Effects of Process Operating Conditions on Performance and Membrane Fouling in Submerged Anaerobic Membrane Bioreactors (AnMBRs)

By

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A thesis submitted to the faculty of graduate studies of

Lakehead University

in partial fulfillment of the requirements for the degree of

Master of Science in Engineering

Environmental Engineering

Lakehead University

Abstract

Submerged anaerobic membrane bioreactor (SAnMBR) technology is becoming an attractive alternative for industrial wastewater treatment as it improves the biological process while allowing for the recovery of energy through biogas production. However, membrane fouling presents one of the main drawbacks of the technology. It is generally believed that operating below the critical flux can reduce the fouling rate. Another drawback hampering the wide-spread application of the SAnMBR technology is its competitors, mainly conventional high-rate anaerobic systems, like up-flow anaerobic sludge blanket (UASB) reactors which are known for their high OLRs (up to 40 kgCOD/m^3.d).

This Thesis focused on two parts. In the first part, investigated the effects of sparging rates (8.72, 6.0 and 4.38 m^3/m^2.h) and mixed liquor total solids (MLTS) concentrations (15, 10.6, 7.7 and 5.7 g/L) on the critical flux in a short term study. The study concluded that both MLTS concentration and sparging rate are key factors to be considered for optimization of the SAnMBR. Critical flux increased as the sparging rate increased for all MLTS concentrations, but no further increase was noted above (6.0 m^3/m^2.h). The relationship between the critical flux and MLTS concentrations of 5.7, 7.7 and 10.6 g/L can be approximated by a linear relationship for all the sparging intensities tested (the critical flux decreased as MLTS concentrations increased), but no further decrease in the critical flux was noted at MLTS concentration of 15.0 g/L. The short term study was followed by a long term study to validate the concept of the critical flux. The SAnMBR was operated at sub-

critical flux but membrane fouling occurred (decreased flux and increased TMP) within five weeks operation mainly caused by a gel layer formation. The results suggest that the concept of critical flux is not valid for SAnMBRs.

In the second part, a high-rate SAnMBR was developed. The results were stunning as the SAnMBR's performance surpassed the UASB's performance. The SAnMBR maintained organic loading rate (OLR) of 39.85 ± 1.14 Kg COD/m^3.d for more than 100 days at chemical oxygen demand (COD) removal efficiency of more than 99.7% (with very low effluent COD concentration of 42 ± 17 mg/L) and excellent biogas production (0.39 ± 0.07 L CH_4 /g COD removed) and CH_4 composition of 66.89% ± 1.52. The results suggest that SAnMBR can compete with UASB and achieved superior effluent quality for system closure or water reuse.

In part I, no membrane fouling was developed under stable operation for over 300 days. In part II, gel layer formation was the main mechanism of fouling. Inorganic fouling was more important than organic fouling in both part I and II studies.

Acknowledgements

It is my pleasure to thank all the people who made this thesis possible. First and foremost, I would like to express my sincere gratitude and appreciation to my academic advisor, Dr. Baoqiang Liao, for his continuous encouragement, support, and understanding and for his critical thinking and questioning throughout the course of this study. My great appreciation also goes to the following people for their contributions towards the success of my research and study:

- My supervisory committee members Dr. Pedram Fatehi and Dr Wensheng Qin for their valuable advice and guidance.
- GE Power and Water for financial support and namely Dr. Martha Dagnew and Mr. Young seck Hong for their continuous support.
- Faculty Members of Environmental Engineering for their great lectures and help.
- Depts. of Chemical Engineering & Chemistry
- Lakehead University, LUIL staff, Mr. Garry Rathje and Ms. Debbie Puumala at chemical storage.
- Special acknowledgements must be given to the members of Dr. Liao's team: Dr. Weijue Gao and Lin Hao.

Finally, I am ineffably grateful to my wife Safana Omer for her encouragements and taking up the additional responsibilities while I pursued my degree. Special thanks to my Son Satti and daughter Omnia for their share of sacrifice and to my youngest son Yousuf who was born within the last two months of this thesis. Without my family's love and support this work would have been impossible and meaningless.

I would like to dedicate this thesis to my parents, who have been a constant source of spiritual inspiration throughout my life. May Allah show mercy on them and let them rest in paradise as they have nourished me when I was young. All praise to Almighty Allah, for keeping me healthy and inspired throughout my research.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

Abbreviations	Meaning
AFM	Atomic Force Microscopy
AnMBR	Anaerobic Membrane Bioreactor
ANOVA	analysis of variance
BOD	Biochemical Oxygen Demand
CLSM	confocal laser scanning microscopy
CSTR	Completely Stirred Tank Reactor
COD	Chemical Oxygen Demand
EDX	Energy-dispersive X-ray spectroscopy
EPS	Extracellular Polymeric Substances
F	Full scale
F/M	Food/Microorganisms
FS	Flat Sheet
FTIR	Fourier Transform Infrared
GAC	granular activated carbon
HF	Hollow Fibre
HF-SAnMBR	Hollow Fibre Anaerobic Membrane Bioreactor

HRT	Hydraulic Retention Time
L	Laboratory/bench scale
LMH	Litres Per Square Meter Per Hour
LPM	Liters Per Minute
MBRs	Membrane Bioreactors
MF	Microfiltration
MLSS	Mixed Liquor Suspended Solids
MWCO	Molecular Weight Cut-off
NF	Nanofiltration
OLR	Organic Loading Rate
P	Pilot scale
PAC	Powered Activated Carbon
PE	Polyethylene
PSD	Particle Size Distribution
PVC	Polyvinyl Chloride
PVDF	Polyvinylidene Fluoride
RO	Reverse Osmosis
Rt	Total Resistance

SEM	Scanning Electron Microscopy
SMP	Soluble Microbial Products
SRT	Solid Retention Time
SS	Suspended Solids
TMP	Trans-membrane Pressure
TSS	Total Suspended Solids
UASB	Upflow Anaerobic Sludge Blanket
UFAF	Upflow Anaerobic Filter
UV	Ultraviolet

Chapter 1 : Introduction

1.1 Overview of the present study

Environmental contamination is one of the major challenges facing human beings in the twenty-first century. We are also facing the repercussions of climate change, increased global demand on fossil fuels, unstable energy supply, and constant exploitation of the very limited natural resources (Khanal et al., 2008). The conventional methods of pollution control, that focus on removing pollutants from a single medium, that is, transformation of contaminants from liquid to solid or gas phases and vice versa, is no longer considered an attractive option. It has become immensely important to encourage research efforts on sustainable approaches that not only alleviate environmental pollution, but also ease the stress on diminishing natural resources and skyrocketing energy shortage (Khanal et al., 2008). Anaerobic wastewater treatment process has long been considered as a more cost effective treatment technology than the aerobic treatment of various kinds of wastewater ranging from low to medium to high strength, including municipal and industrial wastewaters. The success of anaerobic treatment is accredited to low biomass yield, high organic loading potential, less nutrient requirement, smaller reactor volume and low operations & maintenance capitals. Furthermore, biogas recovery from anaerobic treatment can be used as a renewable energy source, thus reducing green house gas emission (Wijekoon et al., 2011). At the present, high rate anaerobic treatment of industrial wastewaters is considered an established effective technology. The success of high rate anaerobic treatment can be attributed to the retention of slow growing methanogenic bacteria in the bioreactor by

effectively decoupling of solids retention time (SRT) and hydraulic retention time (HRT) (Lomte and Bobade., 2013). The commonly used methods of biomass retention are settling, attachment and granulation. The granulation is the most commonly applied process, as substantiated by the profusion of up-flow anaerobic sludge bed (UASB), expanded granular sludge bed (EGSB) and internal circulation (IC) reactors for the treatment of industrial wastewaters (Dereli et al., 2012). Due to the combination of simple construction and a high volumetric treatment capacity, the up-flow anaerobic sludge blanket (UASB) is the most dominant high rate anaerobic reactor (Chong et al., 2012). UASB reactors are extensively applied in treating most of the wastewaters containing high concentrations of soluble organic matter. However, UASB still faces many challenges such as long duration for start-up period, biomass wash-out, requirement for effluent polishing and failure to treat wastewaters at extreme conditions (e.g. high temperature, high salinity and presence of toxicity) (Lomte and Bobade (2013); Martinez-Sosa et al., 2011; An et al., 2009; Najafpour et al., 2008).

In recent years, the Anaerobic membrane bioreactors (AnMBRs) has gained popularity and emerged as a competitive high rate technology as it offers in addition to the advantages of conventional high rate reactors; superior effluent quality (free of solids and pathogens), complete retention of biomass, decouple SRT from HRT and more importantly overcomes the weaknesses of the UASB (Dereli et al., 2012). Nonetheless membrane fouling and low organic loading rate are a synonym for AnMBRs. So far, AnMBRs have been operated at much lower OLRs compared to UASB despite the potentials to be developed further. In order for the AnMBRs to compete with UASB, high rate AnMBRs need to be developed to convince the market to

switch to AnMBRs. We must stress that there is no any other technology that can beat AnMBR in terms of overall performance with the exception of OLR.

The deterioration of the membrane performances due to membrane fouling remains the major obstacle hampering the extensive application of AnMBRs. Membrane fouling is responsible for the rapid decline of permeation flux or an increase in trans-membrane pressure (TMP), higher energy consumption, more frequent membrane cleaning and replacement eventually increasing the operational cost of the AnMBR process. Due to the complexity, variability and interaction of the membrane properties, operational and the environmental conditions, membrane fouling have not been fully understood and explained. Further research on membrane fouling mechanisms is imperative to develop effective membrane fouling control strategies.

Based on membrane integration into the bioreactors, two MBR process configurations have been developed: side-stream and submerged (see section 2.1.5). In side-stream MBRs, membrane modules are located outside the reactor (external cross flow), and the mixed liquor of the reactor circulates over a recirculation loop containing the membrane and the permeation is obtained through pressure. In submerged MBRs, the membranes are situated inside the reactor (submerged) and a vacuum pump is used to draw the effluent through the membrane. Side-stream MBRs are energy intensive process while submerged MBRs involve lower energy needs. Thus, submerged MBRs are gaining popularity. However, biogas sparging is needed to scour the membrane surface as a fouling control strategy. Biogas sparging rate has been proved to influence the/ membrane fouling but the optimum sparging intensities are not

fully understood yet and more research needs to be conducted (Stuckey (2012); Bornare et al., 2014; Watanabe et al., 2014)

Biomass properties such as particle size distribution (PSD), mixed liquor suspended solids (MLSS) concentration and extracellular polymeric substance (EPS) can seriously affect the biological performance and membrane fouling (Meng et al., 2006). Higher MLSS concentrations may increase energy demand, as well as increasing the risk of membrane fouling (Judd (2008)). However, no guidelines have established on recommended MLSS concentrations due to its complex effect on the overall performance of AnMBRs.

1.2 Novelty of the study

- No high OLR anMBR over 24 kg COD/m^2.d has been developed with excellent performance to compete with UASB.
- The limited studies of MLSS effect on critical flux were achieved by varying the SRT to change MLSS concentration which also changes sludge properties. We have carried on an accelerated study on the effect of MLSS on critical flux by minimizing the change of sludge properties.

1.3 Research objectives

The overall goal of this study was to investigate and develop the next generation of SAnMBR technology for industrial wastewater treatment and benefit from the biogas production and the superior quality of the AnMBR effluent that can be re-used or

recycled without further treatment and be fully integrated in the much desired system enclosure of the industrial processes.

The specific objectives of the study were designed to:

- Develop a high-rate AnMBR to compete with conventional anaerobic wastewater treatment, namely, up-flow anaerobic sludge blanket (UASB)
- Investigate the effect of mixed liquor suspended solids (MLSS) and biogas sparging rate on critical flux and membrane fouling
- Study membrane fouling and its control
- Characterize membrane fouling and foulants

1.4 Outline of this thesis

This thesis is organized in five chapters. Chapter 1 includes the general introduction, the motivation and research objectives of this study. Chapter 2 presents a comprehensive literature review of previous studies on AnMBR, including details on the evolution of anaerobic membrane treatment process, MBR configurations, operation, application and membrane fouling and fouling control strategies. In Chapter 3, a flat sheet membrane was submerged in a laboratory-scale anaerobic bioreactor (FS-SAnMBR) and was operated for petro-chemical synthetic wastewater treatment. The effect of MLSS concentration and biogas sparging intensity on the critical flux of submerged anaerobic membrane bioreactor (SAnMBR) was studied. The critical fluxes at various MLSS concentrations and spraging intensities were investigated in a short term studies followed with a long term operation to evaluate one of the critical fluxes measured in the short term study. In Chapter 4 a hollow fibre-submerged anaerobic

membrane bioreactor (HF-SAnMBR) was used to develop a high rate SAnMBR to compete with the conventional high rate anaerobic treatment processes mainly the up-flow anaerobic sludge blanket (UASB). The overall performance of the HF-SAnMBR was monitored in terms of organic loading rates (OLRs), chemical oxygen demand (COD) removal efficiency, biogas production and composition. Sludge properties role in membrane fouling was investigated and finally, the membrane fouling characterisation in terms of resistances was performed. The general conclusions from these studies and recommendations for future research are summarized in Chapter 5.

1.5 References

An, Y., Yang, F., Bucciali, B., & Wong, F. (2009). Municipal wastewater treatment using a UASB coupled with cross-flow membrane filtration. Journal of Environmental Engineering, 135(2), 86-91.

Bornare, J. B., Raman, V. K., Sapkal, V. S., Sapkal, R. S., Minde, G., & Sapkal, P. V. (2014). An Overview of Membrane Bioreactors for Anaerobic Treatment of Wastewaters.

