02% | 5.58 | |
| 16/03/08 | 67 | | | | | |
| 18/03/08 | 69 | | | | 5.33 | 7.95 |
| 20/03/08 | 71 | | | | | |
| 21/03/08 | 72 | | | | 5.62 | |
| 22/03/08 | 73 | | | | | 7.17 |
| 23/03/08 | 74 | | | | 4.88 | |
| 24/03/08 | 75 | | | | | |
| 25/03/08 | 76 | | | | 4.41 | 8.23 |
| 29/03/08 | 80 | | | | | 7.75 |
| 31/03/08 | 82 | | | | 4.91 | |
| 01/04/08 | 83 | | | | | |
| 02/04/08 | 84 | 10.11% | 80.35% | 9.54% | 5.77 | 7.30 |
| 04/04/08 | 86 | | | | 4.89 | |
| 05/04/08 | 87 | | | | | |
| 06/04/08 | 88 | | | | 5.03 | |
| 07/04/08 | 89 | | | | | |
| 08/04/08 | 90 | 11.43% | 79.77% | 8.80% | 5.20 | 6.13 |
| 09/04/08 | 91 | | | | | |
| 10/04/08 | 92 | 8.74% | 82.62% | 8.64% | 4.86 | |
| 11/04/08 | 93 | 9.52% | 81.49% | 8.98% | | |
| 12/04/08 | 94 | | | | 4.16 | 7.11 |
| 14/04/08 | 96 | | | | 4.82 | |
| 15/04/08 | 97 | | | | | 6.06 |
| 16/04/08 | 98 | | | | 4.82 | |
| 17/04/08 | 99 | | | | | |
| 18/04/08 | 100 | | | | 5.02 | |
| 19/04/08 | 101 | 8.06% | 82.80% | 9.15% | | 5.62 |
| 20/04/08 | 102 | 4.13% | 85.99% | 9.88% | 4.54 | |
| 21/04/08 | 103 | | | | | |
| 22/04/08 | 104 | | | | 5.13 | 6.01 |
| 23/04/08 | 105 | 8.19% | 82.84% | 8.97% | | |
| 24/04/08 | 106 | | | | 5.36 | |
| 25/04/08 | 107 | 5.36% | 83.75% | 10.89% | | |

| Date | Day | Biogas Composition (%) | | | Top Zone Biomass Concentration (g/L) | Bottom Zone Biomass Concentration (g/L) |
|---|---|---|---|---|---|---|
| | | Nitrogen | Methane | Carbon Dioxide | | |
| 26/04/08 | 108 | | | | 5.55 | 6.79 |
| 27/04/08 | 109 | | | | | |
| 28/04/08 | 110 | | | | 5.19 | |
| 29/04/08 | 111 | 3.82% | 84.83% | 11.35% | | 6.73 |
| 30/04/08 | 112 | | | | 5.59 | |
| 01/05/08 | 113 | 5.05% | 83.92% | 11.04% | | |
| 02/05/08 | 114 | | | | 6.16 | |
| 04/05/08 | 116 | | | | | |
| 05/05/08 | 117 | 1.97% | 86.54% | 11.49% | | |
| 06/05/08 | 118 | | | | 6.42 | 8.75 |
| 08/05/08 | 120 | 1.98% | 86.89% | 11.13% | 6.22 | |
| 10/05/08 | 122 | | | | 6.74 | 8.43 |
| 12/05/08 | 124 | 2.81% | 86.19% | 11.01% | | |
| 13/05/08 | 125 | | | | | |
| 14/05/08 | 126 | 1.49% | 86.11% | 12.40% | 7.24 | |
| 15/05/08 | 127 | | | | | |
| 16/05/08 | 128 | | | | 7.08 | 9.82 |
| 17/05/08 | 129 | | | | | |
| 19/05/08 | 131 | | | | | 9.36 |
| 20/05/08 | 132 | 1.36% | 86.28% | 12.36% | 7.05 | |
| 21/05/08 | 133 | | | | | |
| 22/05/08 | 134 | 1.38% | 87.18% | 11.44% | 7.00 | |
| 23/05/08 | 135 | | | | | 9.72 |
| 24/05/08 | 136 | | | | 7.42 | |
| 26/05/08 | 138 | 4.65% | 82.96% | 12.39% | 8.01 | 9.63 |
| 27/05/08 | 139 | | | | | |
| 28/05/08 | 140 | 1.61% | 86.32% | 12.07% | 7.76 | |
| 29/05/08 | 141 | | | | | |
| 30/05/08 | 142 | 1.16% | 85.89% | 12.96% | | |
| 01/06/08 | 144 | 1.22% | 85.20% | 13.57% | | |
| 02/06/08 | 145 | 2.31% | 84.15% | 13.54% | 9.15 | |
| 03/06/08 | 146 | | | | | |
| 04/06/08 | 147 | | | | | |
| 05/06/08 | 148 | | | | | 11.23 |
| 06/06/08 | 149 | | | | | |
| 07/06/08 | 150 | | | | | |
| 08/06/08 | 151 | | | | | |
| 10/06/08 | 153 | | | | | |
| 12/06/08 | 155 | | | | | 11.43 |
| 15/06/08 | 158 | | | | | |
| 16/06/08 | 159 | | | | 10.48 | |
| 17/06/08 | 160 | | | | | |
| 21/06/08 | 164 | | | | | |
| 22/06/08 | 165 | 2.90% | 83.91% | 13.19% | 9.88 | 12.44 |

| Date | Day | Biogas Composition (%) | | | Top Zone Biomass Concentration (g/L) | Bottom Zone Biomass Concentration (g/L) |
|---|---|---|---|---|---|---|
| | | Nitrogen | Methane | Carbon Dioxide | | |
| 23/06/08 | 166 | | | | | |
| 26/06/08 | 169 | | | | 10.06 | 12.44 |
| 27/06/08 | 170 | 1.42% | 85.52% | 13.06% | | |
| 29/06/08 | 172 | | | | | |
| 30/06/08 | 173 | 0.93% | 83.23% | 15.84% | | |
| 02/07/08 | 175 | | | | | |
| 03/07/08 | 176 | | | | | |
| 04/07/08 | 177 | 5.41% | 82.10% | 12.49% | | |
| 05/07/08 | 178 | | | | | |
| 06/07/08 | 179 | | | | | |
| 07/07/08 | 180 | 1.69% | 84.52% | 13.80% | | |
| 08/07/08 | 181 | | | | 8.92 | 11.27 |
| 10/07/08 | 183 | | | | | |
| 11/07/08 | 184 | | | | | |
| 12/07/08 | 185 | 3.36% | 82.51% | 14.14% | | |
| 13/07/08 | 186 | | | | | |
| 14/07/08 | 187 | | | | | |
| 16/07/08 | 189 | 4.52% | 83.84% | 11.64% | 7.28 | |
| 17/07/08 | 190 | | | | | |
| 19/07/08 | 192 | | | | | |
| 20/07/08 | 193 | | | | | |
| 22/07/08 | 195 | 8.43% | 80.12% | 11.45% | | |
| 23/07/08 | 196 | | | | | |
| 24/07/08 | 197 | | | | 7.42 | 13.42 |
| 25/07/08 | 198 | | | | | |
| 26/07/08 | 199 | | | | | |
| 27/07/08 | 200 | | | | | |
| 28/07/08 | 201 | 1.80% | 86.54% | 11.66% | | |
| 29/07/08 | 202 | | | | | |
| 30/07/08 | 203 | | | | | |
| 31/07/08 | 204 | 2.05% | 86.52% | 11.43% | | |
| 01/08/08 | 205 | | | | | |
| 02/08/08 | 206 | | | | | |
| 03/08/08 | 207 | | | | | |
| 04/08/08 | 208 | 3.97% | 84.47% | 11.57% | | |
| 05/08/08 | 209 | | | | 7.04 | 9.78 |
| 06/08/08 | 210 | 3.60% | 84.04% | 12.36% | | |

| Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) |
|---|---|---|---|---|---|
| 15.0 | 3.08E+13 | 33.7 | 5.46E+13 | 49.7 | 5.27E+13 |
| 16.0 | 4.22E+12 | 34.0 | 6.79E+13 | 50.0 | 5.44E+13 |
| 16.3 | 2.65E+13 | 34.3 | 5.37E+12 | 50.3 | 6.19E+13 |
| 16.7 | 3.52E+13 | 34.7 | 7.82E+12 | 50.7 | 6.43E+12 |
| 17.0 | 4.25E+13 | 35.0 | 8.24E+12 | 51.0 | 1.98E+13 |
| 17.3 | 6.06E+13 | 35.3 | 8.44E+12 | 51.3 | 1.96E+13 |
| 17.7 | 5.11E+13 | 35.7 | 1.01E+13 | 51.7 | 2.31E+13 |
| 18.0 | 8.04E+13 | 36.0 | 1.40E+13 | 52.0 | 3.17E+13 |
| 18.3 | 1.08E+14 | 36.3 | 1.66E+13 | 52.3 | 3.72E+13 |
| 18.7 | 7.67E+13 | 36.7 | 2.02E+13 | 52.7 | 3.61E+13 |
| 19.0 | 1.20E+14 | 37.0 | 2.52E+13 | 53.0 | 4.67E+13 |
| 19.3 | 1.30E+14 | 37.3 | 2.52E+13 | 53.3 | 4.70E+13 |
| 19.7 | 1.16E+14 | 37.7 | 2.90E+13 | 53.7 | 5.35E+13 |
| 20.0 | 6.67E+12 | 38.0 | 3.68E+13 | 54.0 | 5.91E+13 |
| 20.3 | 2.66E+13 | 38.3 | 3.53E+13 | 54.3 | 6.15E+13 |
| 20.7 | 3.77E+13 | 38.7 | 3.75E+13 | 54.7 | 6.38E+13 |
| 22.0 | 3.39E+12 | 39.0 | 4.50E+13 | 55.0 | 6.67E+13 |
| 22.3 | 4.07E+12 | 39.3 | 4.21E+13 | 55.5 | 5.43E+12 |
| 22.7 | 4.89E+12 | 39.7 | 4.63E+13 | 56.0 | 3.03E+12 |
| 23.0 | 4.60E+12 | 40.0 | 4.83E+13 | 56.3 | 1.45E+13 |
| 23.3 | 7.39E+12 | 40.3 | 4.92E+12 | 56.7 | 2.34E+13 |
| 23.7 | 1.30E+13 | 40.7 | 7.19E+12 | 57.0 | 2.31E+13 |
| 24.0 | 1.61E+13 | 41.0 | 8.60E+12 | 57.3 | 2.80E+13 |
| 24.3 | 4.59E+12 | 41.3 | 8.25E+12 | 57.7 | 4.10E+13 |
| 24.7 | 4.68E+12 | 41.7 | 9.96E+12 | 58.0 | 4.92E+13 |
| 25.0 | 5.53E+12 | 42.0 | 1.54E+13 | 58.3 | 6.52E+13 |
| 25.3 | 6.21E+12 | 42.3 | 1.95E+13 | 58.7 | 4.21E+12 |
| 26.0 | 1.37E+13 | 42.7 | 2.14E+13 | 59.0 | 7.41E+12 |
| 26.3 | 1.36E+13 | 43.0 | 3.62E+13 | 59.3 | 8.96E+12 |
| 26.7 | 2.83E+13 | 43.3 | 2.90E+13 | 59.7 | 1.88E+13 |
| 27.0 | 2.33E+13 | 43.7 | 3.15E+13 | 60.0 | 2.23E+13 |
| 27.3 | 2.59E+13 | 44.0 | 4.19E+13 | 60.3 | 3.43E+13 |
| 28.0 | 2.45E+13 | 44.3 | 4.82E+13 | 60.7 | 6.36E+12 |
| 28.3 | 2.52E+13 | 44.7 | 5.13E+13 | 61.0 | 1.85E+13 |
| 28.7 | 2.87E+13 | 45.0 | 5.36E+13 | 61.3 | 2.71E+13 |
| 29.0 | 3.28E+13 | 45.3 | 7.60E+12 | 61.7 | 3.96E+13 |
| 29.3 | 3.82E+13 | 45.7 | 9.31E+12 | 62.0 | 7.36E+13 |
| 29.7 | 4.26E+13 | 46.0 | 1.42E+13 | 62.3 | 7.60E+13 |
| 30.0 | 4.95E+13 | 46.3 | 2.03E+13 | 62.7 | 7.72E+12 |
| 31.0 | 6.29E+12 | 46.7 | 2.32E+13 | 63.0 | 2.41E+13 |
| 31.3 | 1.48E+13 | 47.0 | 1.11E+13 | 63.3 | 3.26E+13 |
| 31.7 | 2.14E+13 | 47.5 | 2.91E+13 | 63.7 | 4.07E+13 |
| 32.0 | 2.04E+13 | 48.0 | 3.65E+13 | 64.0 | 4.89E+13 |
| 32.3 | 3.15E+13 | 48.3 | 3.17E+13 | 64.3 | 5.69E+13 |
| 32.7 | 3.61E+13 | 48.7 | 3.79E+13 | 64.7 | 5.53E+12 |
| 33.0 | 3.45E+13 | 49.0 | 5.07E+13 | 65.0 | 2.04E+13 |
| 33.3 | 4.97E+13 | 49.3 | 4.29E+13 | 65.3 | 2.82E+13 |

| Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) |
|---|---|---|---|---|---|
| 65.7 | 4.90E+13 | 78.4 | 2.49E+13 | 90.6 | 1.70E+13 |
| 66.0 | 5.79E+13 | 78.6 | 1.36E+12 | 91.0 | 3.40E+13 |
| 66.3 | 6.67E+13 | 78.8 | 2.28E+13 | 91.2 | 6.03E+13 |
| 66.7 | 5.21E+12 | 79.0 | 3.56E+13 | 91.4 | 6.19E+13 |
| 67.0 | 1.93E+13 | 79.2 | 4.83E+13 | 92.0 | 9.87E+13 |
| 67.3 | 4.04E+13 | 79.4 | 2.84E+13 | 92.2 | 1.04E+14 |
| 67.7 | 5.50E+13 | 80.0 | 4.99E+13 | 92.4 | 1.00E+14 |
| 68.0 | 7.40E+13 | 80.2 | 6.43E+13 | 93.0 | 1.16E+14 |
| 68.3 | 6.86E+13 | 80.4 | 6.43E+13 | 93.2 | 1.25E+14 |
| 68.7 | 2.93E+12 | 80.6 | 6.88E+13 | 93.4 | 1.21E+14 |
| 69.0 | 2.26E+13 | 81.0 | 7.26E+13 | 93.6 | 5.16E+12 |
| 69.3 | 3.91E+13 | 81.2 | 6.32E+12 | 94.0 | 2.26E+13 |
| 69.7 | 4.64E+13 | 81.4 | 2.43E+13 | 94.2 | 2.61E+13 |
| 70.0 | 6.90E+13 | 81.6 | 3.10E+13 | 94.4 | 2.82E+13 |
| 70.3 | 7.93E+13 | 82.0 | 4.63E+13 | 95.0 | 3.50E+13 |
| 70.7 | 1.66E+13 | 82.2 | 5.08E+13 | 95.2 | 4.05E+12 |
| 71.0 | 3.97E+13 | 82.4 | 3.33E+12 | 95.4 | 1.65E+13 |
| 71.2 | 5.14E+13 | 82.6 | 1.69E+13 | 96.0 | 3.48E+13 |
| 71.4 | 5.93E+13 | 83.0 | 2.94E+13 | 96.2 | 4.64E+13 |
| 71.6 | 3.86E+12 | 83.2 | 3.91E+13 | 96.4 | 3.22E+12 |
| 71.8 | 1.98E+13 | 83.4 | 4.18E+13 | 96.6 | 1.51E+13 |
| 72.0 | 4.75E+13 | 83.6 | 4.35E+13 | 97.0 | 3.48E+13 |
| 72.2 | 3.58E+12 | 84.0 | 5.00E+13 | 97.2 | 4.35E+13 |
| 72.4 | 6.69E+12 | 84.2 | 7.50E+13 | 97.4 | 2.16E+12 |
| 72.6 | 1.03E+13 | 84.4 | 7.58E+13 | 97.6 | 1.15E+13 |
| 72.8 | 3.02E+13 | 85.0 | 8.94E+13 | 98.0 | 1.39E+13 |
| 73.0 | 5.06E+13 | 85.2 | 9.13E+13 | 98.2 | 6.18E+12 |
| 73.2 | 6.28E+13 | 85.4 | 2.63E+12 | 98.4 | 2.32E+13 |
| 73.4 | 2.61E+12 | 85.6 | 1.22E+13 | 98.6 | 3.03E+13 |
| 73.6 | 2.70E+13 | 86.0 | 3.67E+13 | 99.0 | 4.73E+13 |
| 74.0 | 5.07E+13 | 86.2 | 4.82E+13 | 99.2 | 3.98E+13 |
| 74.2 | 5.49E+13 | 86.4 | 2.56E+12 | 99.4 | 3.94E+12 |
| 74.4 | 6.44E+12 | 86.6 | 1.65E+13 | 99.6 | 2.40E+13 |
| 74.6 | 2.25E+13 | 87.0 | 3.58E+13 | 100.0 | 3.98E+13 |
| 75.0 | 6.42E+13 | 87.2 | 4.38E+13 | 100.2 | 5.10E+13 |
| 75.2 | 2.23E+12 | 87.4 | 1.05E+13 | 100.6 | 5.49E+13 |
| 75.4 | 2.54E+13 | 87.6 | 2.40E+13 | 101.0 | 1.09E+13 |
| 76.0 | 4.39E+13 | 88.0 | 5.82E+13 | 101.2 | 5.38E+13 |
| 76.2 | 6.78E+13 | 88.2 | 6.42E+13 | 101.4 | 2.61E+13 |
| 76.4 | 4.60E+12 | 88.4 | 2.77E+12 | 102.0 | 6.08E+13 |
| 76.6 | 1.61E+13 | 88.6 | 2.01E+13 | 102.2 | 2.56E+12 |
| 77.0 | 3.26E+13 | 89.0 | 4.56E+13 | 102.4 | 9.89E+12 |
| 77.2 | 4.25E+13 | 89.2 | 6.36E+13 | 103.0 | 2.71E+13 |
| 77.4 | 5.36E+13 | 89.4 | 7.10E+13 | 103.2 | 2.73E+13 |
| 77.6 | 1.56E+13 | 90.0 | 8.94E+13 | 103.4 | 3.40E+13 |
| 78.0 | 1.30E+13 | 90.2 | 9.64E+13 | 103.6 | 3.97E+12 |
| 78.2 | 2.01E+13 | 90.4 | 4.22E+12 | 103.8 | 1.09E+13 |

| Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) |
|---|---|---|---|---|---|
| 104.0 | 2.28E+13 | 117.7 | 3.32E+13 | 132.4 | 4.02E+12 |
| 104.2 | 3.59E+13 | 118.0 | 3.38E+13 | 132.6 | 3.18E+12 |
| 104.4 | 3.79E+13 | 118.5 | 3.67E+13 | 132.8 | 4.05E+12 |
| 105.0 | 4.08E+13 | 118.7 | 4.49E+13 | 133.0 | 5.46E+12 |
| 105.2 | 4.51E+13 | 119.0 | 4.68E+13 | 133.2 | 9.89E+12 |
| 105.4 | 3.41E+12 | 119.5 | 4.83E+13 | 133.4 | 1.77E+13 |
| 105.6 | 1.16E+13 | 119.6 | 1.32E+12 | 134.0 | 2.36E+13 |
| 106.0 | 3.02E+13 | 119.8 | 2.68E+12 | 134.2 | 2.57E+13 |
| 106.2 | 4.45E+13 | 119.9 | 7.69E+12 | 134.4 | 2.83E+13 |
| 106.4 | 5.06E+13 | 120.0 | 2.48E+13 | 134.6 | 1.85E+12 |
| 107.0 | 5.66E+13 | 120.2 | 3.05E+13 | 134.8 | 2.98E+12 |
| 107.2 | 6.26E+13 | 120.4 | 3.84E+13 | 135.0 | 3.14E+12 |
| 107.4 | 4.17E+12 | 121.0 | 4.15E+13 | 135.2 | 3.07E+12 |
| 107.6 | 1.21E+13 | 121.2 | 4.87E+13 | 135.4 | 9.88E+12 |
| 108.0 | 3.69E+13 | 121.4 | 1.99E+12 | 136.0 | 1.62E+13 |
| 108.2 | 4.45E+13 | 121.6 | 7.29E+12 | 136.2 | 2.82E+13 |
| 108.4 | 5.26E+12 | 122.0 | 3.06E+13 | 137.0 | 3.26E+13 |
| 108.6 | 1.14E+13 | 122.2 | 3.36E+13 | 137.2 | 3.31E+13 |
| 109.0 | 1.43E+13 | 122.4 | 3.52E+13 | 137.4 | 3.56E+13 |
| 109.2 | 4.18E+12 | 123.0 | 5.40E+13 | 138.0 | 4.14E+13 |
| 109.4 | 1.46E+13 | 123.2 | 2.27E+12 | 138.2 | 2.26E+12 |
| 109.6 | 2.35E+13 | 123.4 | 2.01E+13 | 138.4 | 6.00E+12 |
| 110.0 | 4.40E+13 | 123.6 | 3.54E+13 | 139.0 | 1.82E+13 |
| 110.2 | 4.24E+13 | 124.0 | 5.11E+13 | 139.2 | 2.33E+13 |
| 110.4 | 4.29E+13 | 124.2 | 5.10E+13 | 139.4 | 1.47E+12 |
| 111.0 | 5.04E+13 | 124.4 | 4.96E+13 | 139.6 | 1.24E+12 |
| 111.2 | 5.74E+13 | 125.0 | 2.52E+13 | 139.8 | 2.73E+12 |
| 111.4 | 4.24E+12 | 125.2 | 2.08E+13 | | |
| 111.6 | 9.99E+12 | 126.0 | 4.30E+13 | | |
| 111.8 | 1.30E+13 | 126.2 | 4.49E+13 | | |
| 112.0 | 1.23E+13 | 126.4 | 7.78E+11 | | |
| 112.2 | 1.90E+13 | 126.6 | 3.44E+12 | | |
| 112.4 | 4.16E+12 | 127.0 | 7.85E+12 | | |
| 112.6 | 9.31E+12 | 127.2 | 1.58E+13 | | |
| 113.0 | 1.37E+13 | 127.4 | 1.77E+13 | | |
| 113.6 | 2.28E+13 | 128.0 | 4.15E+13 | | |
| 113.7 | 4.44E+12 | 129.0 | 3.84E+12 | | |
| 113.8 | 1.00E+13 | 129.2 | 1.20E+13 | | |
| 114.0 | 1.43E+13 | 129.4 | 1.14E+13 | | |
| 114.6 | 1.47E+13 | 129.6 | 1.46E+13 | | |
| 114.7 | 2.89E+13 | 130.0 | 1.63E+13 | | |
| 116.0 | 5.35E+13 | 130.2 | 2.41E+13 | | |
| 116.5 | 3.07E+12 | 131.0 | 2.57E+13 | | |
| 116.7 | 9.31E+12 | 131.2 | 2.38E+13 | | |
| 116.9 | 2.20E+13 | 131.4 | 2.81E+13 | | |
| 117.0 | 2.12E+13 | 132.0 | 2.67E+13 | | |
| 117.5 | 2.61E+13 | 132.2 | 2.21E+12 | | |

## Appendix II Evaluation of Methodology for Thermophilic SAnMBR

| Date | Day | Hydraulic Retention Time (hr) | Thermophilic SAnMBR Flux ($L/m^2/hr$) | Organic Loading Rate ($kg\ COD/m^3/day$) | Organic Removal Rate ($kg\ COD/m^3/day$) |
|---|---|---|---|---|---|
| 11/01/08 | 2 | | 5.25 | | |
| 12/01/08 | 3 | | 4.05 | | |
| 18/01/08 | 9 | 21.43 | 6.81 | 2.99 | 2.82 |
| 19/01/08 | 10 | 27.18 | 5.36 | 2.35 | 2.23 |
| 20/01/08 | 11 | 32.06 | 4.55 | 2.00 | 1.90 |
| 21/01/08 | 12 | 36.36 | 4.01 | 1.76 | 1.64 |
| 22/01/08 | 13 | 21.76 | 6.70 | 2.94 | 2.70 |
| 23/01/08 | 14 | 28.28 | 5.16 | 2.26 | 2.10 |
| 24/01/08 | 15 | 31.23 | 4.67 | 2.05 | 1.93 |
| 25/01/08 | 16 | 24.85 | 5.87 | 2.58 | 2.47 |
| 26/01/08 | 17 | 33.20 | 4.39 | 1.93 | 1.88 |
| 27/01/08 | 18 | | | | |
| 28/01/08 | 19 | | | | |
| 29/01/08 | 20 | 23.60 | 6.18 | 2.71 | 2.55 |
| 30/01/08 | 21 | | | | |
| 31/01/08 | 22 | 24.00 | 6.08 | 2.67 | 2.49 |
| 01/02/08 | 23 | 31.70 | 4.60 | 2.02 | 1.91 |
| 02/02/08 | 24 | 36.84 | 3.96 | 1.74 | 1.60 |
| 03/02/08 | 25 | 24.00 | 6.08 | 2.67 | 2.39 |
| 04/02/08 | 26 | 32.06 | 4.55 | 2.00 | 1.71 |
| 05/02/08 | 27 | 33.07 | 4.41 | 1.94 | 1.58 |
| 06/02/08 | 28 | 29.37 | 4.97 | 2.18 | 1.87 |
| 07/02/08 | 29 | 36.84 | 3.96 | 1.74 | 1.55 |
| 09/02/08 | 31 | 25.93 | 5.63 | 2.47 | 2.12 |
| 11/02/08 | 33 | | | | |
| 13/02/08 | 35 | 28.00 | 5.21 | 2.22 | 1.82 |
| 14/02/08 | 36 | 31.11 | 4.69 | 2.00 | 1.69 |
| 15/02/08 | 37 | 31.23 | 4.67 | 1.99 | 1.74 |
| 16/02/08 | 38 | 29.79 | 4.90 | 2.09 | 1.90 |
| 17/02/08 | 39 | 33.07 | 4.41 | 1.88 | 1.78 |
| 18/02/08 | 40 | 33.73 | 4.32 | 1.85 | 1.71 |
| 19/02/08 | 41 | 21.27 | 6.86 | 2.93 | 2.67 |
| 20/02/08 | 42 | 35.00 | 4.17 | 1.78 | 1.66 |
| 21/02/08 | 43 | 38.89 | 3.75 | 1.60 | 1.52 |
| 22/02/08 | 44 | 31.11 | 4.69 | 2.00 | 1.90 |
| 23/02/08 | 45 | 36.52 | 3.99 | 1.70 | 1.62 |
| 24/02/08 | 46 | | | | |
| 25/02/08 | 47 | 18.14 | | 7.75 | 6.79 |
| 26/02/08 | 48 | 20.69 | 7.05 | 6.79 | 6.18 |
| 27/02/08 | 49 | 29.37 | 4.97 | 4.79 | 4.52 |
| 28/02/08 | 50 | 30.32 | 4.81 | 4.63 | 4.39 |
| 29/02/08 | 51 | 20.90 | 6.98 | 6.73 | 6.40 |
| 01/03/08 | 52 | 21.93 | 6.65 | 6.41 | 6.14 |
| 02/03/08 | 53 | 25.30 | 5.76 | 5.55 | 5.35 |

| Date | Day | Hydraulic Retention Time (hr) | Thermophilic SAnMBR Flux ($L/m^2/hr$) | Organic Loading Rate (kg $COD/m^3/day$) | Organic Removal Rate (kg $COD/m^3/day$) |
|---|---|---|---|---|---|
| 03/03/08 | 54 | 26.84 | 5.43 | 5.24 | 5.08 |
| 04/03/08 | 55 | 28.09 | 5.19 | 5.00 | 4.88 |
| 05/03/08 | 56 | 23.08 | 6.32 | 6.09 | 5.95 |
| 06/03/08 | 57 | 26.67 | 5.47 | 5.27 | 5.15 |
| 07/03/08 | 58 | 34.29 | 4.25 | 4.10 | 4.00 |
| 08/03/08 | 59 | 22.40 | 6.51 | 6.27 | 6.11 |
| 09/03/08 | 60 | 23.80 | 6.13 | 5.91 | 5.77 |
| 10/03/08 | 61 | 25.77 | 5.66 | 5.45 | 5.34 |
| 11/03/08 | 62 | 30.55 | 4.77 | 4.60 | 4.30 |
| 12/03/08 | 63 | 19.40 | 7.52 | 7.24 | 6.44 |
| 13/03/08 | 64 | 21.32 | 6.84 | 6.59 | 6.12 |
| 14/03/08 | 65 | 23.40 | 6.23 | 6.01 | 5.81 |
| 15/03/08 | 66 | 28.00 | 5.21 | 5.02 | 4.86 |
| 16/03/08 | 67 | 24.93 | 5.85 | 5.64 | 5.46 |
| 18/03/08 | 69 | 18.14 |  | 7.75 | 7.54 |
| 19/03/08 | 70 | 22.22 | 6.56 | 5.98 | 5.82 |
| 20/03/08 | 71 | 22.89 | 6.37 | 5.81 | 5.66 |
| 21/03/08 | 72 | 17.32 |  | 7.67 | 7.46 |
| 22/03/08 | 73 | 24.63 | 5.92 | 5.39 | 5.23 |
| 23/03/08 | 74 | 23.53 | 6.20 | 5.65 | 5.46 |
| 24/03/08 | 75 | 25.00 | 5.83 | 5.32 | 5.12 |
| 25/03/08 | 76 | 27.18 | 5.36 | 4.89 | 4.68 |
| 26/03/08 | 77 | 27.18 | 5.36 | 4.89 | 4.68 |
| 27/03/08 | 78 | 26.42 | 5.52 | 5.03 | 4.64 |
| 28/03/08 | 79 | 23.33 | 6.25 | 5.70 | 5.04 |
| 29/03/08 | 80 | 30.32 | 4.81 | 4.38 | 3.62 |
| 31/03/08 | 82 | 25.15 | 5.80 | 5.28 | 3.46 |
| 01/04/08 | 83 | 22.95 | 6.35 | 5.79 | 3.79 |
| 02/04/08 | 84 | 29.79 | 4.90 | 4.46 | 2.46 |
| 04/04/08 | 86 | 24.93 | 5.85 | 5.33 | 2.90 |
| 05/04/08 | 87 | 24.63 | 5.92 | 4.80 | 2.39 |
| 06/04/08 | 88 | 25.00 | 5.83 | 4.73 | 2.36 |
| 07/04/08 | 89 | 30.22 | 4.83 | 3.91 | 1.87 |
| 09/04/08 | 91 | 28.77 | 5.07 | 4.11 | 2.52 |
| 10/04/08 | 92 |  |  |  |  |
| 12/04/08 | 94 | 28.95 | 5.04 | 4.09 | 1.89 |
| 13/04/08 | 95 | 32.00 | 4.56 |  |  |
| 15/04/08 | 97 | 118.31 | 1.23 |  |  |
| 16/04/08 | 98 |  | 1.23 |  |  |
| 17/04/08 | 99 |  | 0.94 |  |  |
| 18/04/08 | 100 | 135.48 | 1.08 | 0.99 | 0.79 |
| 19/04/08 | 101 | 101.20 | 1.44 | 1.32 | 0.98 |
| 20/04/08 | 102 | 137.70 | 1.06 | 0.97 | 0.80 |
| 21/04/08 | 103 | 137.70 | 1.06 | 0.97 | 0.79 |
| 22/04/08 | 104 | 83.17 | 1.75 | 1.61 | 1.31 |
| 23/04/08 | 105 | 104.05 | 1.40 | 1.29 | 1.06 |