Chong, S., Sen, T. K., Kayaalp, A., & Ang, H. M. (2012). The performance enhancements of upflow anaerobic sludge blanket (UASB) reactors for domestic sludge treatment–A State-of-the-art review. Water research, 46(11), 3434-3470.

Dereli, R. K., Ersahin, M. E., Ozgun, H., Ozturk, I., Jeison, D., van der Zee, F., & van Lier, J. B. (2012). Potentials of anaerobic membrane bioreactors to overcome treatment limitations induced by industrial wastewaters. Bioresource technology, 122, 160-170.

Judd, Simon. "The status of membrane bioreactor technology." Trends in biotechnology 26.2 (2008): 109-116.

Khanal, S. K. (2008). Overview of anaerobic biotechnology. Anaerobic biotechnology for bioenergy production: principles and applications. Wiley–Blackwell Publishing, New York http://www. wiley. com/WileyCDA/WileyTitle/productCd0813823463. html, 20, 385-406.

Lomte, A. T., & Bobade, V. V. Suitability of UASB Reactor System in Tropical Developing Countries like India.

Martinez-Sosa, D., Helmreich, B., Netter, T., Paris, S., Bischof, F., & Horn, H. (2011). Anaerobic submerged membrane bioreactor (AnSMBR) for municipal wastewater treatment under mesophilic and psychrophilic temperature conditions. Bioresource technology, 102(22), 10377-10385.

Meng, F., Chae, S. R., Drews, A., Kraume, M., Shin, H. S., & Yang, F. (2009). Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material. Water research, 43(6), 1489-1512.

Najafpour, G. D., Hashemiyeh, B. A., Asadi, M., & Ghasemi, M. B. (2008). Biological treatment of dairy wastewater in an upflow anaerobic sludge-fixed film bioreactor. Am. Eurasian J. Agric. Environ. Sci, 4, 251-257.

Stuckey, D. C. (2012). Recent developments in anaerobic membrane reactors.Bioresource technology, 122, 137-148.

Watanabea, R., Qiaoa, W., Nortond, M., Wakaharae, S., & Lia, Y. Y. (2014). Recent Developments in Municipal Wastewater Treatment Using Anaerobic Membrane Bioreactor: A Review. Journal of Water Sustainability, 4(2), 101-122.

Wijekoon, K. C., Visvanathan, C., & Abeynayaka, A. (2011). Effect of organic loading rate on VFA production, organic matter removal and microbial activity of a two-stage thermophilic anaerobic membrane bioreactor. Bioresource Technology, 102(9), 5353-5360.

Chapter 2 : Literature Review

2.1 Anaerobic Membrane Bioreactor (AnMBR)

2.1.1 Introduction

The Anaerobic membrane bioreactor (AnMBR) process can be simply defined as a biological treatment process operated in the absence of oxygen and using a membrane to provide complete solid-liquid filtration (Visvanathan and Abeynayaka., 2012). The first known commercial Anaerobic Membrane Bioreactor (AnMBR) was built in the early 1980s, by Dorr-Oliver for high-strength whey processing wastewater treatment, the development was named membrane anaerobic reactor system (MARS) (Lin et al., 2013; Skouteris et al., 2012; Liao et al, 2006). Since then, AnMBRs have been widely studied for application in the treatment of municipal and industrial wastewaters of various strengths (Skouteris et al., 2012). As the AnMBRs could operate independently in relation to the SRTs, it becomes capable of tolerating high organic loading rates. This is an advantage which makes it an attractive option for low (i.e., municipal wastewater) to high strength industrial wastewater treatment, energy recovery and low excess sludge production (Visvanathan and Abeynayaka., 2012).

2.1.2 What is Membrane?

A membrane can be defined as a material forming a thin wall having the capability of selectively resisting the transfer of fluids with different constituents and can effectively separate these constituents from the liquid. Hence, membranes must be produced with materials having a reasonable mechanical strength that can sustain a

high throughput of a desired permeate with a high degree of selectivity. The most effective physical structure of the membrane material is rested on a thin layer of material with a narrow range of pore size and a high surface porosity (Visvanathan and Aim., 2002). Based on membrane pore sizes, there are four types of membranes: microfiltration (MF; 0.05~10 μm), ultrafiltration (UF; 0.002~0.01 μm), nanofiltration (NF; 0.001~0.002 μm) and reverse osmosis (RO; ~0.002 μm) (Watanabe et al., 2014).

2.1.3 Membrane Bioreactor

Membrane Bioreactor (MBR) technology is the combination of the biological degradation process with solid-liquid separation or membrane filtration process. Generally, micro or ultra-filtration membranes with pore sizes in the range of 0.1 to 0.4 μm are employed in MBRs (Zhu et al., 2014; Bornare et al., 2014). The overall quality of water treated by the MBR technology equates the combination of secondary clarification and effluent microfiltration. Therefore, the MBR systems are becoming an attractive option for the treatment and reuse of various types of wastewaters such as industrial and municipal wastewaters (Zhu et al., 2014).

2.1.4 The Anaerobic Digestion Process

Anaerobic digestion (AD) is considered a very complex reduction process consisting of a number of biochemical reactions taking place under anaerobic conditions and several types of microorganisms are involved in the complex process. During the anaerobic process, biogas (mainly composed of methane and carbon dioxide) is produced as the end product. Methane formation in the anaerobic digestion occurs in

four different steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Adekunle and Okolie., 2015).

Hydrolysis: It is the first step in the anaerobic digestion process initiating transformation of insoluble organic materials and large molecular compounds such as proteins, lipids, polyssacharides, cellulose, fats etc. into soluble organic compounds suitable for the use as an energy source and cell carbon (e.g., glucose, monosaccharides, fatty acids, amino acids and other simple organic materials.

Acidogenesis (Fermentation): In this step, the monomers produced in the previous step are further digested by different anaerobic bacteria (acidogenic bacteria) and converted into short chain organic acids (e.g., formic, butyric, lactic, propanoic, acetic), alcohols, acetate, hydrogen, ketones and carbon dioxide.

Acetogenesis: In this phase the fermentation products are consumed as substrate for the microorganisms (acetogenic bacteria) and through a biological reaction are broken-down into acetate, hydrogen, and carbon dioxide (CO_2).

Methanogenesis: This is the final phase of the anaerobic digestion where the production of methane and carbon dioxide from intermediate products takes place. The biological reaction is carried out by methanogenic bacteria under strict anaerobic conditions. It is important to note that the methanogenesis is a very critical step in the whole anaerobic digestion process as it is the slowest biochemical reaction of the process. Figure 2-1 shows the overall biochemical process.
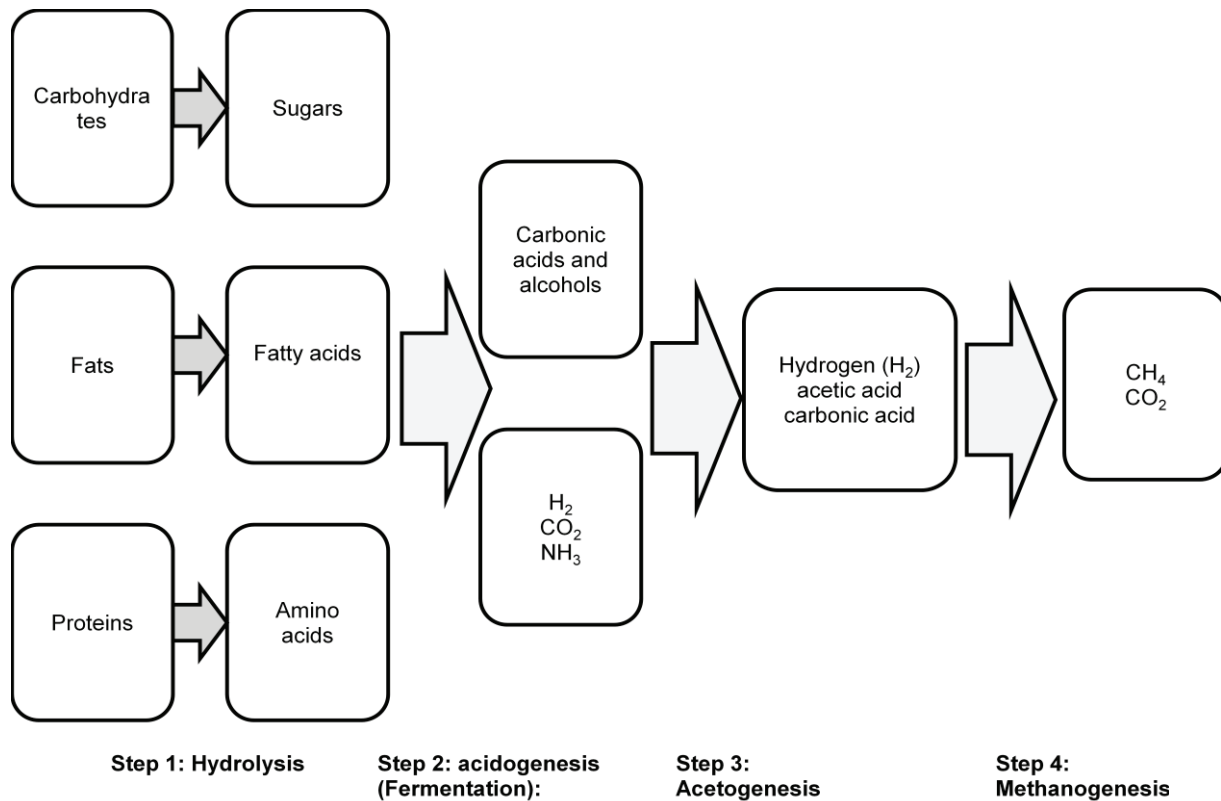
Figure 2-1: Anaerobic digestion biochemical conversion pathways

(Adapted from Adekunle and Okolie., 2015)

It is important to note that anaerobic microorganisms particularly the methanogens are very sensitive to environmental changes. Since methanogenesis is a rate limiting reaction in anaerobic digestion process, its stability directly depends on the environmental conditions such as operating pH, temperature, nutrients and trace elements and toxicity. Besides, methanogens are greatly susceptible to the variations in substrate loading. For example, changes in temperature in anaerobic reactors should not exceed 0.6-1.2 $^{\circ}$C per day. The optimum pH range of acetogens / acidogens is 5.5-7.2 while methanogens have a very narrow pH range of 6.8-7.8. As a result, it is imperative to maintain reactor pH around the neutral to optimize the methanogenic activity (Visvanathan and Abeynayaka., 2012).

2.1.5 Integration of membrane modules into the AnMBR systems

In general there are two principle methods of integrating the membrane modules into the AnMBR process: the side-stream configuration (also termed external cross-flow) and the submerged configuration. In the first case, the membrane is isolated from the bioreactor and a pump is employed to push bioreactor effluent into the membrane modules and permeate through the membrane (Figure 2-2). This type of configuration is also called an external cross-flow. The cross-flow velocity of the liquid (in the range of 1–4 m/s) across the membrane surface produces a turbulent cross-flow and serves as the main mechanism to disrupt cake formation on the membrane. This method is a very energy intensive process; therefore, the attention is shifting towards the submerged configuration. In the second option, the membranes are submerged in the mixed liquor, and permeate is obtained by mechanical suction or by gravity flow. Due to the interaction of mixed liquor with the membrane, fouling can occur and needs to be controlled. This can be done by biogas sparging to disrupt the cake layer formation. Off course in case of aerobic MBRs, air can be used to scour the membrane surface and provide aeration. The major advantage of having the membrane submerged in the bioreactor is that the energy required for pumping and recycling the sludge is eliminated. On the other hand, biogas must to be recycled from the headspace to underneath of the membrane modules to provide biogas scouring for fouling control.

The submerged (also called vacuum-driven) membrane approach can be installed in two configurations. The membrane may be submerged directly into the bioreactor (Figure 2-3) or submerged into a separate filtration tank (Figure 2-4). The latter configuration resembles the external membrane configuration, thus, requiring a

pump to return the retentate to the bioreactor to maintain constant sludge concentration. Nevertheless, unlike the external cross-flow membrane configuration, permeate here is obtained by suction instead of pressure. The separate tank configuration (Figure 2-4) is mostly applied in for full-scale aerobic wastewater treatment plants (WWTPs) as it simplifies cleaning of the submerged membranes, because the chambers can be isolated instead of physically removing the membranes. In general, submerged configurations have proved to be more cost and energy effective than the side-stream configurations (Stuckey (2012); Li et al., 2008; Liao et al., 2006).