| Date | Day | Hydraulic Retention Time (hr) | Thermophilic SAnMBR Flux ($L/m^2/hr$) | Organic Loading Rate (kg $COD/m^3/day$) | Organic Removal Rate (kg $COD/m^3/day$) |
|---|---|---|---|---|---|
| 24/04/08 | 106 | 88.42 | 1.65 | 1.51 | 1.25 |
| 25/04/08 | 107 | 110.53 | 1.32 | 1.21 | 0.91 |
| 26/04/08 | 108 | 77.78 | 1.88 | 1.72 | 1.41 |
| 27/04/08 | 109 | 131.25 | 1.11 | 1.02 | 0.83 |
| 28/04/08 | 110 | 115.07 | 1.27 | 1.16 | 0.92 |
| 29/04/08 | 111 | | 0.87 | 0.80 | 0.70 |
| 30/04/08 | 112 | 82.35 | 1.77 | 1.63 | 1.37 |
| 01/05/08 | 113 | 123.53 | 1.18 | 1.08 | 0.92 |
| 02/05/08 | 114 | 118.38 | 1.23 | 1.13 | 1.00 |
| 04/05/08 | 116 | 115.38 | 1.26 | 1.16 | 1.04 |
| 05/05/08 | 117 | 87.50 | 1.67 | 1.53 | 1.42 |
| 06/05/08 | 118 | 124.66 | 1.17 | | |
| 07/05/08 | 119 | 137.25 | 1.06 | | |
| 08/05/08 | 120 | 79.25 | 1.84 | 1.69 | 1.50 |
| 09/05/08 | 121 | 100.30 | 1.45 | 1.33 | 1.26 |
| 10/05/08 | 122 | 78.39 | 1.86 | 1.71 | 1.60 |
| 12/05/08 | 124 | | | | |
| 13/05/08 | 125 | 83.23 | 1.75 | 1.72 | 1.64 |
| 14/05/08 | 126 | 88.73 | 1.64 | 1.62 | 1.55 |
| 15/05/08 | 127 | 50.00 | 2.92 | 2.87 | 2.76 |
| 16/05/08 | 128 | 62.82 | 2.32 | 2.28 | 2.21 |
| 17/05/08 | 129 | 41.93 | 3.48 | 3.42 | 3.30 |
| 18/05/08 | 130 | 48.00 | 3.04 | 2.99 | 2.89 |
| 19/05/08 | 131 | 53.76 | 2.71 | 2.67 | 2.59 |
| 20/05/08 | 132 | 53.44 | 2.73 | 2.69 | 2.59 |
| 21/05/08 | 133 | 46.10 | 3.16 | 3.11 | 3.02 |
| 22/05/08 | 134 | 55.68 | 2.62 | 2.58 | 2.51 |
| 23/05/08 | 135 | 78.24 | 1.86 | | |
| 24/05/08 | 136 | | | | |
| 26/05/08 | 138 | | | | |
| 27/05/08 | 139 | 73.68 | 1.98 | | |
| 28/05/08 | 140 | 81.31 | 1.79 | | |
| 29/05/08 | 141 | 52.27 | 2.79 | | |
| 30/05/08 | 142 | | | | |
| 02/06/08 | 145 | | | | |
| 03/06/08 | 146 | 75.36 | 1.94 | 3.15 | 3.06 |
| 04/06/08 | 147 | 93.33 | 1.56 | 2.54 | 2.48 |
| 05/06/08 | 148 | 94.38 | 1.55 | 2.51 | 2.45 |
| 06/06/08 | 149 | 95.45 | 1.53 | 2.48 | 2.43 |
| 07/06/08 | 150 | 97.73 | 1.49 | 2.43 | 2.37 |
| 09/06/08 | 152 | | | 3.01 | 2.93 |
| 10/06/08 | 153 | 101.11 | 1.44 | 2.34 | 2.28 |
| 11/06/08 | 154 | 97.67 | 1.49 | 2.43 | 2.37 |
| 12/06/08 | 155 | 73.55 | 1.98 | | |
| 13/06/08 | 156 | 59.36 | 2.46 | 3.99 | 3.96 |
| 14/06/08 | 157 | 90.28 | 1.62 | 2.63 | 2.60 |

| Date | Day | Hydraulic Retention Time (hr) | Thermophilic SAnMBR Flux ($L/m^2/hr$) | Organic Loading Rate (kg $COD/m^3/day$) | Organic Removal Rate (kg $COD/m^3/day$) |
|---|---|---|---|---|---|
| 16/06/08 | 159 | | | | |
| 17/06/08 | 160 | 50.11 | 2.91 | 4.73 | 4.69 |
| 18/06/08 | 161 | 55.97 | 2.61 | | |
| 19/06/08 | 162 | 50.62 | 2.88 | 4.68 | 4.64 |
| 20/06/08 | 163 | 75.89 | 1.92 | 3.12 | 3.09 |
| 21/06/08 | 164 | 49.07 | 2.97 | 4.83 | 4.78 |
| 22/06/08 | 165 | 44.49 | 3.28 | | |
| 23/06/08 | 166 | 101.90 | 1.43 | 2.33 | 2.22 |
| 24/06/08 | 167 | | | | |
| 25/06/08 | 168 | 86.42 | 1.69 | 2.74 | 2.42 |
| 26/06/08 | 169 | 61.45 | 2.37 | 3.86 | 3.26 |
| 27/06/08 | 170 | 70.00 | 2.08 | 3.39 | 2.81 |
| 28/06/08 | 171 | 69.03 | 2.11 | 3.43 | 2.79 |
| 10/07/08 | 183 | | 1.38 | | |
| 11/07/08 | 184 | 70.44 | 2.07 | 3.36 | 3.14 |
| 12/07/08 | 185 | 87.50 | 1.67 | 2.71 | 2.55 |
| 13/07/08 | 186 | 101.62 | 1.44 | 2.33 | 2.22 |
| 14/07/08 | 187 | 105.00 | 1.39 | 2.26 | 2.16 |
| 15/07/08 | 188 | | | | |
| 17/07/08 | 190 | | | | |
| 18/07/08 | 191 | 77.78 | 1.88 | 3.05 | 2.97 |
| 19/07/08 | 192 | | | | |
| 20/07/08 | 193 | 58.85 | 2.48 | 4.03 | 3.95 |
| 21/07/08 | 194 | 68.29 | 2.14 | 3.47 | 3.39 |
| 22/07/08 | 195 | 71.42 | 2.04 | 3.32 | 3.23 |
| 23/07/08 | 196 | 43.68 | 3.34 | | |
| 24/07/08 | 197 | 69.42 | 2.10 | | |
| 25/07/08 | 198 | 91.35 | 1.60 | | |
| 26/07/08 | 199 | 72.79 | 2.00 | | |
| 27/07/08 | 200 | 81.19 | 1.80 | | |
| 28/07/08 | 201 | 89.74 | 1.63 | | |
| 29/07/08 | 202 | 45.34 | 3.22 | | |
| 30/07/08 | 203 | 63.16 | 2.31 | | |
| 31/07/08 | 204 | 59.87 | 2.44 | | |
| 01/08/08 | 205 | | | | |
| 02/08/08 | 206 | 74.45 | 1.96 | | |
| 03/08/08 | 207 | 70.34 | 2.07 | | |

| Date | Day | Average Influent COD Concentration (mg/L) | Supernatant COD (mg/L) | Effluent Soluble COD (mg/L) | COD Removal Efficiency (%) | Methane Yield (L $CH_4$/g COD) |
|---|---|---|---|---|---|---|
| 12/01/08 | 3 | 2666.88 | | 104.95 | 96.06 | |
| 13/01/08 | 4 | 2666.88 | | 116.75 | 95.62 | |
| 14/01/08 | 5 | 2666.88 | | 147.41 | 94.47 | 0.38 |
| 16/01/08 | 7 | 2666.88 | | 154.23 | 94.22 | 0.30 |
| 18/01/08 | 9 | 2666.88 | | 151.74 | 94.31 | |
| 19/01/08 | 10 | 2666.88 | | | | 0.33 |
| 20/01/08 | 11 | 2666.88 | | 133.97 | 94.98 | 0.30 |
| 21/01/08 | 12 | 2666.88 | | | | 0.31 |
| 22/01/08 | 13 | 2666.88 | | 217.70 | 91.84 | 0.33 |
| 23/01/08 | 14 | 2666.88 | | | | 0.33 |
| 24/01/08 | 15 | 2666.88 | | 161.48 | 93.94 | |
| 25/01/08 | 16 | 2666.88 | | | | |
| 26/01/08 | 17 | 2666.88 | | 64.79 | 97.57 | |
| 28/01/08 | 19 | 2666.88 | | 111.78 | 95.81 | |
| 29/01/08 | 20 | 2666.88 | | | | 0.34 |
| 30/01/08 | 21 | 2666.88 | | 201.20 | 92.46 | |
| 31/01/08 | 22 | 2666.88 | | | | 0.28 |
| 01/02/08 | 23 | 2666.88 | | 150.28 | 94.36 | 0.30 |
| 02/02/08 | 24 | 2666.88 | | | | 0.30 |
| 03/02/08 | 25 | 2666.88 | | 276.78 | 89.62 | |
| 04/02/08 | 26 | 2666.88 | | | | |
| 05/02/08 | 27 | 2666.88 | | 485.55 | 81.79 | 0.27 |
| 06/02/08 | 28 | 2666.88 | | | | |
| 07/02/08 | 29 | 2666.88 | | 282.74 | 89.40 | 0.26 |
| 09/02/08 | 31 | 2666.88 | | 381.76 | 85.69 | 0.27 |
| 11/02/08 | 33 | 2666.88 | | 344.34 | 87.09 | |
| 12/02/08 | 34 | 2666.88 | | | | 0.32 |
| 13/02/08 | 35 | 2593.44 | | 472.08 | 81.80 | |
| 14/02/08 | 36 | 2593.44 | | | | |
| 15/02/08 | 37 | 2593.44 | | 333.39 | 87.14 | 0.30 |
| 16/02/08 | 38 | 2593.44 | | | | 0.29 |
| 17/02/08 | 39 | 2593.44 | | 139.83 | 94.61 | 0.27 |
| 18/02/08 | 40 | 2593.44 | | | | 0.26 |
| 19/02/08 | 41 | 2593.44 | | 231.52 | 91.07 | 0.30 |
| 20/02/08 | 42 | 2593.44 | | | | 0.26 |
| 21/02/08 | 43 | 2593.44 | | 125.16 | 95.17 | 0.27 |
| 22/02/08 | 44 | 2593.44 | | | | 0.29 |
| 23/02/08 | 45 | 2593.44 | | 123.94 | 95.22 | 0.29 |
| 24/02/08 | 46 | 5855.87 | | | | |
| 25/02/08 | 47 | 5855.87 | | 723.16 | 87.65 | |
| 26/02/08 | 48 | 5855.87 | | | | 0.25 |
| 27/02/08 | 49 | 5855.87 | | 328.56 | 94.39 | 0.29 |
| 28/02/08 | 50 | 5855.87 | | | | 0.31 |
| 29/02/08 | 51 | 5855.87 | | 286.14 | 95.11 | |
| 01/03/08 | 52 | 5855.87 | | | | |
| 02/03/08 | 53 | 5855.87 | | 212.79 | 96.37 | 0.30 |

| Date | Day | Average Influent COD Concentration (mg/L) | Supernatant COD (mg/L) | Effluent Soluble COD (mg/L) | COD Removal Efficiency (%) | Methane Yield (L $CH_4$/g COD) |
|---|---|---|---|---|---|---|
| 03/03/08 | 54 | 5855.87 | | | | 0.32 |
| 04/03/08 | 55 | 5855.87 | | 138.37 | 97.64 | 0.29 |
| 05/03/08 | 56 | 5855.87 | | | | 0.32 |
| 06/03/08 | 57 | 5855.87 | | 137.21 | 97.66 | 0.27 |
| 07/03/08 | 58 | 5855.87 | | | | 0.33 |
| 08/03/08 | 59 | 5855.87 | | 151.16 | 97.42 | 0.33 |
| 09/03/08 | 60 | 5855.87 | | | | 0.32 |
| 10/03/08 | 61 | 5855.87 | | 122.82 | 97.90 | 0.26 |
| 13/03/08 | 64 | 5855.87 | | | | 0.37 |
| 14/03/08 | 65 | 5855.87 | | 188.76 | 96.78 | 0.32 |
| 15/03/08 | 66 | 5855.87 | | | | 0.31 |
| 16/03/08 | 67 | 5855.87 | | 186.10 | 96.82 | |
| 18/03/08 | 69 | 5855.87 | | 155.46 | 97.35 | |
| 20/03/08 | 71 | 5537.26 | | 140.76 | 97.46 | |
| 22/03/08 | 73 | 5537.26 | | 168.89 | 96.95 | 0.23 |
| 24/03/08 | 75 | 5537.26 | | 201.52 | 96.36 | 0.25 |
| 25/03/08 | 76 | 5537.26 | | 232.99 | 95.79 | 0.17 |
| 26/03/08 | 77 | 5537.26 | | 233.08 | 95.79 | 0.15 |
| 27/03/08 | 78 | 5537.26 | | | | 0.14 |
| 28/03/08 | 79 | 5537.26 | | 633.80 | 88.55 | 0.02 |
| 29/03/08 | 80 | 5537.26 | | | | 0.01 |
| 31/03/08 | 82 | 5537.26 | | 1916.27 | 65.39 | |
| 01/04/08 | 83 | 5537.26 | | 1890.04 | 65.46 | 0.03 |
| 02/04/08 | 84 | 5537.26 | 2450.29 | 2450.29 | 55.23 | 0.06 |
| 04/04/08 | 86 | 5537.26 | 2432.00 | 2491.43 | 54.47 | 0.09 |
| 05/04/08 | 87 | 4927.94 | | 2466.90 | 49.75 | 0.06 |
| 06/04/08 | 88 | 4927.94 | 2499.42 | 2457.61 | 49.94 | 0.00 |
| 07/04/08 | 89 | 4927.94 | | 2569.11 | 47.66 | 0.00 |
| 08/04/08 | 90 | 4927.94 | 2494.77 | 2480.84 | 49.46 | |
| 09/04/08 | 91 | 4927.94 | | 1910.74 | 61.40 | 0.02 |
| 10/04/08 | 92 | 4927.94 | 3640.17 | 2426.78 | 50.70 | 0.05 |
| 12/04/08 | 94 | 4927.94 | 2249.14 | 2646.86 | 46.29 | 0.01 |
| 13/04/08 | 95 | 4927.94 | | 1673.14 | 66.05 | |
| 14/04/08 | 96 | 4927.94 | 3805.71 | 1865.14 | 62.15 | 6.27 |
| 15/04/08 | 97 | 4927.94 | | 2016.00 | 59.09 | 5.08 |
| 16/04/08 | 98 | 3891.61 | 3655.67 | 1523.19 | 60.86 | 0.73 |
| 17/04/08 | 99 | 4734.30 | | 1654.74 | 65.05 | 1.48 |
| 18/04/08 | 100 | 5576.99 | 3773.37 | 1107.78 | 80.14 | 0.51 |
| 19/04/08 | 101 | 5576.99 | | 1456.94 | 73.88 | |
| 20/04/08 | 102 | 5576.99 | 3983.25 | 968.90 | 82.63 | |
| 21/04/08 | 103 | 5576.99 | | 1040.67 | 81.34 | |
| 22/04/08 | 104 | 5576.99 | 3818.18 | 1026.32 | 81.60 | 0.49 |
| 23/04/08 | 105 | 5576.99 | | 972.97 | 82.55 | 0.49 |

| Date | Day | Average Influent COD Concentration (mg/L) | Supernatant COD (mg/L) | Effluent Soluble COD (mg/L) | COD Removal Efficiency (%) | Methane Yield (L CH4/g COD) |
|---|---|---|---|---|---|---|
| 24/04/08 | 106 | 5576.99 | 3701.53 | 980.02 | 82.43 | 0.46 |
| 25/04/08 | 107 | 5576.99 | | 1388.95 | 75.09 | |
| 26/04/08 | 108 | 5576.99 | 3308.20 | 1010.84 | 81.87 | |
| 27/04/08 | 109 | 5576.99 | | 1053.25 | 81.11 | 0.44 |
| 28/04/08 | 110 | 5576.99 | 3329.41 | 1187.56 | 78.71 | |
| 29/04/08 | 111 | 5576.99 | | 706.88 | 87.33 | |
| 30/04/08 | 112 | 5576.99 | 3286.88 | 879.38 | 84.23 | |
| 01/05/08 | 113 | 5576.99 | | 836.14 | 85.01 | |
| 02/05/08 | 114 | 5576.99 | 2515.62 | 663.14 | 88.11 | |
| 04/05/08 | 116 | 5576.99 | | 568.48 | 89.81 | |
| 05/05/08 | 117 | 5576.99 | 2043.66 | 402.97 | 92.77 | 0.51 |
| 06/05/08 | 118 | 5576.99 | 2065.24 | 345.41 | 93.81 | |
| 07/05/08 | 119 | 5576.99 | | 381.45 | 93.16 | 0.52 |
| 08/05/08 | 120 | 5576.99 | 1645.87 | 621.62 | 88.85 | |
| 09/05/08 | 121 | 5576.99 | | 324.94 | 94.17 | 0.49 |
| 10/05/08 | 122 | 5576.99 | 1503.18 | 343.45 | 93.84 | 0.41 |
| 12/05/08 | 124 | 5978.06 | 1452.68 | 425.53 | 92.88 | 0.42 |
| 13/05/08 | 125 | 5978.06 | | 300.81 | 94.97 | 0.47 |
| 14/05/08 | 126 | 5978.06 | 1261.92 | 251.90 | 95.79 | |
| 15/05/08 | 127 | 5978.06 | | 232.98 | 96.10 | |
| 16/05/08 | 128 | 5978.06 | 1093.67 | 191.94 | 96.79 | |
| 17/05/08 | 129 | 5978.06 | | 215.04 | 96.40 | 0.44 |
| 18/05/08 | 130 | 5978.06 | 1196.54 | 192.22 | 96.78 | |
| 19/05/08 | 131 | 5978.06 | | 180.20 | 96.99 | |
| 20/05/08 | 132 | 5978.06 | 1643.44 | 212.64 | 96.44 | |
| 21/05/08 | 133 | 5978.06 | | 177.10 | 97.04 | 0.34 |
| 22/05/08 | 134 | 5978.06 | 975.25 | 162.54 | 97.28 | 0.33 |
| 23/05/08 | 135 | 5978.06 | | 242.60 | 95.94 | |
| 24/05/08 | 136 | 5978.06 | 1016.42 | 276.44 | 95.38 | 0.36 |
| 26/05/08 | 138 | 5978.06 | 997.10 | 261.95 | 95.62 | |
| 27/05/08 | 139 | 5978.06 | | 228.15 | 96.18 | 0.34 |
| 28/05/08 | 140 | 5978.06 | | | | |
| 29/05/08 | 141 | 5978.06 | | | | |
| 30/05/08 | 142 | 5978.06 | | | | |
| 31/05/08 | 143 | 5978.06 | | | | |
| 01/06/08 | 144 | 5978.06 | | | | |
| 02/06/08 | 145 | 5978.06 | | | | |
| 03/06/08 | 146 | 9876.30 | | 272.23 | 97.24 | 0.35 |
| 04/06/08 | 147 | 9876.30 | | | | 0.43 |
| 05/06/08 | 148 | 9876.30 | | | | 0.35 |
| 06/06/08 | 149 | 9876.30 | 803.13 | 203.25 | 97.94 | 0.42 |
| 07/06/08 | 150 | 9876.30 | | | | |
| 09/06/08 | 152 | 9876.30 | | | | 0.32 |
| 10/06/08 | 153 | 9876.30 | 704.59 | 284.55 | 97.12 | 0.41 |
| 11/06/08 | 154 | 9876.30 | | | | 0.34 |
| 12/06/08 | 155 | 9876.30 | | | | |
| 13/06/08 | 156 | 9876.30 | 435.38 | 93.64 | 99.05 | |
| 14/06/08 | 157 | 9876.30 | | | | |