In terms of membrane shape configurations, there are three common shapes: hollow fiber, flat sheet and tubular. The most common shapes are the hollow fiber and flat sheet for micro-filtration (MF) and ultra-filtration (UF) application in the AnMBR technology (Judd (2010)).
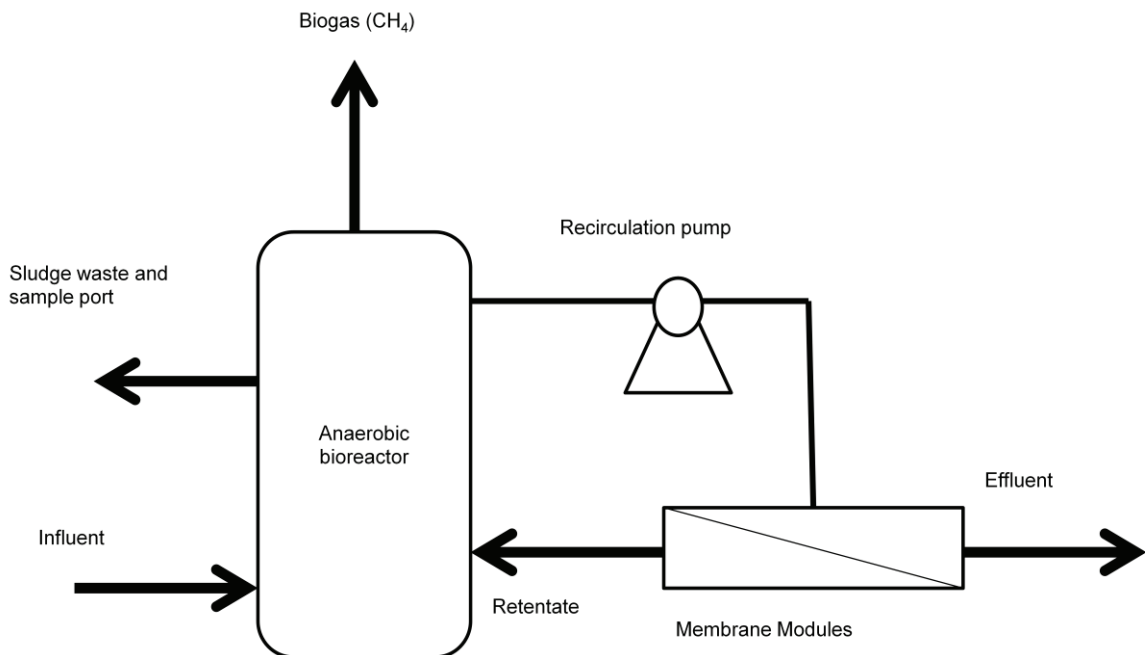
Figure 2-2: Side-stream process configuration (External cross-flow)

(Adapted from Liao et al, 2006)
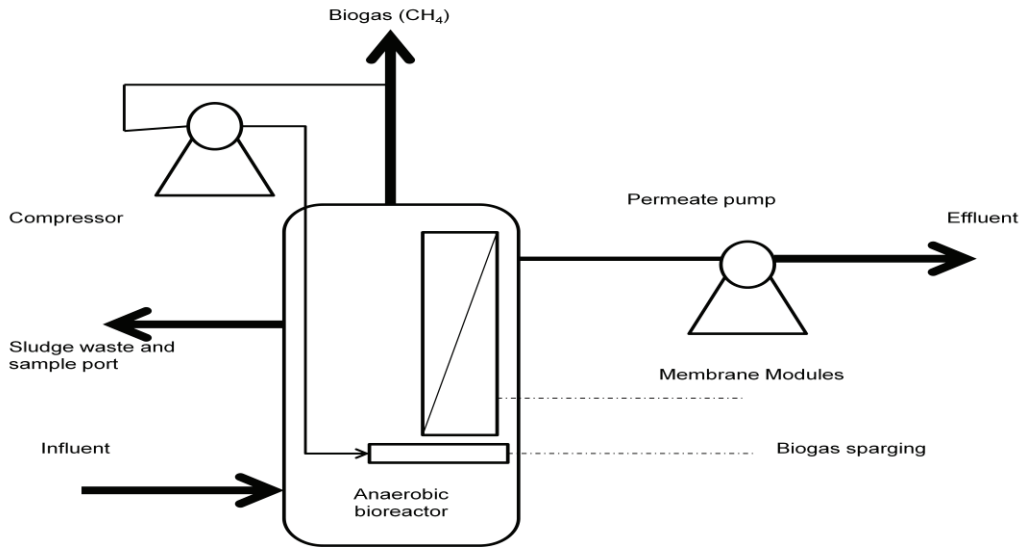
Figure 2-3: Submerged membrane configuration

(Membrane submerged inside the reactor- Adapted from Liao et al, 2006)
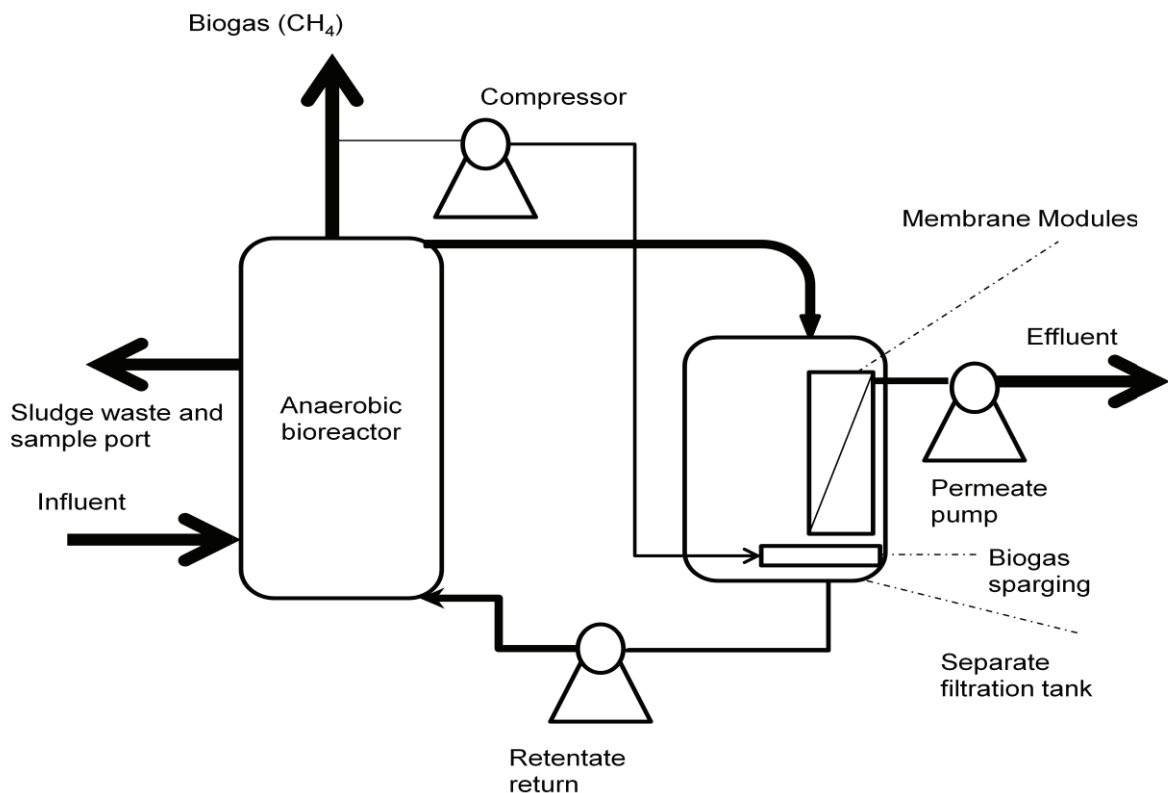
Figure 2-4: Membrane configuration (membrane submerged in a separate filtration tank) - (Adapted from Liao et al, 2006)

2.2 Anaerobic membrane bioreactor (AnMBR) for treatment of industrial wastewaters

Due to their outstanding advantages like high quality effluent, biogas production and low sludge yield, anaerobic membrane bioreactors (AnMBRs), which is a combination of anaerobic bioreactors and membrane filtration units for biomass retention in a single step, have proved to become state-of-the-art technology in wastewater treatment and are increasingly gaining popularity (Lin et al., 2012; Drews et al., 2010; Judd (2008); Liao et al., 2006). So far, AnMBR technology has been applied to treat various types of wastewaters such as synthetic wastewaters, food processing wastewaters, industrial wastewaters, high-solids-content waste streams and municipal wastewaters (Liao et al., 2006). The term industrial wastewaters may refer to the wastewaters generated from industries such as food, pulp and paper, textile, tannery, pharmaceutical, oil and petrochemical, landfill leachate and other industries (Lin et al., 2013; Lin et al., 2012). As the disposal of wastewaters generated from the industries into the municipal sewer systems is no longer permitted, integration of on-site wastewater treatment plants into the process of industrial operations is becoming the norm. In recent years, the success of submerged MBR technology in municipal wastewater treatment has greatly influenced the application of MBRs in the industrial wastewater treatments (Lin et al., 2012).

Furthermore, the rapid industrialization has resulted in the generation of a large quantity of effluents from the industrial sectors. Some of these effluents are characterized by high organic strength and/or extreme physical–chemical nature (e.g., pH, temperature, salinity, high calcium concentrations, FOG content, high SS content),

and containing synthetic and natural compounds that may inhibit (be toxic to) the biological treatment processes. At these extreme conditions, AnMBRs can be viewed as an attractive and the only viable option for treatment as the traditional high-rate conventional reactors such as upflow anaerobic sludge bed (UASB) have poorly performed due to the failure of the sludge bed formation (Lin et al., 2013; Dereli et al., 2012).

Wastewaters generated from food processing industries are rich in organics (COD concentration of 1000 – 85,000 mg/L) with a wide range of suspended solids concentration ranging from 50 to 17,000 mg/L. Hence, they are easily biodegradable, making the anaerobic treatment the most suitable treatment option. In general COD removal efficiency in treating these industrial wastewaters was more than 90%, with applied OLRs ranging from 2-15 kg COD/m^3/day (Liao et al., 2006).

Evaporator condensate (EC), one of the major constituents of the effluent produced from pulp and paper industry, was studied by various researchers using both mesophilic (37 °C) and thermophilic (55 °C) AnMBRs. The results showed more than 93% COD removal efficiency at influent COD concentration of 10,000 mg/L and OLRs in the range of 1-24 kg COD/m3/day (Lin et al., 2013).

Treatment of simulated petrochemical industrial wastewater by a submerged (SAnMBR) using a flat sheet MF membrane resulted in a very high COD removal efficiency at high organic loading rates of 25 kg COD/m3/day in a long term operation. Slaughterhouse wastewater treatment by an AnMBR was also investigated at high organic loading rates in the range of 4.4 and 13.3 kg COD/m3/day. However, a process failure was observed when OLR reached 16.3 kg COD/m3/day due to volatile fatty acid

(VFA) accumulation in the bioreactor. Interestingly, AnMBR treating palm oil mill (POM) wastewater recorded very high COD removal rate of more than 96% at OLRs of 1–11 kg COD/m3/day and HRTs ranging from 7 to 600 days (Dereli et al., 2012).

As discussed above, AnMBR technology can be successfully applied for the various types of industrial wastewaters with efficient performance, this success is expected to lead to a tremendous growth in the full-scale application of the anMBR technology in the near future.

2.3 Effect of operating and environmental conditions on performance and membrane fouling in AnMBRs

Anaerobic treatment process is a complicated system which is greatly influenced by many factors such as operating conditions (organic loading rate (OLR), HRT, SRT and membrane flux) and environmental conditions (pH and temperature).

2.3.1 Operating temperature

Generally, most of the AnMBRs systems are operated either in the mesophilic range at around 35 ºC or at around 55 ºC in the thermophilic range, mainly due to their slow growth rate. These high temperatures can be very helpful due to the nature of hot industrial wastewaters by eliminating the cooling process. In addition, the lower viscosity of the biomass suspension at higher temperatures can lead to higher fluxes (Skouteris et al., 2012; Stuckey (2012)). The mixed-liquor temperature also impacts the COD removal efficiencies; higher temperatures lead to increased COD removal efficiencies. For example, Skouteris et al (2012) documented that total COD removal efficiency of

95% and 85% were achieved at 25 ºC and 15 ºC respectively. Psychrophilic temperatures of around 20 ºC have also been tested by some researchers. However, there may be issues about the loss of methane in the effluent due to its enhanced solubility at low temperatures (Skouteris et al., 2012; Stuckey (2012)).

2.3.2 Operating pH

There are two groups of anaerobic bacteria in terms of optimum pH: acid-producing bacteria (acidogens) and methane-producing bacteria (methanogens). The acidogens can be optimized in the pH range of 5.5–6.5, while methanogens prefer a higher pH range of 7.8–8.2. In typical anaerobic environment where both cultures must coexist, the optimal pH range is between 6.8 and 7.4. As the methanogenesis is the rate-limiting step, when both groups of microorganisms are present, it is imperative to keep the reactor pH close to neutral (Khanal (2008)).

2.3.3 Organic loading rate (OLR)

The organic loading rate (OLR) is a measure of treatment capability of the bioreactor per unit volume of the digester and typically expressed in the units of (Kg COD/m^3.day). It can be mathematically calculated as:

$$\text{OLR} = \frac{Q * C}{V}$$

Where Q represents the flow rate (m^3/day), C represents the COD concentration of the influent (mg/L), and V represents the volume of the bioreactor (m^3).

Modern high-rate anaerobic bioreactors have the capability of treating wastewater at very high organic loading rates (typically 10 – 40 kg COD/m^3.day). These high OLRs translate to more wastewater being treated per unit volume of the bioreactor. This is mainly attributed to the fact that, oxygen transfer is not a limitation in the anaerobic digestion processes (Khanal (2008)). Fakhru'l-Razi (1994) discussed the following procedures of increasing the OLR in an AnMBR:

i.   Increase the influent COD concentration

ii. Increase the membrane flux (if possible), or increase the membrane area at a fixed flux

iii. Decrease the volume of the bioreactor at a given influent COD concentration

iv. Increase the wasting rate of the mixed liquor

High OLRs and short HRTs are theoretically applicable in AnMBRs. Nonetheless, the OLR of the AnMBR system is not an independent parameter and it should be considered along with SRT and activity of the sludge. In other words, high biomass concentrations do not always necessarily translate into application of high OLR (Dereli et al., 2012). AnMBR systems have the major advantage of tolerating fluctuations in organic loading similar to its tolerance to the changes in temperature.