| Date | Day | Average Influent COD Concentration (mg/L) | Supernatant COD (mg/L) | Effluent Soluble COD (mg/L) | COD Removal Efficiency (%) | Methane Yield (L CH4/g COD) |
|---|---|---|---|---|---|---|
| 16/06/08 | 159 | 9876.30 | | | | |
| 17/06/08 | 160 | 9876.30 | 374.46 | 74.24 | 99.25 | |
| 18/06/08 | 161 | 9876.30 | | | | |
| 19/06/08 | 162 | 9876.30 | | | | 0.35 |
| 20/06/08 | 163 | 9876.30 | | | | 0.41 |
| 21/06/08 | 164 | 9876.30 | | | | 0.31 |
| 22/06/08 | 165 | 9876.30 | 527.54 | 108.41 | 98.90 | |
| 23/06/08 | 166 | 9876.30 | | | | 0.03 |
| 24/06/08 | 167 | 9876.30 | | | | |
| 25/06/08 | 168 | 9876.30 | | | | 0.02 |
| 26/06/08 | 169 | 9876.30 | 1851.11 | 1533.17 | 84.48 | 0.04 |
| 27/06/08 | 170 | 9876.30 | | | | 0.03 |
| 28/06/08 | 171 | 9876.30 | | | | 0.11 |
| 29/06/08 | 172 | 9876.30 | | | | 0.03 |
| 01/07/08 | 174 | 9876.30 | | | | 0.07 |
| 02/07/08 | 175 | 9876.30 | | | | 0.10 |
| 03/07/08 | 176 | 9876.30 | 5063.04 | 2637.49 | 73.29 | 0.14 |
| 05/07/08 | 178 | 9876.30 | | 182.15 | 98.16 | 0.30 |
| 07/07/08 | 180 | 9876.30 | | | | 0.38 |
| 08/07/08 | 181 | 9876.30 | | 206.43 | 97.91 | |
| 10/07/08 | 183 | 9876.30 | 1032.16 | 758.94 | 92.32 | |
| 11/07/08 | 184 | 9876.30 | | | | 0.39 |
| 12/07/08 | 185 | 9876.30 | | | | |
| 13/07/08 | 186 | 9876.30 | 1032.16 | 473.58 | 95.20 | 0.28 |
| 14/07/08 | 187 | 9876.30 | | | | 0.37 |
| 15/07/08 | 188 | 9876.30 | | | | 0.32 |
| 17/07/08 | 190 | 9876.30 | 967.64 | 262.07 | 97.35 | |
| 18/07/08 | 191 | 9876.30 | | | | |
| 19/07/08 | 192 | 9876.30 | | | | |
| 20/07/08 | 193 | 9876.30 | 860.13 | 188.15 | 98.09 | |
| 21/07/08 | 194 | 9876.30 | | | | |
| 22/07/08 | 195 | 9876.30 | | | | |
| 23/07/08 | 196 | 9876.30 | | | | |
| 24/07/08 | 197 | 9876.30 | 927.33 | 329.27 | 96.67 | |
| 25/07/08 | 198 | 9876.30 | | | | |
| 26/07/08 | 199 | 9876.30 | | | | |
| 27/07/08 | 200 | 9876.30 | | | | |
| 28/07/08 | 201 | 9876.30 | | | | |
| 29/07/08 | 202 | 9876.30 | | | | |
| 30/07/08 | 203 | 9876.30 | | | | |
| 31/07/08 | 204 | 9876.30 | | | | |
| 01/08/08 | 205 | 9876.30 | | | | |
| 02/08/08 | 206 | 9876.30 | | | | |
| 03/08/08 | 207 | 9876.30 | | | | |

| Date | Day | Biogas Composition (%) | | | Top Zone Biomass Concentration (g/L) | Bottom Zone Biomass Concentration (g/L) |
|---|---|---|---|---|---|---|
| | | Nitrogen | Methane | Carbon Dioxide | | |
| 13/01/08 | 4 | | | | 0.56 | |
| 14/01/08 | 5 | | | | 1.12 | 19.01 |
| 16/01/08 | 7 | | | | | |
| 18/01/08 | 9 | | | | 2.69 | |
| 19/01/08 | 10 | | | | | 18.90 |
| 20/01/08 | 11 | 14.84% | 82.72% | 2.44% | 2.46 | |
| 21/01/08 | 12 | 10.14% | 87.49% | 2.37% | | |
| 22/01/08 | 13 | | | | 5.74 | |
| 23/01/08 | 14 | 16.64% | 80.98% | 2.39% | | |
| 24/01/08 | 15 | 12.98% | 84.58% | 2.44% | 1.12 | |
| 25/01/08 | 16 | | | | | |
| 26/01/08 | 17 | | | | 2.25 | 12.06 |
| 27/01/08 | 18 | 14.23% | 82.85% | 2.92% | | |
| 28/01/08 | 19 | | | | 3.07 | |
| 29/01/08 | 20 | | | | | |
| 30/01/08 | 21 | | | | 2.72 | |
| 31/01/08 | 22 | | | | | |
| 01/02/08 | 23 | | | | 1.50 | |
| 02/02/08 | 24 | 13.76% | 83.79% | 2.44% | 1.40 | 11.19 |
| 03/02/08 | 25 | | | | | |
| 04/02/08 | 26 | | | | 4.54 | |
| 05/02/08 | 27 | | | | | 11.18 |
| 06/02/08 | 28 | | | | 4.33 | 7.94 |
| 07/02/08 | 29 | | | | | |
| 09/02/08 | 31 | | | | | 8.35 |
| 11/02/08 | 33 | | | | | |
| 12/02/08 | 34 | | | | 0.39 | 10.99 |
| 13/02/08 | 35 | | | | | |
| 14/02/08 | 36 | | | | 2.30 | |
| 15/02/08 | 37 | | | | | |
| 16/02/08 | 38 | 15.33% | 81.87% | 2.81% | 1.78 | 7.14 |
| 17/02/08 | 39 | 3.92% | 92.87% | 3.20% | | |
| 18/02/08 | 40 | 3.57% | 93.33% | 3.09% | 1.12 | |
| 19/02/08 | 41 | | | | | |
| 21/02/08 | 43 | 9.68% | 87.24% | 3.08% | | |
| 22/02/08 | 44 | 6.06% | 91.48% | 2.46% | 1.95 | |
| 23/02/08 | 45 | 5.97% | 91.72% | 2.31% | | |
| 24/02/08 | 46 | | | | 3.66 | 6.48 |
| 25/02/08 | 47 | 5.04% | 91.62% | 3.34% | | |
| 26/02/08 | 48 | 17.94% | 81.52% | 0.54% | 2.81 | 6.95 |
| 27/02/08 | 49 | 5.59% | 89.31% | 5.10% | | |
| 28/02/08 | 50 | | | | 2.74 | |
| 29/02/08 | 51 | | | | | |
| 01/03/08 | 52 | | | | 3.18 | 5.68 |
| 02/03/08 | 53 | 3.39% | 92.87% | 3.73% | | |

| Date | Day | Biogas Composition (%) | | | Top Zone Biomass Concentration (g/L) | Bottom Zone Biomass Concentration (g/L) |
|---|---|---|---|---|---|---|
| | | Nitrogen | Methane | Carbon Dioxide | | |
| 03/03/08 | 54 | 2.77% | 93.10% | 4.13% | 3.02 | |
| 04/03/08 | 55 | | | | | |
| 05/03/08 | 56 | | | | 2.84 | 6.50 |
| 06/03/08 | 57 | | | | | |
| 07/03/08 | 58 | | | | 2.90 | |
| 08/03/08 | 59 | | | | | 5.66 |
| 09/03/08 | 60 | 4.74% | 83.42% | 11.84% | 3.54 | |
| 10/03/08 | 61 | 4.84% | 84.49% | 10.66% | | |
| 11/03/08 | 62 | | | | 4.68 | 5.79 |
| 12/03/08 | 63 | | | | | |
| 13/03/08 | 64 | 16.42% | 81.45% | 2.13% | 5.17 | |
| 14/03/08 | 65 | | | | | |
| 15/03/08 | 66 | 2.41% | 88.53% | 9.06% | 4.42 | 8.41 |
| 16/03/08 | 67 | | | | | |
| 18/03/08 | 69 | | | | 4.93 | 7.09 |
| 19/03/08 | 70 | 4.88% | 83.22% | 11.90% | 5.12 | |
| 20/03/08 | 71 | | | | | |
| 21/03/08 | 72 | | | | 4.38 | |
| 22/03/08 | 73 | | | | | 7.67 |
| 23/03/08 | 74 | | | | | |
| 25/03/08 | 76 | | | | | 8.67 |
| 26/03/08 | 77 | | | | | |
| 27/03/08 | 78 | | | | 4.50 | |
| 28/03/08 | 79 | | | | | |
| 29/03/08 | 80 | | | | 5.56 | |
| 31/03/08 | 82 | | | | | |
| 01/04/08 | 83 | | | | | |
| 02/04/08 | 84 | | | | 5.22 | 6.43 |
| 04/04/08 | 86 | | | | 3.80 | |
| 05/04/08 | 87 | | | | | |
| 06/04/08 | 88 | | | | 3.56 | 6.34 |
| 07/04/08 | 89 | | | | | |
| 08/04/08 | 90 | | | | 3.05 | 6.16 |
| 09/04/08 | 91 | | | | | |
| 10/04/08 | 92 | | | | | |
| 12/04/08 | 94 | | | | 4.22 | 6.66 |
| 13/04/08 | 95 | | | | | |
| 14/04/08 | 96 | | | | 4.86 | |
| 15/04/08 | 97 | | | | | 59.24 |
| 16/04/08 | 98 | | | | 6.92 | |
| 17/04/08 | 99 | | | | | |
| 18/04/08 | 100 | | | | 8.95 | |
| 19/04/08 | 101 | | | | | 36.49 |
| 20/04/08 | 102 | | | | 9.45 | |
| 22/04/08 | 104 | | | | 9.38 | |