2.3.4 Sludge retention time (SRT)

The sludge retention time (SRT) refers to the average time the activated-sludge solids spend in the treatment system. The SRT is an important parameter in design and operating of the biological systems and is usually expressed in days

(Rittmann & McCarty., 2012). In general, as a rule of thumb, SRTs in high-rate anaerobic bioreactors are equal or greater than 3 times the doubling time of the rate limiting biomass. Thus, assuming doubling times of 4–10 days of acetotrophic methanogenic bacteria, a SRT of more than 20 days is generally recommended for mesophilic anaerobic high-rate reactors. AnMBRs offer the major advantage of a SRT completely independent from HRT, allowing full control of the SRT regardless of the sludge quality. Typical SRTs applied in AnMBRs are between 30 to 300 days. Infinite SRTs also have been reported, indicating that no sludge wasting practically occurred during the MBR operation. Generally, high SRTs are preferred since it leads to less sludge waste and higher sludge concentrations in the bioreactor. On the other hand, long SRTs may also influence the activity of the methanogenic sludge owing to a decrease in viable microorganism concentration (Dereli et al., 2012; Skouteris et al., 2012).

2.3.5 Hydraulic retention time (HRT)

The hydraulic retention time (HRT) refers to the average length of time the wastewater spends in the treatment system (Rittmann & McCarty., 2012). The HRT is key parameter in performance optimisation of an AnMBR as low HRTs translate to smaller reactor volume and thus lower construction and maintenance costs. Hence, the influence of HRT on the biological performance of AnMBRs has been investigated by many researchers. HRT values ranging from a few hours (i.e. 2 h) to a few days (i.e. 20 d) have been reported in literature. In general, COD concentrations both within the bioreactor and effluent increases slightly with a decrease in HRT due to the increased organic load (OLR) (Ozgun et al., 2013; Skouteris et al., 2012; Stuckey et al 2012; Liao

et al., 2006). Ozgun et al (2013) hypothesized that there is an optimum HRT for each application, which is determined by various parameters such as system hydraulics, wastewater characteristics, temperature, F/M ratio, reactor design and sludge properties, to obtain both efficient biological removal and filtration performance.

2.3.6 Critical Flux

Critical flux is known as the flux below no membrane fouling occurs (Field *et al.*, 1995). Membrane flux is an important parameter affecting the fouling rate. In General, operating below the critical flux can reduce the fouling rate. The concept of the critical flux in MBRs was first introduced by Field et al. (1995); the authors defined the critical flux as: "The critical flux hypothesis for micro-filtration is that on start-up there exists a flux below which a decline of flux with time does not occur; above it, fouling is observed. This flux is the critical flux and its value depends on hydrodynamics and probably other variables." Two forms of the concept were introduced: strong form and weak form. The strong form states that the flux acquired during sub-critical flux is equated to the clean water flux attained under the equivalent conditions (Le Clech et al., 2003a). The weak form defines the sub-critical flux as the flux immediately established and maintained during the start-up of the biomass filtration, though it does not certainly equate to the clean water flux (Le Clech et al., 2003a). Since then the concept of the critical flux and the various factors influencing the critical flux has been extensively studied by many researchers (Monclus et al., 2010; Robles et al., 2012; Fox and Stuckey., 2015). These factors affecting the critical flux include: biomass properties, environmental conditions (pH and temperature), membrane properties and hydrodynamic conditions.

Numerous methods have been used to measure the critical flux, such as direct membrane observation, mass balances, and TMP observation in flux step method (or cycling experiments). Mass balances and microscopic observations are less likely to be applied in full-scale plants or in submerged MBR systems. Nevertheless, pressure increase at constant flux operation (or pressure step method) and flux step method can be smoothly applied for critical flux measurement in any type of MBR process, both at lab and full-scale (Jeison (2007)).

Table 2-1 (modified from Robles et al., 2012) summarises some of the critical studies reported in literature under different operating conditions: wastewater type, reactor scale, membrane type and pore size, reactor type, operating MLSS concentration, air and or biogas sparging intensity

2.3.7 Biogas sparging rate

Biogas sparging is the most common way to provide shear stress over the membrane surface in order to reduce the fouling rate or to restrict foulants interaction with the membrane (Dereli et al., 2012). Robles et al. (2012) investigated effect of various sparging intensities on the critical flux of SAnMBR at MLSS concentration of 23 g/L and noted a linear dependency between the critical flux and the biogas sparging intensity. Increasing the biogas sparging rate in submerged AnMBRs enhances the hydrodynamic conditions but also increases energy cost, disrupts sludge flocs and negatively impacts membrane fouling (Lin et al., 2012). Therefore; optimisation of the biogas sparging rate is a critical factor in economical success of the AnMBRs.

Table 2-1: Summary of some critical flux studies published in literature (Modified from Robles et al., 2012).

Wastewater (type)	MBR (type)	Type of Membrane	Pore size (μm)	MLSS (gL^{-1})	$J_{C,20}$ (LMH)	Sparging rate (m^{3}m^{-2}h^{-1})	Reference
Synthetic	UASB	FS	0.22	0.3–0.55	30-50	-	Cho and Fane (2002)
Synthetic	Aerobic	FS	0.4	20	10-22	-	Howell et al. (2004)
Municipal	Aerobic	FS	0.4	8	17.5	8.6	Wu et al. (2008)
Municipal	Aerobic	FS	0.8	8	29.5	8.6	Wu et al. (2008)
Municipal	Aerobic	FS	0.2	8	41.5	8.6	Wu et al. (2008)
Synthetic	Aerobic	FS	0.45	10	25	-	Guo et al. (2008)
Municipal	Aerobic	FS	0.37	14	5	-	Bottino et al. (2009)
Municipal	Aerobic	FS	0.1	10	50	-	Van der Marel et al. (2009)
Synthetic	Aerobic	Tubular	0.2	3	10	1.9	Le-Clech et al. (2003)
Municipal	Aerobic	Tubular	0.2	3	10	1.9	Le-Clech et al. (2003)
Synthetic	Anaerobic	Tubular	0.2	25	16-22	-	Guglielmi et al. (2006)
Synthetic	Anaerobic	Tubular	0.2	35	3-6	-	Jeison and Van Lier (2007)
Domestic	Aerobic	HF	0.1	12-19	19	-	Guglielmi (2002)
Domestic	Aerobic	HF	0.4	10-18	20	-	Guglielmi (2002)
Municipal	Aerobic	HF	0.04	10	25-31	0.3–1.0	Stephenson et al. (2000)
Municipal	Aerobic	HF	0.04	10	28	0.35	Guglielmi et al. (2007)
Municipal	Anaerobic	HF	0.05	23	12–19	0.17–0.5	Robles et al. (2012)

Notes: FS: flat-sheet; HF: hollow-fibre; MLSS: mixed liquor suspended solids concentration; J_{C20}: 20 ºC-normalised critical flux; and S(A/G)D$_m$: specific air/gas demand per m^2 of membrane area.

2.4 Membrane fouling and fouling mitigation techniques in AnMBRs

2.4.1 What is membrane fouling?

Membrane fouling is a process where solute or particles deposit onto a membrane surface or into membrane pores in a way that degrades the membrane's performance. Membrane fouling leads to serious flux decline and may affect the quality

of the produced water. Intense fouling may necessitate vigorous chemical cleaning or membrane replacement which in turn increases the operating costs of a treatment plant (Franken (2009)). Membrane fouling is regarded as the major obstacle to the widespread use of this technology. Because of the economical impacts, fouling has been the main issue in membrane and specifically MBR research in the last decade or so. There has been steady increase in the number of published articles on fouling, with approx. 30% of all MBR research focused on fouling (Drews (2010)).

Based on removability of foulants, Meng et al (2009) introduced three classes of fouling: removable fouling, irremovable fouling and irreversible fouling. In removable fouling, foulants can be easily removed from the membrane surface by application of physical cleaning (like backwashing) while chemical cleaning is required for the elimination of the irremovable fouling. The irremovable fouling is a result of pore blockage and strongly adsorbed foulants on the membrane

surface during the membrane filtration operation. The irreversible fouling (or permanent fouling) is represented by the foulants which cannot be removed during physical and chemical cleanings and it is believed to occur over a long period of membrane filtration operation (Drews (2010)). According to the location, membrane fouling can be classified into internal (due to membrane pore blockage) and external (due to cake layer formation) with cake layers meaning porous layers formed by rejected particles on the membrane surface. Internal fouling is normally irreversible, while cake layer formation is reversible (Skouteris et al., 2012).

Based on fouling components, membrane fouling can be divided into three main categories; biofouling, organic and inorganic fouling. These three fouling mechanisms occur simultaneously; however, contribution of each type depends on several factors such as membrane characteristics, sludge characteristics, environmental conditions, reactor design and operating strategy (Meng et al., 2009; Liao et al., 2006).

Biofouling: Biofouling occurs due to the interactions of the components of biological treatment broth with membrane surfaces which leads to deposition and growth of microorganisms on the surface of membranes. Biofouling can be classified as pore clogging, sludge cake formation or adsorption of extracellular polymeric substances (EPS).

Inorganic fouling: Inorganic fouling (or scaling) in AnMBRs occurs due to the chemical precipitation of inorganic colloids and crystals and /or biological precipitation of inorganic-organic compounds. Cat-ions like Ca^{2+}, Mg^{2+}, Fe^{3+}, and

Al^{3+} can react with anions such as CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and OH^- and lead to chemical precipitation once the saturation concentrations are exceeded on the membrane surfaces. Furthermore, the inorganic materials existing in the systems can also be attracted to the membrane surfaces or clog membrane pores causing inorganic fouling (Wang et al., 2014). Precipitation of Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is the most common inorganic foulant, and it can precipitate on organic and inorganic membranes. In addition, there are other inorganic foulants such as $K_2NH_4PO_4$ and $CaCO_3$ (Liao et al., 2006). AnMBRs are vulnerable to inorganic fouling much more than aerobic MBRs, partially because of greater chances for pH shifts attributable to carbon dioxide partial pressure changes and the production of ammonia and phosphate in high concentrations, mostly during sludge digestion (Liao et al., 2006).

Organic fouling: The term of organic fouling refers to those organic substances that are mainly dissolved in the feed solution and have the tendency of sticking to the membrane surface. Foulants such as oil, humic acids, macromolecules, proteins, polysaccharides, anti-foaming agents are all contributors to formation of an organic gel layer on top of the membrane surface or in pores. Adsorption is the main cause of the built-up of the initial layer (Franken (2009); Wang et al., 2014). The somewhat high chemical oxygen demand (COD) concentrations in AnMBRs effluent (in comparison to aerobic MBR systems) increases the relative contribution of organic fouling in AnMBRs. As higher organic loading rates (OLRs) tend to produce higher residual CODs and it is the residual COD not the COD removal rate that affects the membrane

fouling. Operations with higher solids retention time (SRT) may decrease organic fouling as it leads to lower effluent concentration (Liao et al., 2009).

2.4.2 Modeling of membrane fouling

For porous membranes, pores are the active area of the membrane. Thus, most fouling mechanisms are linked to the pores and the processes which lead to a reduction in the number or area of the active pores. Based on this theory, mainly four fouling mechanisms for porous membranes can be identified. As illustrated in figure 2-5, these fouling mechanisms are (Field (2010)):

i.   complete pore blockage

ii.   internal pore blockage

iii.   partial pore blockage

iv.   cake layer filtration
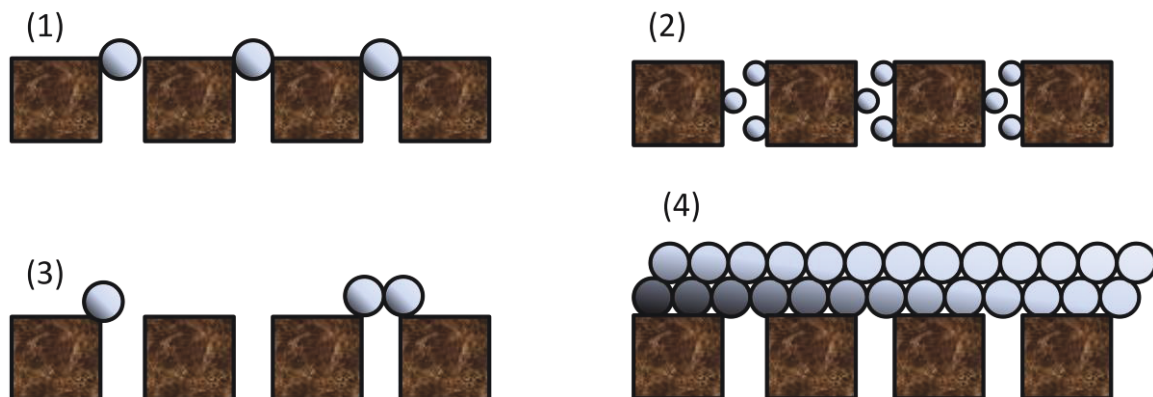
Figure 2-5: Fouling mechanisms of membranes

(Adapted from Field (2010)).

(1) Complete pore blockage; (2) Internal pore blockage; (3) Partial pore blockage; (4) Cake layer filtration.

2.4.3 Factors affecting treatment performance and membrane fouling in AnMBR

There are many factors affecting treatment performance and membrane fouling of AnMBRs as illustrated in figure. 2-6.They can be grouped into five main categories of factors which strongly influence the nature and complexity of membrane fouling and the biological performance: membrane properties, sludge characteristics, hydrodynamic conditions, operating conditions, and environmental conditions. The complex interactions of these factors in AnMBRs are not fully understood (Hai et al., 2013).

2.4.3.1 Membrane properties

Membrane properties such as membrane material, pore size or molecular weight cut-off (MWCO), porosity, roughness, surface charge and hydrophilicity / hydrophobicity can impede MBR performance by impacting on the membrane fouling (Hai et al., 2013;Peeva., 2011; Meng et al., 2009; Liao et al., 2006). The most common commercial pore size of anaerobic MBRs is in the range of coarse Ultrafiltration (UF) to fine Microfiltration range (MF) (Stuckey (2012)). The membrane pore size or molecular weight cut-off can significantly affect the membrane flux, with the larger pore size (or higher molecular weight cut-off) leading to an increase in the flux (Liao et al., 2006). However, Stuckey (2012) reported conflicting results, noting no consistency between membrane pore size and hydraulic performance. He attributed the contradictions to the complexity of the biological suspensions in the MBR process along with operational

parameters such as hydrodynamics and the duration of the test. Membrane materials can be categorized into three main types: organic (polymeric), metallic and inorganic (ceramic) (Lin et al., 2012). Various membrane materials have been reported in MBR studies. The most common materials are: organic polymers (e.g. polyethylene (PE), polyvinylidene fluoride (PVDF) and polyvinyl chloride (PVC)), inorganic materials (like ceramic and porous glass) and metals (stainless steel) (Huang et al, 2010). Membrane materials can significantly affect the membrane fouling. Bérubé et al (2006) reported that the cake layer formation on organic membrane surfaces in an AnMBRs consisted of both biological/organic compounds and inorganic precipitates while struvite was the main inorganic constituent of the cake layer. Membrane shape may also impact the membrane fouling. As documented by Skouteris et al., (2012), Trans-membrane pressure (TMP) values were observed to be higher across HF membranes than across FS membranes when operated under comparable conditions, suggesting HF membranes are more prone to fouling. Surface modification of membranes (by means of coating or grafting) can alter membrane properties while maintaining their macro-porous structure. The surface modifications can increase the surface hydrophilicity, change the surface charge, or subsidize the surface with an anti-bacterial function (Stuckey (2012)). According to Jung and Kang (2003); permeate flux decline rate was higher in hydrophobic membrane than hydrophilic membrane, they observed approximately 10-30% flux drop for hydrophobic membranes than for hydrophilic membranes operated under the same identical conditions.

2.4.3.2 Biomass properties

Biomass properties can greatly influence biological performance of the AnMBR and the membrane fouling. MLSS properties include particle size distribution (PSD), mixed liquor suspended solids (MLSS) concentration, sludge charge, extracellular polymeric substance (EPS), soluble microbial products (SMP), suspended solids (SS) in supernatant, dynamic viscosity (μ), relative hydrophobicity (RH), and zeta potential (Meng et al., 2006).

Studies conducted on PSDs of the mixed liquor have generally identified supernatant of the mixed liquor (specifically the colloidal fraction) as the contributor of the greatest permanent fouling propensity (Jud (2008)). Hai et al (2013) reported that larger particle size on the membrane surface can be removed much more easily at the same shear condition compared to smaller floccs, thus, reduces the impact on membrane fouling. Jeison and Lier (2008) observed lower critical fluxes of 6-7 LMH for smaller sludge particle size whereas larger particles yielded critical flux of 20 LMH and concluded that particle size was a key factor controlling the attainable fluxes.

Extracellular polymeric substance (EPS) concentrations, both bound and soluble (or SMP), is often regarded as the sludge factor of prime influence in relation to membrane fouling. Membrane inner pore accumulation and adsorption of EPS and SMP prefer biomass attachment and cake layer formation and may cause severe fouling. Operational conditions such as HRT, SRT, OLR, temperature, pH and shear rate are the most important parameters affecting both the concentration and composition of EPS and SMP (Ozgun et al., 2013; Meng et

al., 2006). Huang et al (2011) investigated the effect of HRT and SRT on treatment performance and membrane fouling of SAnMBR and concluded that, at 8 and 10 hour HRTs, infinite SRT in SAnMBR produced highest MLSS and SMP concentrations and accelerated particle deposition and biocake/biofilm formation on the membrane surface. Also at longer SRT, lower extracellular polymeric substances (EPS) decreased flocculation of particulates and particle sizes, further deteriorate membrane performance.

Mixed liquor suspended solids (MLSS) concentration directly affects cake layer formation on the membrane surface, therefore decreases the permeate flux (Chang and Kim. 2005). Higher sludge concentrations may increase energy demand, as well as increasing the risk of membrane clogging (Judd (2008)). Damayanti et al. (2011) investigated effect of mixed liquor suspended solids (MLSS) concentration on critical flux in aerobic MBR and concluded that when MLSS concentration increased from 5 to 20 g/L the critical flux became four times lower. Trussell et al. (2007) studied the effects of various factors on membrane fouling in aerobic SMBR by monitoring the membrane flux and reported that, the mixed liquor viscosity increased as the MLSS concentration increased ultimately affecting the membrane flux.
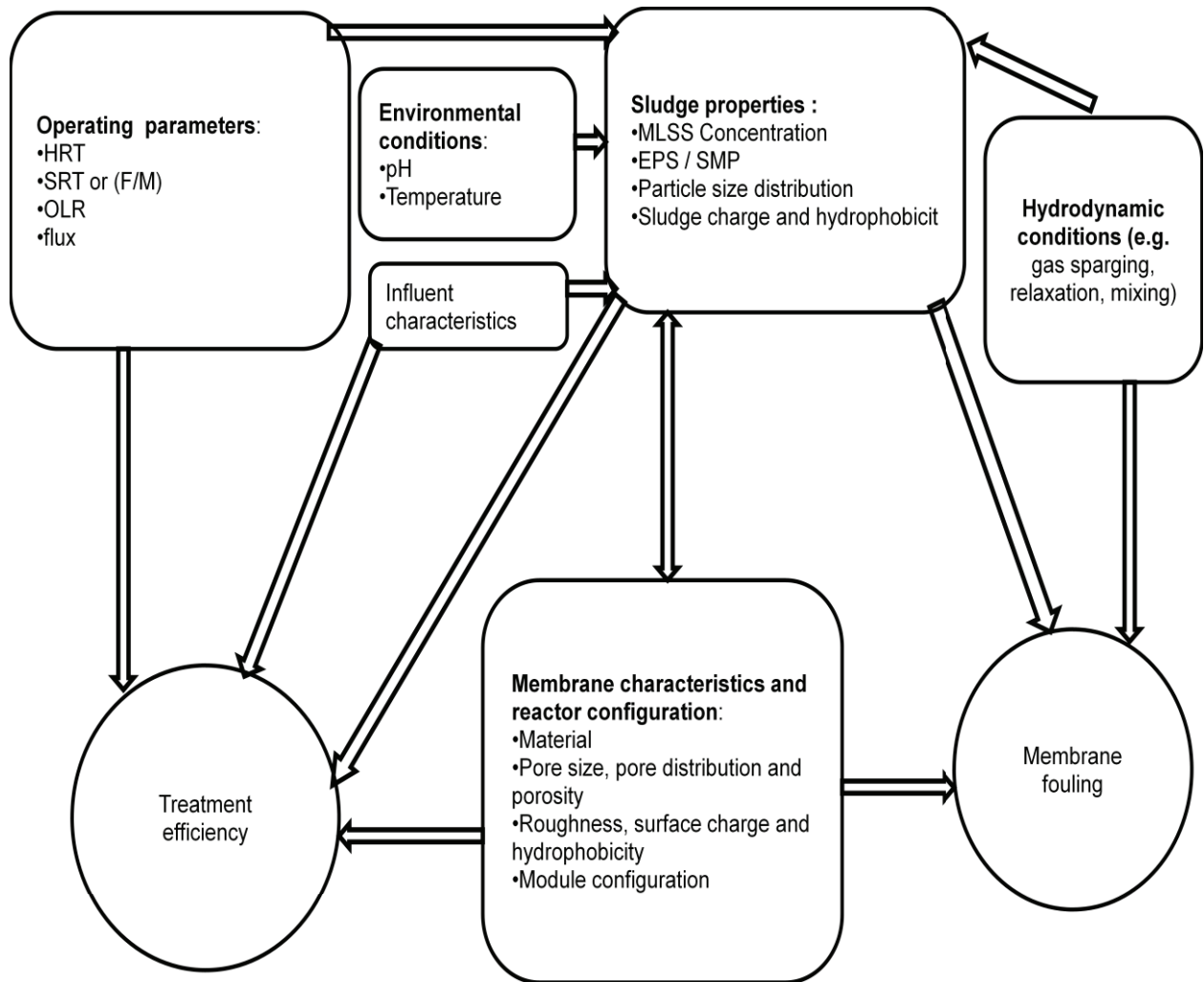
Figure 2-6: Factors influencing the treatment performance and membrane fouling in AnMBRs - (Adapted from Hai et al., 2013)

2.4.4 Membrane fouling mitigation techniques

Membrane fouling decreases productivity as it reduces flux, increases operational energy by increasing the trans-membrane pressure (TMP), necessitates frequent cleaning and my lead to membrane replacement. Due to

these economical impacts, membrane fouling is regarded as the major obstacle for wider application and use of the technology. Thus, it has received extensive attention from researchers across the globe. Membrane fouling control strategies in AnMBRs boils down to reducing the fouling rate and cleaning the fouled membrane (Hai et al., 2013, Liao et al., 2006).

Reducing the fouling rate techniques include: membrane modification, operating below critical flux, Relaxation, biogas sparging, Backwashing with (permeate, air or biogas), control of operating conditions (e.g. SRT, HRT, biomass concentration) and addition of coagulants/flocculants such as activated carbon (AC) and granular activated carbon (GAC) to modify the mixed liquor (Hai et al., 2013).

Backwashing using permeate, air or biogas refers to back-flushing of the membrane. It has been proved very effective in removing most of the reversible fouling caused by pore blocking, pushing particles back into the bioreactor. Additionally, it can partially or fully dislodge the loose cake layer from the membrane surface. Effective utilization of backwashing technique would optimize parameters like frequency, duration and intensity of backwashing as different combinations of these factors proved to be more efficient in various studies (Hai et al., 2011).

Unfortunately, reducing the fouling rate cannot eliminate the need for chemical cleaning as the decline in flux or increase in TMP or combination of both caused by the fouling will become unbearable, thus, chemical cleaning will be inevitable. Chemical cleaning has received a considerable attention in recent

studies and is being extensively applied in removing membrane fouling and recovering the permeability of membrane (Wang et al., 2008, Liao et al., 2006). Chemical cleaning includes maintenance and recovery cleaning. Maintenance cleaning refers to the regular cleaning (e.g. every week) using moderate chemical concentration to sustain design permeability and minimize the frequency of intense cleaning. Recovery cleaning (intensive chemical) is usually done once or twice per year when the flux or TMP can no longer be maintained (Hai et al., 2011). Membrane cleaning can be performed in-situ (or in place) and ex-situ based on whether the membrane modules remain within the AnMBR during cleaning (Wang et al., 2008). There are four classes of the chemical reagents used in membrane cleaning: Acids, bases, oxidants and other chemicals (chelating agents, surfactants, etc.). Acids (such as hydrochloric acid, sulfuric acid, citric acid, etc.) are successful in removing inorganic fouling which are formed by chemical precipitation of inorganic compounds (multivalent cations) and biologically- triggered mineralization between the biopolymer and salts. Alkaline cleaning (NaOH) has proved to be efficient in removing biological fouling by breaking large organic particles like colloids and microbes into fine particles. Oxidants and disinfectants (such as sodium hypochlorite, perhydrol, etc.) target removal of organic and biological foulants through oxidation and / or disinfection. Ozone aeration has also been used to disintegrate organic foulants. Other chemical reagents that can be applied for membrane cleaning may include metal chelating chemicals (e.g. citric acid as mentioned above, ethylene diamine tetraacetic acid (EDTA) and sodium tripolyphosphate(STP)), surfactants (e.g.

sodium dodecyl sulfate (SDS)) and other chemical detergents. Much more effective cleaning can be achieved by employing multi-step chemical cleaning, for example, sodium hypochlorite cleaning could be followed by acid cleaning and/or alkaline cleaning. Sodium hypochlorite (NaClO) is the dominant cleaning reagent in full-scale AnMBRs, which is commonly combined with citric acid during cleaning operations. The combination of NaClO with NaOH may also be used (Wang et al., 2014; Huang et al., 2011; Wang et al., 2008; Hai et al., 2013; Liao et al 2006).

Other interesting mechanical cleaning procedures were also investigated and developed. For example, a hollow fiber membrane module integrating self-mechanical-cleaning function was developed in China and found suitable for high biomass concentration and flux operation. Another study investigated removal of the fouling in a submerged flat-sheet MBR by means of sponge scouring (Wang et al., 2008). According to Wang et al (2014) and Lin et al (2012) ultrasonication has been applied successfully for membrane cleaning in various membrane filtration operations. Ultrasonic cleaning was found effective in removing the cake layers and controlling the gel layer in AnMBR.