| Date | Day | Biogas Composition (%) | | | Top Zone Biomass Concentration (g/L) | Bottom Zone Biomass Concentration (g/L) |
|---|---|---|---|---|---|---|
| | | Nitrogen | Methane | Carbon Dioxide | | |
| 24/04/08 | 106 | | | | | |
| 25/04/08 | 107 | | | | | |
| 26/04/08 | 108 | | | | | |
| 27/04/08 | 109 | | | | | |
| 28/04/08 | 110 | | | | 8.43 | |
| 29/04/08 | 111 | | | | | 31.77 |
| 30/04/08 | 112 | | | | 9.19 | |
| 01/05/08 | 113 | | | | | |
| 02/05/08 | 114 | | | | 8.46 | |
| 04/05/08 | 116 | | | | | |
| 05/05/08 | 117 | | | | | |
| 06/05/08 | 118 | | | | 6.73 | 27.19 |
| 07/05/08 | 119 | | | | | |
| 08/05/08 | 120 | | | | 6.47 | |
| 09/05/08 | 121 | | | | | |
| 10/05/08 | 122 | | | | | 21.49 |
| 12/05/08 | 124 | | | | 6.62 | |
| 13/05/08 | 125 | | | | | |
| 14/05/08 | 126 | | | | 8.63 | |
| 15/05/08 | 127 | | | | | |
| 16/05/08 | 128 | | | | | 13.79 |
| 17/05/08 | 129 | | | | | |
| 18/05/08 | 130 | | | | | |
| 19/05/08 | 131 | 3.41% | 88.64% | 7.95% | | 11.85 |
| 20/05/08 | 132 | | | | | |
| 21/05/08 | 133 | | | | | |
| 22/05/08 | 134 | 7.53% | 84.98% | 7.48% | 7.90 | |
| 23/05/08 | 135 | | | | | 10.75 |
| 24/05/08 | 136 | | | | | |
| 26/05/08 | 138 | 10.67% | 80.53% | 8.80% | 7.75 | 10.34 |
| 27/05/08 | 139 | | | | | |
| 28/05/08 | 140 | | | | 8.33 | |
| 29/05/08 | 141 | | | | | |
| 30/05/08 | 142 | 6.14% | 83.98% | 9.88% | | |
| 31/05/08 | 143 | 5.12% | 83.73% | 11.14% | | |
| 01/06/08 | 144 | 4.03% | 86.07% | 9.90% | | |
| 02/06/08 | 145 | 5.51% | 84.17% | 10.32% | 9.08 | |
| 03/06/08 | 146 | | | | | |
| 04/06/08 | 147 | | | | | |
| 05/06/08 | 148 | | | | 9.90 | 11.05 |
| 06/06/08 | 149 | | | | | |
| 07/06/08 | 150 | | | | | |
| 09/06/08 | 152 | | | | 9.09 | 10.33 |
| 10/06/08 | 153 | | | | | |
| 12/06/08 | 155 | | | | 9.93 | 11.40 |

| Date | Day | Biogas Composition (%) | | | Top Zone Biomass Concentration (g/L) | Bottom Zone Biomass Concentration (g/L) |
|---|---|---|---|---|---|---|
| | | Nitrogen | Methane | Carbon Dioxide | | |
| 16/06/08 | 159 | | | | 9.87 | |
| 17/06/08 | 160 | | | | | |
| 21/06/08 | 164 | | | | | |
| 22/06/08 | 165 | | | | 9.21 | 10.42 |
| 23/06/08 | 166 | | | | | |
| 24/06/08 | 167 | | | | | |
| 25/06/08 | 168 | | | | | |
| 26/06/08 | 169 | | | | | 10.42 |
| 07/07/08 | 180 | 4.74% | 79.16% | 16.10% | | |
| 08/07/08 | 181 | | | | 4.63 | |
| 10/07/08 | 183 | | | | | |
| 11/07/08 | 184 | | | | | |
| 12/07/08 | 185 | | | | | |
| 13/07/08 | 186 | | | | | |
| 14/07/08 | 187 | | | | | |
| 15/07/08 | 188 | 6.33% | 81.03% | 12.64% | | |
| 17/07/08 | 190 | | | | | |
| 18/07/08 | 191 | 7.38% | 81.44% | 11.18% | | |
| 19/07/08 | 192 | | | | | |
| 20/07/08 | 193 | | | | | |
| 21/07/08 | 194 | | | | | |
| 22/07/08 | 195 | 2.72% | 82.41% | 14.86% | | |
| 23/07/08 | 196 | | | | | |
| 24/07/08 | 197 | | | | 2.70 | 2.76 |
| 30/07/08 | 203 | | | | 6.23 | 5.18 |
| 31/07/08 | 204 | | | | | |
| 01/08/08 | 205 | | | | | |
| 02/08/08 | 206 | | | | | |
| 03/08/08 | 207 | | | | | |

| Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) |
|---|---|---|---|---|---|
| 15.0 | 4.31E+13 | 33.3 | 1.51E+14 | 49.7 | 5.39E+13 |
| 16.0 | 3.70E+12 | 33.7 | 1.62E+14 | 50.0 | 5.80E+13 |
| 16.3 | 2.48E+13 | 34.0 | 2.02E+14 | 50.3 | 6.35E+13 |
| 16.7 | 3.19E+13 | 34.3 | 3.69E+12 | 50.7 | 4.45E+12 |
| 17.0 | 3.97E+13 | 34.7 | 8.56E+12 | 51.0 | 2.11E+13 |
| 17.3 | 6.04E+13 | 35.0 | 3.41E+13 | 51.3 | 2.20E+13 |
| 17.7 | 4.72E+13 | 35.3 | 2.70E+13 | 51.7 | 2.48E+13 |
| 18.0 | 7.09E+13 | 35.7 | 4.28E+13 | 52.0 | 2.68E+13 |
| 18.3 | 8.91E+13 | 36.0 | 4.85E+13 | 52.3 | 3.18E+13 |
| 18.7 | 5.24E+13 | 36.3 | 4.84E+13 | 52.7 | 3.09E+13 |
| 19.0 | 8.38E+13 | 36.7 | 5.13E+13 | 53.0 | 4.01E+13 |
| 19.3 | 1.02E+14 | 37.0 | 5.90E+13 | 53.3 | 4.21E+13 |
| 19.7 | 1.01E+14 | 37.3 | 5.20E+13 | 53.7 | 4.65E+13 |
| 20.0 | 4.30E+12 | 37.7 | 5.96E+13 | 54.0 | 4.57E+13 |
| 20.3 | 2.73E+13 | 38.0 | 6.62E+13 | 54.3 | 5.03E+13 |
| 20.7 | 3.79E+13 | 38.3 | 6.11E+13 | 54.7 | 5.02E+13 |
| 22.0 | 6.21E+11 | 38.7 | 6.24E+13 | 55.0 | 5.13E+13 |
| 22.3 | 1.63E+13 | 39.0 | 6.84E+13 | 55.5 | 6.29E+12 |
| 22.7 | 3.32E+13 | 39.3 | 5.71E+13 | 56.0 | 1.24E+13 |
| 23.0 | 3.37E+13 | 39.7 | 6.80E+13 | 56.3 | 2.02E+13 |
| 23.3 | 4.41E+13 | 40.0 | 7.03E+13 | 56.7 | 2.27E+13 |
| 23.7 | 4.65E+13 | 40.3 | 7.45E+12 | 57.0 | 3.52E+13 |
| 24.0 | 6.08E+13 | 40.7 | 8.62E+12 | 57.3 | 3.19E+13 |
| 24.3 | 3.55E+12 | 41.0 | 3.21E+13 | 57.7 | 5.85E+13 |
| 24.7 | 4.18E+12 | 41.3 | 3.34E+13 | 58.0 | 5.99E+13 |
| 25.0 | 1.34E+13 | 41.7 | 3.81E+13 | 58.3 | 7.01E+13 |
| 25.3 | 3.14E+13 | 42.0 | 4.82E+13 | 58.7 | 5.18E+12 |
| 25.7 | 3.06E+13 | 42.3 | 5.63E+13 | 59.0 | 8.98E+12 |
| 26.0 | 4.02E+13 | 42.7 | 5.77E+13 | 59.3 | 6.42E+12 |
| 26.3 | 4.35E+13 | 43.0 | 6.51E+13 | 59.7 | 1.01E+13 |
| 26.7 | 5.19E+13 | 43.3 | 2.76E+13 | 60.0 | 9.54E+12 |
| 27.0 | 4.31E+13 | 43.7 | 2.62E+13 | 60.3 | 1.81E+13 |
| 27.3 | 5.14E+13 | 44.0 | 6.96E+13 | 60.7 | 1.95E+13 |
| 28.0 | 2.07E+12 | 44.3 | 6.22E+13 | 61.0 | 2.41E+13 |
| 28.3 | 4.38E+13 | 44.7 | 6.71E+13 | 61.3 | 2.50E+13 |
| 28.7 | 6.69E+13 | 45.0 | 6.62E+13 | 61.7 | 4.37E+12 |
| 29.0 | 6.81E+13 | 45.3 | 3.78E+13 | 62.0 | 3.59E+13 |
| 29.3 | 8.98E+13 | 45.7 | 4.45E+13 | 62.3 | 4.96E+13 |
| 29.7 | 1.03E+14 | 46.3 | 4.67E+12 | 62.7 | 5.07E+12 |
| 30.0 | 9.44E+13 | 46.7 | 6.45E+12 | 63.0 | 1.30E+13 |
| 31.0 | 5.08E+12 | 47.0 | 3.73E+13 | 63.3 | 5.28E+12 |
| 31.3 | 5.54E+13 | 47.5 | 8.48E+12 | 63.7 | 1.46E+13 |
| 31.7 | 8.03E+13 | 48.0 | 1.95E+13 | 64.0 | 3.32E+13 |
| 32.0 | 5.32E+13 | 48.3 | 2.73E+13 | 64.3 | 5.56E+13 |
| 32.3 | 1.00E+14 | 48.7 | 3.13E+13 | 64.7 | 6.49E+12 |
| 32.7 | 1.40E+14 | 49.0 | 4.58E+13 | 65.0 | 1.59E+13 |
| 33.0 | 1.20E+14 | 49.3 | 3.72E+13 | 65.3 | 2.32E+13 |

| Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) |
|---|---|---|---|---|---|
| 65.7 | 4.04E+13 | 78.4 | 8.20E+13 | 90.6 | 3.45E+13 |
| 66.0 | 5.28E+13 | 78.6 | 2.20E+12 | 91.0 | 6.34E+13 |
| 66.3 | 6.12E+13 | 78.8 | 2.21E+13 | 91.2 | 1.05E+14 |
| 66.7 | 6.45E+12 | 79.0 | 5.23E+13 | 91.4 | 1.02E+14 |
| 67.0 | 5.81E+13 | 79.2 | 5.47E+13 | 92.0 | 1.24E+14 |
| 67.3 | 8.63E+13 | 79.4 | 4.79E+13 | 92.2 | 1.45E+14 |
| 67.7 | 1.02E+14 | 80.0 | 8.47E+13 | 92.4 | 1.53E+14 |
| 68.0 | 1.21E+14 | 80.2 | 9.54E+13 | 93.0 | 1.68E+14 |
| 68.3 | 1.01E+14 | 80.4 | 8.98E+13 | 93.2 | 1.96E+14 |
| 68.7 | 2.71E+12 | 80.6 | 1.10E+14 | 93.4 | 1.80E+14 |
| 69.0 | 2.06E+13 | 81.0 | 1.22E+14 | 93.6 | 5.92E+12 |
| 69.3 | 2.60E+13 | 81.2 | 4.79E+12 | 94.0 | 6.40E+13 |
| 69.7 | 2.85E+13 | 81.4 | 3.59E+13 | 94.2 | 5.19E+13 |
| 70.0 | 4.28E+13 | 81.6 | 4.58E+13 | 94.4 | 5.86E+13 |
| 70.3 | 5.17E+13 | 82.0 | 6.11E+13 | 95.0 | 6.55E+13 |
| 70.7 | 1.90E+13 | 82.2 | 6.88E+13 | 95.2 | 1.52E+13 |
| 71.0 | 3.74E+13 | 82.4 | 4.47E+12 | 95.4 | 1.08E+14 |
| 71.2 | 3.80E+13 | 82.6 | 2.82E+13 | 96.0 | 1.63E+14 |
| 71.4 | 3.70E+13 | 83.0 | 4.08E+13 | 96.2 | 1.85E+14 |
| 71.6 | 3.49E+12 | 83.2 | 4.74E+13 | 96.4 | 2.15E+13 |
| 71.8 | 1.73E+13 | 83.4 | 5.30E+13 | 96.6 | 2.04E+14 |
| 72.0 | 3.73E+13 | 83.6 | 5.69E+13 | 97.0 | 2.87E+14 |
| 72.2 | 7.54E+12 | 84.0 | 5.68E+13 | 97.2 | 3.42E+14 |
| 72.4 | 2.22E+13 | 84.2 | 7.97E+13 | 97.4 | 2.24E+13 |
| 72.6 | 1.50E+13 | 84.4 | 6.47E+13 | 98.2 | 3.14E+13 |
| 72.8 | 3.79E+13 | 85.0 | 1.18E+14 | 98.4 | 1.77E+14 |
| 73.0 | 7.40E+13 | 85.2 | 1.38E+14 | 98.6 | 2.96E+14 |
| 73.2 | 1.15E+14 | 85.4 | 4.10E+12 | 99.0 | 3.14E+14 |
| 73.4 | 1.63E+12 | 85.6 | 3.06E+13 | 99.2 | 2.74E+14 |
| 73.6 | 2.41E+13 | 86.0 | 4.49E+13 | 99.4 | 2.30E+13 |
| 74.0 | 6.13E+13 | 86.2 | 6.49E+13 | 99.6 | 1.86E+14 |
| 74.2 | 7.19E+13 | 86.4 | 3.86E+12 | 100.0 | 2.87E+14 |
| 74.4 | 5.13E+12 | 86.6 | 3.42E+13 | 100.2 | 3.07E+14 |
| 74.6 | 2.90E+13 | 87.0 | 4.08E+13 | 100.4 | 2.52E+13 |
| 75.0 | 6.40E+13 | 87.2 | 4.54E+13 | 100.6 | 1.08E+14 |
| 75.2 | 5.59E+12 | 87.4 | 5.03E+12 | 101.0 | 1.26E+14 |
| 75.4 | 3.89E+13 | 87.6 | 3.59E+13 | 101.2 | 1.86E+14 |
| 76.0 | 6.74E+13 | 88.0 | 6.43E+13 | 101.4 | 2.52E+14 |
| 76.2 | 8.98E+13 | 88.2 | 8.27E+13 | 102.0 | 3.29E+14 |
| 76.4 | 7.70E+12 | 88.4 | 3.77E+12 | 102.2 | 2.00E+13 |
| 76.6 | 2.53E+13 | 88.6 | 4.66E+13 | 102.4 | 1.52E+14 |
| 77.0 | 5.47E+13 | 89.0 | 7.28E+13 | 103.0 | 1.74E+14 |
| 77.2 | 6.81E+13 | 89.2 | 9.58E+13 | 103.2 | 2.78E+14 |
| 77.4 | 8.31E+13 | 89.4 | 1.03E+14 | 103.4 | 3.17E+14 |
| 77.6 | 2.77E+13 | 90.0 | 1.08E+14 | 103.6 | 1.43E+13 |
| 78.0 | 4.88E+13 | 90.2 | 1.14E+14 | 103.8 | 1.04E+14 |
| 78.2 | 6.29E+13 | 90.4 | 3.69E+12 | 104.0 | 1.28E+14 |

| Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) | Day | Total Transmembrane Resistance ($m^{-1}$) |
|---|---|---|---|---|---|
| 104.2 | 1.66E+14 | 118.0 | 1.36E+14 | 132.6 | 8.85E+13 |
| 104.4 | 1.85E+14 | 118.5 | 1.26E+14 | 132.8 | 1.08E+14 |
| 105.0 | 1.74E+14 | 118.7 | 1.18E+14 | 133.0 | 1.10E+14 |
| 105.2 | 1.91E+14 | 119.0 | 1.17E+14 | 133.2 | 1.24E+14 |
| 105.4 | 9.68E+12 | 119.5 | 2.00E+14 | 133.4 | 1.50E+14 |
| 105.6 | 8.53E+13 | 119.6 | 1.44E+13 | 134.0 | 1.32E+14 |
| 106.0 | 1.08E+14 | 119.8 | 3.51E+13 | 134.2 | 1.40E+14 |
| 106.2 | 1.17E+14 | 119.9 | 9.82E+13 | 134.4 | 1.66E+14 |
| 106.4 | 1.59E+14 | 120.0 | 1.26E+14 | 134.6 | 8.98E+12 |
| 107.0 | 1.69E+14 | 120.2 | 1.44E+14 | 134.8 | 1.17E+14 |
| 107.2 | 2.05E+14 | 120.4 | 1.61E+14 | 135.0 | 1.68E+14 |
| 107.4 | 1.78E+13 | 121.0 | 1.95E+14 | 135.2 | 1.74E+14 |
| 107.6 | 8.09E+13 | 121.2 | 2.32E+14 | 135.4 | 1.98E+14 |
| 108.0 | 1.13E+14 | 121.4 | 5.42E+12 | 136.0 | 2.02E+14 |
| 108.2 | 1.25E+14 | 121.6 | 1.21E+14 | 136.2 | 1.95E+14 |
| 108.4 | 2.50E+13 | 122.0 | 9.58E+13 | 137.0 | 2.87E+14 |
| 108.6 | 1.44E+14 | 122.2 | 2.07E+14 | 137.2 | 3.18E+14 |
| 109.0 | 1.80E+14 | 122.4 | 1.33E+14 | 137.4 | 2.54E+14 |
| 109.2 | 2.02E+13 | 123.0 | 2.38E+14 | 138.0 | 3.59E+14 |
| 109.4 | 1.28E+14 | 123.2 | 1.74E+13 | 138.2 | 2.42E+13 |
| 109.6 | 1.50E+14 | 123.4 | 1.56E+14 | 138.4 | 9.88E+13 |
| 110.0 | 1.62E+14 | 123.6 | 1.62E+14 | 139.0 | 1.33E+14 |
| 110.2 | 1.92E+14 | 124.0 | 4.11E+14 | 139.2 | 1.43E+14 |
| 110.4 | 2.30E+14 | 124.2 | 2.37E+14 | 139.4 | 9.14E+12 |
| 111.0 | 3.59E+14 | 124.4 | 3.29E+14 | 139.6 | 9.64E+13 |
| 111.2 | 3.17E+14 | 125.0 | 1.46E+14 | 139.8 | 1.15E+14 |
| 111.4 | 1.45E+13 | 125.2 | 1.02E+14 | | |
| 111.6 | 8.09E+13 | 126.0 | 2.03E+14 | | |
| 111.8 | 1.39E+14 | 126.2 | 2.25E+14 | | |
| 112.0 | 1.20E+14 | 126.4 | 4.38E+12 | | |
| 112.2 | 1.39E+14 | 126.6 | 7.75E+13 | | |
| 112.4 | 1.39E+13 | 127.0 | 8.81E+13 | | |
| 112.6 | 1.60E+14 | 127.2 | 7.19E+13 | | |
| 113.0 | 2.52E+14 | 127.4 | 9.67E+13 | | |
| 113.6 | 3.29E+14 | 128.0 | 1.10E+14 | | |
| 113.7 | 1.30E+13 | 129.0 | 1.20E+14 | | |
| 113.8 | 1.33E+14 | 129.2 | 6.28E+13 | | |
| 114.0 | 1.87E+14 | 129.4 | 6.79E+13 | | |
| 114.6 | 2.61E+14 | 129.6 | 6.99E+13 | | |
| 114.7 | 1.70E+13 | 130.0 | 9.85E+13 | | |
| 116.0 | 2.57E+14 | 130.2 | 1.16E+14 | | |
| 116.5 | 2.15E+13 | 131.0 | 1.36E+14 | | |
| 116.7 | 7.77E+13 | 131.2 | 1.15E+14 | | |
| 116.9 | 1.15E+14 | 131.4 | 9.12E+13 | | |
| 117.0 | 8.21E+13 | 132.0 | 1.11E+14 | | |
| 117.5 | 9.24E+13 | 132.2 | 3.72E+12 | | |
| 117.7 | 1.08E+14 | 132.4 | 5.60E+13 | | |