2.4.5 Membrane fouling characterization in AnMBRs

The introduction of new innovative techniques and enhancing the existing ones for characterization of membrane fouling has greatly contributed in advancing the knowledge of mechanisms involved in membrane fouling (Ferrando et al., 2005). Currently there are several visualization techniques used for membrane fouling characterization such as scanning electron microscopy

(SEM), confocal scanning laser microscopy (CSLM), atomic force microscopy (AFM), fourier transform infrared (FTIR) spectroscopy and direct observation (DO). Scanning electron microscopy (SEM) is one of the most common instruments which can prove high resolution images at nano/micro-meter scale. SEM was employed for direct observation of the fouling layer and to evaluate the effectiveness of the fouling mitigation methods. However, due to the pre-treatment protocols (such as drying and gold coating) needed by SEM it is impossible to maintain the natural state of the fouling layer during the characterization (Hai et al., 2013). As drying of samples for SEM analysis may cause shrinkage of membrane pores and a collapse of foulants off the fouling layers, an improvement was made by introduction of the environmental scanning electron microscope (ESEM) which can be used for wet samples. On the contrary, ESEM provides much lower resolution of 0.5 μm compared to 0.01 μm for SEM. In addition no cross-section can be obtained using ESEM (Drews (2010)). Confocal scanning laser microscopy (CSLM) is one of the optical microscopic techniques that were commercially introduced in the early nineties. CSLM in addition to other benefits provides high-resolution images captured from different depths of a three-dimensional (3D) object, thus rendering invasive techniques unnecessary for sample preparation. One of the major advantages of CSLM over most of the other characterization techniques is its ability to distinguish among different species (depending on their fluorescent emission) and visualize on-line the adsorption–desorption processes that occur at different depths of the membrane (Ferrando et al., 2005). Zator et al (2007) was able to

calculate the portion of pore surface where protein and/or dextran were detected using data obtained from CSLM. The data obtained was up to a depth of 3 µm inside the membrane, and provided valuable information about the membrane pore blockage. Atomic force microscopy (AFM), also known as scanning force microscopy, this instrumental technique is mainly used to examine surface topography and interactions on the molecular scale. It can convert the scanning signals into a three-dimensional topographical map of the surface. AFM renders a horizontal resolution of 0.1 nm and a vertical resolution of 0.01 nm. AFM has been widely used in characterizing the structure and morphology (or topography) of different types of clean microfiltration (MF) and ultrafiltration (UF) membranes. Specifically, most of the studies were conducted on examining pore size, porosity, pore size distribution and membrane surface roughness (Chan and Chen, 2004). Fourier transform infrared (FTIR) spectroscopy is another instrument commonly used to characterize functional groups of organic molecules adsorbed on the surface of the membrane (Drews (2010)). Direct observation (DO) also known as direct observation through the membrane (DOTM) offers non-invasive, in situ, visualisation and quantification of fouling development and the removal process from hollow fiber membranes in real-time, however, is limited to visually accessible systems such as dilute suspensions and single fibres (Drews (2010); Marselina et al., 2009).

These instruments can be used in combination or as individual tools. For example, DOTM and CLSM have been extensively used in characterising membrane biofouling (Meng et al., 2009). Similarly, energy-dispersive X-ray

spectroscopy (EDX) and SEM were used by Berube et al (2006) to characterise an inorganic precipitate of AnMBR. The results indicated that the inorganic precipitate was composed of struvite ($MgNH_4PO_4 \cdot 6H_2O$), calcite, and clay which were induced by production of ammonium and phosphate ions during anaerobic digestion of the organic materials.

2.5 References

Adekunle, K. F., & Okolie, J. A. (2015). A Review of Biochemical Process of Anaerobic Digestion. Advances in Bioscience and Biotechnology, 6(03), 205.

Berube, P.R., Hall, E.R. and Sutton, P.M. (2006) Parameters governing permeate flux in an anaerobic membrane bioreactor treating low-strength municipal wastewaters: A literature review. Water Environment Research 78(8), 887-896.

Bornare, J. B., Raman, V. K., Sapkal, V. S., Sapkal, R. S., Minde, G., & Sapkal, P. V. (2014). An Overview of Membrane Bioreactors for Anaerobic Treatment of Wastewaters.

Bottino, A., Capannelli, G., Comite, A., Margano, R., 2009. Critical flux in submerged membrane bioreactors for municipal wastewater treatment. Desalination 245, 748–753.

Chan, R., & Chen, V. (2004). Characterization of protein fouling on membranes: opportunities and challenges. Journal of Membrane Science, 242(1), 169-188.

Chang, I. S., & Kim, S. N. (2005). Wastewater treatment using membrane filtration—effect of biosolids concentration on cake resistance. Process Biochemistry, 40(3), 1307-1314.

Cho, B.D., Fane, A.G., 2002. Fouling transients in nominally sub-critical flux operation of a membrane bioreactor. J. Membr. Sci. 209, 391–403. 1307-1314.

Damayanti A, Ujang Z, Salim M R, Olsson G. The effect of mixed liquor suspended solids (MLSS) on biofouling in a hybrid membrane bioreactor for the treatment of high concentration organic wastewater. Water science and technology 2011;63(8):1701-6.

Dereli, R. K., Ersahin, M. E., Ozgun, H., Ozturk, I., Jeison, D., van der Zee, F., & van Lier, J. B. (2012). Potentials of anaerobic membrane bioreactors to overcome treatment limitations induced by industrial wastewaters. Bioresource technology, 122, 160-170.

Drews, A. (2010). Membrane fouling in membrane bioreactors—characterisation, contradictions, cause and cures. Journal of Membrane Science, 363(1), 1-28.

Fakhru'l-Razi, A. (1994). Ultrafiltration membrane separation for anaerobic wastewater treatment. Water Science and Technology, 30(12), 321-327.

Ferrando, M., Rǒżek, A., Zator, M., Lopez, F., & Güell, C. (2005). An approach to membrane fouling characterization by confocal scanning laser microscopy.Journal of Membrane Science, 250(1), 283-293.

Field, R. (2010). Fundamentals of fouling. Membranes for Water Treatment, 4, 1-23.

Field, R.W., Wu, D., Howell, J.A., Gupta, B.B., 1995. Critical flux concept for microfiltration fouling. J. Membr. Sci. 100, 259–272.

Fox, R. A., & Stuckey, D. C. (2015). The effect of sparging rate on transmembrane pressure and critical flux in an AnMBR. Journal of environmental management, 151, 280-285.

Franken, A. C. M. (2009). Prevention and control of membrane fouling: practical implications and examining recent innovations. Amersfoort, Netherlands: Institute for Sustainable Process Technology.

Guglielmi G. (2002) Membrane bioreactors for municipal wastewater treatment. Ph.D. thesis, Universita' di Trento, Italy.

Guglielmi, G., Chiarani, D., Judd, S.J., Andreottola, G., 2006. Flux criticality and sustainability in a hollow fibre submerged membrane bioreactor for municipal wastewater treatment. J. Membr. Sci. 289, 241–248.

Guglielmi, G., Saroj, D.P., Chiarani, D., Andreottola, G., 2007. Sub-critical fouling in a membrane bioreactor for municipal wastewater treatment: experimental investigation and mathematical modelling. Water Res. 41, 3903–3914.

Guo, W.S., Vigneswaran, S., Ngo, H.H., Xing, W., 2008. Comparison of membrane bioreactor systems in wastewater treatment. Desalination 231, 61–70.

Hai, F. I., Yamamoto, K., & Lee, C. H. (Eds.). (2013). Membrane Biological Reactors: Theory, Modeling, Design, Management and Applications to Wastewater Reuse. IWA Publishing.

Hai, F. I. & Yamamoto, K. (2011). Membrane Biological Reactors. In P. Wilderer (Eds.), Treatise on Water Science (pp. 571-613). UK: Elsevier.

Howell, J.A., Chua, H.C., Arnot, T.C., 2004. In situ manipulation of critical flux in a submerged membrane bioreactor using variable rates, and effects of membrane history. J. Membr. Sci. 242, 13–19.

Huang, X., Xiao, K., & Shen, Y. (2010). Recent advances in membrane bioreactor technology for wastewater treatment in China. Frontiers of Environmental Science & Engineering in China, 4(3), 245-271.

Huang, Z., Ong, S. L., & Ng, H. Y. (2011). Submerged anaerobic membrane bioreactor for low-strength wastewater treatment: effect of HRT and SRT on treatment performance and membrane fouling. Water research, 45(2), 705-713.

Jeison, D., 2007. Anaerobic membrane bioreactors for wastewater treatment: Feasibility and potential applications. PhD-Thesis Wageningen University, Wageningen, The Netherlands – with references – with summaries in English and Dutch. ISBN: 978-90-8504-699-8.

Jeison, D., van Lier, J.B., 2007. Cake formation and consolidation: main factors governing the applicable flux in anaerobic submerged membrane bioreactors (AnSMBR) treating acidified wastewaters. Sep. Purif. Technol. 56, 71–78.

Jeison, D., & Lier, J. V. (2008). Anaerobic wastewater treatment and membrane filtration: a one night stand or a sustainable relationship?. Water Science and Technology, 57(4), 527-532.

Judd, S. (2010). The MBR book: principles and applications of membrane bioreactors for water and wastewater treatment. Elsevier.

Judd, Simon. "The status of membrane bioreactor technology." Trends in biotechnology 26.2 (2008): 109-116.

Jung, C.W. and Kang, L.S. (2003) Application of combined coagulation-ultrafiltration membrane process for water treatment. Korean Journal of Chemical Engineering 20(5), 855-861.

Khanal, S. K. (2008). Overview of anaerobic biotechnology. Anaerobic biotechnology for bioenergy production: principles and applications. Wiley–Blackwell Publishing, New York http://www. wiley. com/WileyCDA/WileyTitle/productCd0813823463. html, 20, 385-406.

Le Clech, P., Jefferson, B., Chang, I. S., & Judd, S. J. (2003). Critical flux determination by the flux-step method in a submerged membrane bioreactor.Journal of Membrane Science, 227(1), 81-93.

Li, N. N., Fane, A. G., Ho, W. S. W. and Matsuura, T. (eds) (2008) Frontmatter, in Advanced Membrane Technology and Applications, John Wiley & Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9780470276280.fmatte.

Liao, B. Q., Kraemer, J. T., & Bagley, D. M. (2006). Anaerobic membrane bioreactors: applications and research directions. Critical Reviews in Environmental Science and Technology, 36(6), 489-530.

Lin, H., Gao, W., Meng, F., Liao, B. Q., Leung, K. T., Zhao, L., ... & Hong, H. (2012). Membrane bioreactors for industrial wastewater treatment: a critical review. Critical reviews in environmental science and technology, 42(7), 677-740.

Lin, H., Peng, W., Zhang, M., Chen, J., Hong, H., & Zhang, Y. (2013). A review on anaerobic membrane bioreactors: applications, membrane fouling and future perspectives. Desalination, 314, 169-188.

Marselina, Y., Le-Clech, P., Stuetz, R. M., & Chen, V. (2009). Characterisation of membrane fouling deposition and removal by direct observation technique. Journal of Membrane Science, 341(1), 163-17.

Meng, F., Chae, S. R., Drews, A., Kraume, M., Shin, H. S., & Yang, F. (2009). Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material. Water research, 43(6), 1489-1512.

Meng, F., Zhang, H., Yang, F., Zhang, S., Li, Y., & Zhang, X. (2006). Identification of activated sludge properties affecting membrane fouling in submerged membrane bioreactors. Separation and Purification Technology, 51(1), 95-103.

Monclus, H., Zacharias, S., Santos, A., Pidou, M., & Judd, S. (2010). Criticality of flux and aeration for a hollow fiber membrane bioreactor. Separation Science and Technology, 45(7), 956-961.

Ozgun, H., Dereli, R. K., Ersahin, M. E., Kinaci, C., Spanjers, H., & van Lier, J. B. (2013). A review of anaerobic membrane bioreactors for municipal wastewater

treatment: integration options, limitations and expectations. Separation and Purification Technology, 118, 89-104.

Peeva, P. D., Palupi, A. E., & Ulbricht, M. (2011). Ultrafiltration of humic acid solutions through unmodified and surface functionalized low-fouling polyethersulfone membranes–Effects of feed properties, molecular weight cut-off and membrane chemistry on fouling behavior and cleanability. Separation and Purification Technology, 81(2), 124-133.

Rittmann, B. E., & McCarty, P. L. (2012). Environmental biotechnology: principles and applications. Tata McGraw-Hill Education.

Robles A, Ruano M V, Garcia Usach F, Ferrer J, García Usach F. Sub-critical filtration conditions of commercial hollow-fibre membranes in a submerged anaerobic MBR (HF-SAnMBR) system: The effect of gas sparging intensity. Bioresource technology 2012;114:247-254.

Skouteris, G., Hermosilla, D., López, P., Negro, C., & Blanco, Á. (2012). Anaerobic membrane bioreactors for wastewater treatment: a review. Chemical Engineering Journal, 198, 138-148.

Stephenson, T., Judd, S., Jefferson, B., Brindle, K., 2000. Membrane Bioreactors for Wastewater Treatment. IWA publishing, London, UK.

Stuckey, D. C. (2012). Recent developments in anaerobic membrane reactors.Bioresource technology, 122, 137-148.

Trussell, R. S., Merlo, R. P., Hermanowicz, S. W., & Jenkins, D. (2007). Influence of mixed liquor properties and aeration intensity on membrane fouling in a submerged membrane bioreactor at high mixed liquor suspended solids concentrations. Water research, 41(5), 947-958.

Van der Marel, P., Zwijnenburg, A., Kemperman, A., Wessling, M., Temmink, H., Van der Meer, W., 2009. An improved flux-step method to determinate the critical flux and the critical flux for irreversibility in a membrane bioreactor. J. Membr.Sci. 332, 24–29.

Visvanathan, C., & Abeynayaka, A. (2012). Developments and future potentials of anaerobic membrane bioreactors (AnMBRs). Membr Water Treat, 3, 31-23.

Visvanathan, C., & Aim, R. B. (2002). Membrane Bioreactor Applications in Wastewater Treatment.

Wang, Z., Ma, J., Tang, C. Y., Kimura, K., Wang, Q., & Han, X. (2014). Membrane cleaning in membrane bioreactors: a review. Journal of Membrane Science, 468, 276-307.

Wang, Z., Wu, Z., Mai, S., Yang, C., Wang, X., An, Y., & Zhou, Z. (2008). Research and applications of membrane bioreactors in China: progress and prospect. Separation and Purification Technology, 62(2), 249-263.

Watanabea, R., Qiaoa, W., Nortond, M., Wakaharae, S., & Lia, Y. Y. (2014). Recent Developments in Municipal Wastewater Treatment Using Anaerobic Membrane Bioreactor: A Review. Journal of Water Sustainability, 4(2), 101-122.

Wu, Z., Wang, Z., Huang, S., Mai, S., Yang, C., Wang, X., Zhou, Z., 2008. Effects of various factors on critical flux in submerged membrane bioreactors for municipal wastewater treatment. Sep. Purif. Technol. 62, 56–63

Zator, M., Ferrando, M., Lopez, F., & Güell, C. (2007). Membrane fouling characterization by confocal microscopy during filtration of BSA/dextran mixtures. Journal of Membrane Science, 301(1), 57-66.

Zhu, L., M. Yu, L. Delgado Chávez, A. Ulrich and T. Yu, 2014. Review of Bioreactor Designs Applicable to Oil Sands Process-Affected Water Treatment. Oil Sands Research and Information Network, University of Alberta, School of Energy and the Environment, Edmonton, Alberta. OSRIN Report No. TR-52. 39 pp.

Chapter 3 : Effects of MLSS concentration and biogas sparging intensity on critical flux of submerged anaerobic membrane bioreactor (SAnMBR)

3.1 Introduction

In recent years, submerged anaerobic membrane bioreactor (SAnMBR) has been regarded as a novel technology for industrial wastewater treatment as it offers many advantages compared to the conventional wastewater treatment systems. It utilizes a submerged membrane in anaerobic reactor for separation of solids thus providing an excellent effluent quality, low sludge yield, higher-treatment performance, a small footprint, biogas production and lower energy consumption (Liao et al., 2006; Lin et al., 2012; Fox and Stuckey., 2015; Estrada-Arriaga et., al 2015). The application of membrane separation also resolves the difficulty of retaining slow-growth anaerobic microorganisms with short solids hydraulic retention times (HRT) by eliminating unwanted sludge wash-out and decoupling solids retention time (SRT) from hydraulic retention time (HRT). By controlling the SRT it is now possible to achieve desired or high biomass concentration in the SAnMBR which makes it attractive for industrial wastewater treatment (Wu et al., 2008; Monclus et al., 2010; Huang et al., 2011; Lin et al., 2012; Chang (2014); Schwarz et al., 2006). However, membrane technology still faces a major challenge of membrane fouling which directly affects the permeate flux and subsequently operational and energy costs causing frequent membrane replacement, membrane maintenance and membrane cleaning (Espinasse et al.,

2002; Chang and Kim., 2005; Robles et al., 2012; Estrada-Arriaga et al., 2015).

Permeate flux is an important parameter influencing the fouling rate (Yu et al., 2003; Wu et al., 2008).It is generally believed that operating below the critical flux can reduce the fouling rate (Pollice et al., 2005; Damayanti et al., 2011). The concept of the critical flux (J_{crit}) in MBRs was pioneered by Field et al. (1995). Since then the concept has inspired many researchers (Espinasse et al., 2002; Yu et al., 2003; Andreottola & Guglielmi., 2003; Le Clech et al., 2003a; Le Clech et al., 2003b; Kim and DiGiano.,2006; Bacchin et., 2006; Monclus et al., 2010; Robles et al., 2012; Fox and Stuckey., 2015;) who studied the various factors affecting the critical flux. Among these factors affecting the critical flux are the mixed liquor suspended solids (MLSS) concentration and the biogas sparging intensity. MLSS concentration directly impacts cake layer formation on the membrane surface and hence decreases the permeate flux (Chang and Kim. 2005). Increasing the biogas intensity in submerged AnMBRs improves hydrodynamic conditions but also increases energy cost, disrupts sludge flocs and negatively impacts membrane fouling (Lin et al., 2012). The most common approaches to minimize fouling in submerged AnMBRs are adjusting biogas sparging intensity and the permeate flux (Kim and DiGiano., 2006; Lin et al., 2012; Robles et al., 2012). Therefore; optimising the biogas sparging rate and MLSS concentration are critical factors in success of AnMBRs.

A critical review on the critical flux studies suggests that most of the studies focused on aerobic MBRs and only limited studies on AnMBRs. Furthermore, the change in MLSS is achieved by either varying solids retention

time (SRT), which led to the simultaneous changes in other sludge properties, such as extracellular polymeric substances (EPS), particle size distributions, hydrophobicity and surface charge (Liao et al., 2001), or taking MLSS from the activated sludge plants or MBRs and stored in cold temperature until the time of critical flux experiments. However, a number of studies found the storage time and temperature had significant impact on sludge properties as well (Bura et al., 1998; Nielsen et al., 1996). Table 3-1 shows the summary of these studies. Damayanti et al. (2011) found that an increase in MLSS concentration from 5 to 20 g/L led to a decrease in critical flux by four times in an aerobic MBR. Similar results were obtained by Wu et al. (2008). Furthermore; Robles et al. (2012) found a linear dependency between the critical flux (J_{Crit}) and the sparging intensity in an AnMBR. Moreover, several sludge properties, such as EPS, particle sizes, hydrophobicity, and surface charge, have been reported to have significant effects on membrane fouling and consequently the critical flux (Wu et al., 2008). Considering the fact that no consensus has been reached in the literature regarding the effects of sludge properties on membrane critical flux, Wu et al (2008) stressed the importance of carrying out experiments under identical sludge characteristics to facilitate comparison of results. The actual method used to change MLSS concentration can have a significant effect on biomass characteristics, as it can be changed both with and without acclimatisation (Le Clech et al., 2003b).

Even though these intensive studies conducted so far, as summarized in Table 3-1, have significantly contributed in understanding the critical flux concept

and the factors influencing the critical flux in MBRs, However, limited studies have focused on submerged AnMBRs. In fact most of the studies examined submerged aerobic MBRs and side-stream (SS) configurations (Xie et al., 2010; Jeison & Lier., 2007). Therefore, it is desirable to carry out the critical flux experiments under various MLSS concentrations and biogas sparging intensities during the continuous operation of a SAnMBR while minimizing the change of sludge properties except for the MLSS concentration.

The objectives of this paper were to critically investigate the effect of MLSS concentration under various biogas sparging intensity on critical flux in SAnMBRs by designing an accelerated experiment of changing MLSS while minimizing the change of other sludge properties. More importantly, accelerated critical flux tests were carried out during the continuous operation of a SAnMBR while minimizing changes in MLSS properties or taking out the MLSS from the SAnMBR and store in cold temperature. Following the accelerated experiments, a long-term operation under sub-critical condition was executed to evaluate validity of the critical flux concept by operating the SAnMBR in one of the critical flux results attained in the accelerated short-term experiments and membrane fouling characterization was performed at the end of the long term operation.

Table 3-1: Summary of some critical flux studies reported in literature

Type of Wastewater	Scale	Reactor Volume (L)	Membrane	Pore Size (µm)	Reactor Type	Influent COD (mg/L)	MLSS (g/L)	Sparging Rate (m³/m².h)	Flux (LMH)	(HRT) (d)	(SRT) (d)	Reference
Settled sewage	Pilot Scale	2500	HF	0.1	Anaerobic	290	8	0.24 & 0.48	14.5, 17.0	--	--	Monclus et al. (2010)
Municipal	Pilot Scale	1300	HF	0.05	Anaerobic	388 ± 95	23	0.17, 0.23, 0.33, 0.4, 0.5	12-19	0.25-1.083	30-70	Robles et al. (2012)
--	Pilot Scale	40	Tubular	0.01	Aerobic	--	4, 8, 12	6.9, 14.8,21.7	37-109	--	--	Le Clech et al. (2003b)
--	Pilot Scale	40	Tubular	0.1	Aerobic	--	4, 8, 12	7.61, 16.3, 23.9	16-121			Le Clech et al. (2003b)
Raw wastewater	Lab Scale	50	HF	0.22	Aerobic	--	3	0 to 254	7.32 - 50.16	--	--	Yu et al. (2003)
Palm oil mill	Lab Scale	20	FS	0.4	Aerobic	45,000	5,10,15,20	--	9.2, 7.1,4.7, 2.5	--	70	Damayanti et al (2011)
Municipal	Lab Scale	6	HF	UF	Aerobic	--	4.2, 6.15, 7.940[a]	7.14	< 20	--	--	Estrada-Arriaga et al. (2015
Synthetic	Lab Scale	3	Flat sheet	0.4	Anaerobic	460 ± 30	---	1.2, 2.4,3.6	7.2 , 11.8	0.5	--	Fox & Stuckey (2015)
Municipal	Lab Scale	33	FS	0.2	Aerobic	--	4.5	2.86, 5.71, 8.71, 11.43, 14.29	42.5-48.5	0.125	40	Wu et al., (2008)
Municipal	Lab Scale	33	FS	0.2	Aerobic	--	9.6, 12.4, 15.9, 22.6	2.86, 5.71, 8.71, 11.43, 14.29	24-50[b]	0.125	40	Wu et al., (2008)
Synthetic	Lab Scale	--	HF	--	Aerobic	--	3.7, 2.9, 0.25, 0.09	Fixed	--	--	--	Chang and Kim (2005)
Municipal	Pilot Scale	1,514	HF	UF	Aerobic	345	15	0.54, 0.82, 1.08	--	--	10, 20, 30	Trussell et al. (2007)
Real Kraft EC.	Lab Scale	10	FS	0.3	Anaerobic	5600-10000	5-10	0.6-1.5	5.6-12.5	--	--	Xie et al. (2010)
Synthetic	Lab Scale	10	FS	0.30	Anaerobic	17,296 ± 285	15, 10.6, 7.7, 5.7	8.72, 6.0, 4.38	8.02 - 15.06	NA	Not used	This study

Notes:

- (--) Indicates value not reported
- (7,940[a]) Concentration reported in MLVSS
- (24-50[b]) Value is approximate (scaled from graph)

3.2 Material and Methods

3.2.1 Laboratory scale SAnMBR setup and operation

The schematic diagram of the submerged AnMBR used in this study is shown in Fig. 3-1. The SAnMBR has a volume of 10 L and is composed of a bottom (sludge blanket) zone (4 L) and a top (filtration) zone (6 L). A flat sheet microfiltration membrane module with effective filtration area of 0.03 m^2 (10 cm × 15 cm on each of side of the module) was submerged in the top zone of the SAnMBR. The bottom zone was used to form sludge granules acting as the sludge blanket and was intended to replicate the UASB reactor. The flat sheet membranes used in this study were made of polyvinylidene fluoride (PVDF) materials and their molecular weight cut off (MWCO) were characterized as 70,000 Da and the pore sizes was 0.3 μm (Shanghai SINAP Membrane Science &Technology Co. Ltd., China).

Underneath the membrane module on each side, a stainless steel tube diffuser was located and the headspace biogas was recirculated by two gas recycle pumps (Masterflex Console Drive, Model 7520-40, Thermo Fisher Scientific, USA) to provide biogas sparging for fouling control on the membrane surface. The biogas sparging rate was controlled as needed during the experiments by settling the digital pump speeds. Additional gentle mixing was achieved by a magnetic stirrer at the bottom of the reactor.

The seeded sludge was obtained from another SAnMBR treating synthetic wastewater and was stored in -25 °C prior to starting of these experiments. The SAnMBR temperature was maintained constant at 37 ± 1 °C by continuously circulating

warm water through the water jacket of the reactor. The feed wastewater stored at 4°C in a refrigerator was preheated in a water bath to 37 ± 1 °C prior to entering into the SAnMBR.

The pH of the bioreactor was controlled at 7.0 ± 0.2 by adjusting the feed pH. NaOH solution was used to raise the feed pH which was typically around 3.5. The feed wastewater was pumped into the bottom of the bioreactor automatically by a feeding pump (Masterflex Model 7520-50, Barnant Co., USA), which was controlled by a water level sensor (Madison Co., USA), and controller (Flowline, USA) to maintain a constant liquid level in the bioreactor.

Synthetic wastewater (simulation of kraft pulping evaporator condensate) composed of methanol was used for the experiments. Macro-nutrients, nitrogen (NH_4Cl) and phosphorus (KH_2PO_4) were added to the synthetic wastewater in a proportion of COD: N: P of 100:2.6:0.4 to sustain the nutrient concentrations requirement for biomass growth in an anaerobic environment (Vogelaar et al., 2002). According to the recommendation of Welander et al. (1999) a trace element solution was supplemented to the influent to prevent trace metal limitations of the methanogens. The permeate was intermittently obtained by using a peristaltic pump (Masterflex, C/L, Model 77120-70, Barnant Co., USA) operating in three minutes on and two minutes off mode. To control the membrane flux the permeate pump speed was adjusted and calibrations were made when necessary. The trans-membrane pressure (TMP) was measured by a vacuum gauge which was connected to the membrane module in the bioreactor and the permeate suction pump. Nitrogen gas was used to remove oxygen from the bioreactor whenever the system was opened to remove or clean the membranes.
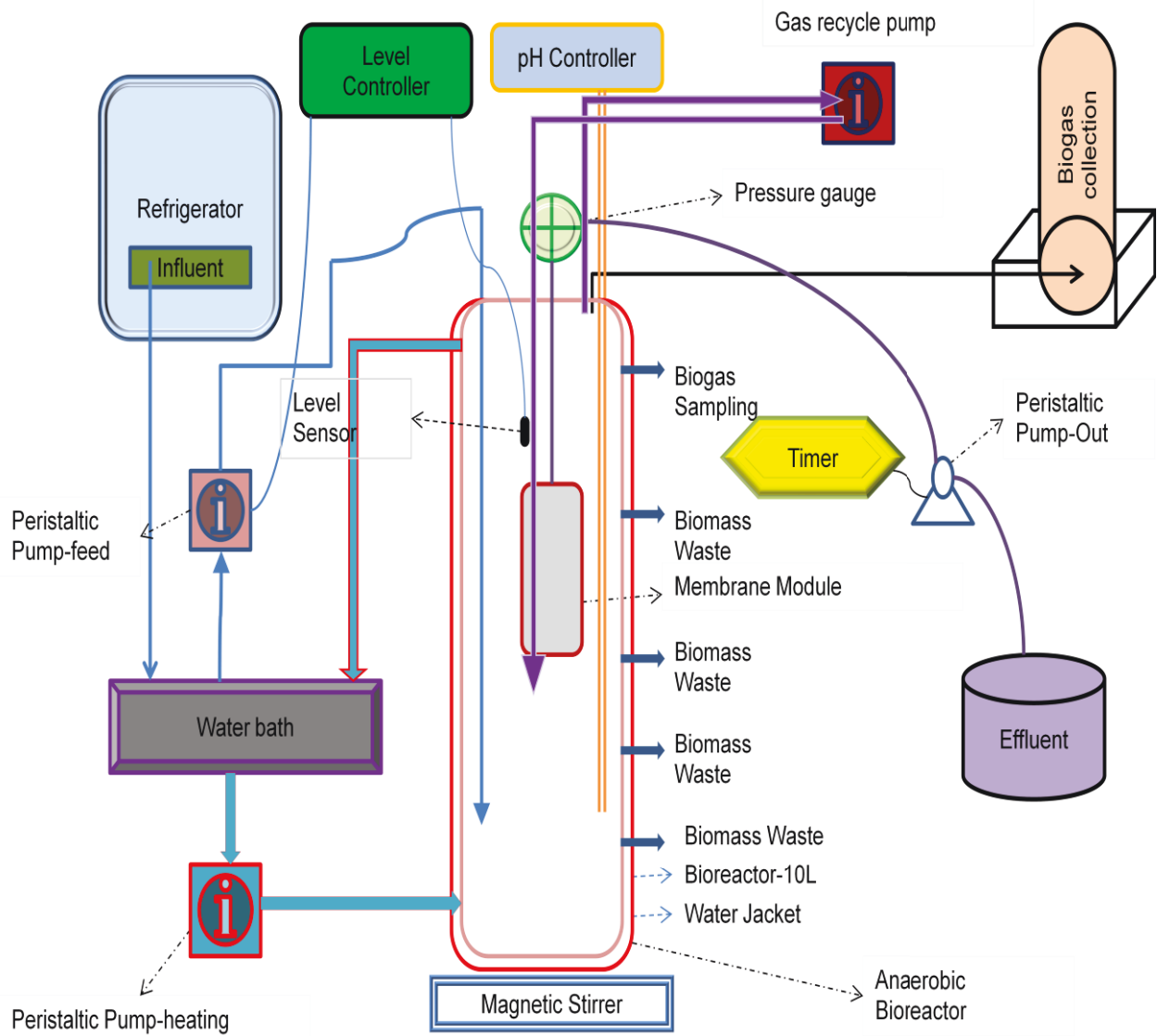
Figure 3-1: Schematic of the laboratory scale submerged anaerobic membrane bioreactor (SAnMBR).

3.2.2 Analytical methods

3.2.2.1. Critical flux determination

The critical flux measurements were conducted on a constant flux basis (using flux-step method) and the corresponding changes in TMP were monitored (Le Clech et al., 2003b; Monclus et al., 2010). Accordingly each flux step was measured for 5 minutes membrane operation cycle (on and off) and was triplicated such that each step was composed of 15 minutes of permeation and relaxation before increasing the flux to the next step. Each run started at a low constant flux and was incrementally increased in step heights of 1 to 2 LMH due to the challenge of changing the permeation pump speed at a fixed interval. If the TMP did not increase within the step length then the flux was stepped up to the next level. The upper limit of the critical flux was taken as the point where the flux–TMP relationship became non-linear (Bacchin et al., 2006) or simply when an ever increasing TMP was observed within the step length. The lower limit of the critical flux was taken as the flux in the previous step. The critical flux was obtained by averaging the lower and upper limits. Each critical flux measurement was conducted three times and the membrane was physically cleaned prior to each critical flux measurement. A new membrane was used for each MLTS concentrations of 15 g/L, 10.6 g/L, 7.7 g/L and 5.7 g/L. Biogas sparging intensities selected were low (4.38 $m^3.m^{-2}.h^{-1}$), intermediate (6.0 $m^3.m^{-2}.h^{-1}$) and high (8.72 $m^3.m^{-2}.h^{-1}$) for each MLTS concentration. After completing the tests with the three sparging intensities and MLTS concentration of 15 g/L, the MLTS was immediately wasted to reach the next level of MLTS concentration of 10.6 g/L and the critical flux measurements were performed as described above. Similar process was followed for MLTS concentrations of 7.7 g/L and

5.7 g/L. The short-term accelerated critical flux experiments were completed within four weeks.

3.2.2.2 MLSS concentrations and biomass acclimation

A synthetic wastewater prepared from methanol with an average COD of 17,296 ± 285 mg/L was used throughout this study. Upon start-up of the reactor the biomass was acclimated to this synthetic wastewater for 136 days to achieve a steady-state operation prior to starting the critical flux experiments. No wasting of MLSS occurred except as per above and as required for sampling. The purpose of immediately wasting the sludge (no control of SRT) to reduce to the desired concentration was to minimize changes in MLSS properties. Changes of MLSS concentration by controlling the SRT has been known to change the MLSS properties (Le-Clech et al., 2003b). Accelerated critical flux experiments were carried out within the shortest possible time to minimize changes in MLSS properties. At the end of critical flux tests, the previously wasted sludge was stored at -25 °C and was used to increase the MLTS concentration to around 11.46 ± 0.92 g/L for the long term operation of SAnMBR to study effect of long term operation.

3.2.2.3 Particle size distributions

The particle size distributions (PSDs) of the mixed liquor samples and supernatant were measured using Malvern Mastersizer 2000 instrument (Worcestershire, UK) which has a detection range of 0.02-2000 μm. The instrument detects the scattered light by means of a detector that converts the signal to a size distribution based on volume or number. Each sample was automatically measured

three times with a standard deviation of 0.1-4.5%. The PSD measurements were measured twice for each set of critical flux tests (i.e. one MLSS concentration & one sparging rate). Samples of mixed liquor were taken from three different zones of the reactor and the supernatant for the top zone mixed liquor. The PSD was routinely monitored for the long term operation.

3.2.2.4 Water samples

COD of (influent, effluent, and supernatant), mixed liquor total solids (MLTS) and mixed liquor suspended solids (MLSS) concentrations were determined according to standard methods (APHA, 2005). MLSS: MLTS ratio was 0.9705. The mixed liquor samples were taken from the top zone of the SAnMBR and centrifuged at a centrifugation force of 18700g for 20 minutes to obtain supernatant for chemical oxygen demand (COD) measurement and particle size distribution (PSD). Samples were measured twice for each set of critical flux tests and were routinely monitored after the end of the critical flux tests for the long term operation.

3.2.2.5 Biogas production and composition measurements

Biogas samples were taken from the headspace of the SAnMBR using a syringe. Biogas composition (methane, nitrogen, and carbon dioxide) was measured by gas chromatography (Shimazu, GC-2014) which is equipped with a thermal conductivity detector and a silica gel packed column. Helium gas at a flow rate of 30 mL/min was used as the carrier for the equipment. Biogas composition was monitored throughout the experimental period of the critical flux tests and thereafter it was measured once a week during the long term operation. Biogas production rate was measured using water

displacement method and was measured two to three times per week through the experimental operation.

3.2.2.6 Analysis of membrane resistance and Permeability

The resistance-in-series model (Rt = Rm + Rc + Rp) was used to evaluate the filtration characteristics. Membrane resistance was analyzed by Darcy's law as follows:

$$R_t = R_m + R_c + R_p = \frac{\Delta P_T}{\eta x J} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (1)$$

Where R_t is the membrane total resistance (1/m), R_m is the new membrane resistance (1/m), R_p is the resistance cause by pore blocking (1/m), R_c is the cake layer resistance formed by the cake layer deposition over the membrane surface during filtration (1/m), ΔP_T is the trans-membrane pressure (Pa), η is the dynamic viscosity of the permeate (Pa.s); and J is the measured membrane flux (m^3/m^2.s). Each resistance value was measured using the same membrane module used in the laboratory-scale SAnMBR for the critical flux tests and the long term operation.

The experimental procedure to measure each resistance value was as follows:(a) R_m was evaluated by measuring the clean water flux of tap water; (b) R_t was obtained from the final flux of the biomass filtration (at the end of the long term operation of the SAnMBR) and the corresponding trans-membrane pressure was similarly obtained; (c) the membrane surface was then gently flushed with tap water and cleaned with a wet sponge to remove the cake layer formed during filtration on SAnMBR. After that, the clean water (tap water) flux was measured again to determine the resistance of the membrane equating to (R_m + $R_{p)}$. From steps (a) to (c), R_t, R_m, R_p and R_c were

calculated. R_t & R_m were directly calculated using equation (1) above; then from step (c) and equation (1), R_c & R_p were calculated. This procedure to determine R_t, R_m, R_p and R_c was used by other researchers (Lin et al., 2009; Chang and Kim, 2005).

The following equation was also used to determine organic fouling resistance, inorganic fouling resistance and permanent fouling (irremovable fouling) resistance:

$$R_p = R_{organic} + R_{inorganic} + P_{permanent} \dotfill (2)$$

Where, $R_{organic}$ is the organic fouling resistance (1/m), $R_{inorganic}$ is the inorganic fouling resistance (1/m) and $P_{permanent}$ is the permanent fouling (irremovable fouling) resistance (1/m). After step (c) above, the membrane was chemically cleaned by submerging in 200 ppm sodium hypochlorite solution for two hours to remove organic foulants. (d) Clean water flux test was done to measure the resistance (R_m + ($R_{inorganic}$ + $P_{permanent}$)) and subsequently $R_{organic}$ was calculated. Finally, after step (d), the membrane was chemically cleaned by submerging in 2000 ppm citric acid solution for two hours at pH 2.5 to remove inorganic foulants. Then (e) clean water flux test was done to measure the resistance (R_m + $P_{permanent}$) so $R_{inorganic}$ & $P_{permanent}$ could be obtained from these steps and equation (2) above.

Membrane performance in terms of permeability was measured by a temperature corrected (to 20 °C) permeability $K_{20°C}$ using the following equation (Trussell et al., 2007).

$$K_{20°C} = J * e^{(-0.0239(T-20))} / \Delta P_T \dotfill (3)$$

$K_{20°C}$ = Permeability of the membrane at 20 °C, L/m^2 *h*bar (LMH/bar)

T = temperature of water, °C

J = membrane flux, $L/m^2 .h$ (LMH) at temperature T

ΔP_T = the trans-membrane pressure (Pa)

From the steps explained above and equation (3) permeability corresponding to each type of resistance can be calculated and their effects evaluated.

3.2.2.7 Statistical analysis

Statistical analysis was carried out using the M*icrosoft Excel* software with a view to characterize the influence of mixed liquor suspended solids (MLSS) concentration and sparging rate on the critical flux. The analysis of variance (ANOVA) and/or student T-Test were used to test for differences between treatment means when investigating the effect of MLSS concentration & sparging rates on the critical flux. The statistical type I error (or alpha) was set at 0.05 for all statistical tests conducted in this study. First, ANOVA was used to test the significance of each factor (MLSS concentration & sparging rates) based on the three observations (n=3, as the critical flux measurement was replicated three times) and the various sparging rates (3 levels) and MLSS concentrations (4 levels). Then, where the treatment means were not equal the student T-Test was used to test each pair of means to find out where the difference lies.

3.3 Results and discussions

### 3.3.1 Accelerated critical flux experiments (Short term study)

3.3.1.1 Overall performance of the SAnMBR

To ensure the consistency of the biological performance during the whole accelerated experimental period; the performance of the SAnMBR was continuously monitored. COD removal efficiency of 99.73 ± 0.05% was observed at influent COD concentration of 17,296 ± 285 mg/L yielding effluent COD concentration of 62 ± 41 mg/L. Biogas yield was 0.42 ± 0.13 L biogas/g COD consumed. The biogas was composed of 76.63 ± 1.27% CH_4 (Methane), 15.55 ± 2.74 % CO_2 and 7.82 ± 3.37 N_2. These values are consistent with the values found in literature (Lin et al., 2010; Lin et al., 2011) and substantiate the normal behaviour of the SAnMBR during the experiments.

3.3.1.2 MLSS properties

Fig. 3-2 shows the particle size distributions (PSDs) of MLTS at a concentration of 15 g/L under various biogas sparging rates (4.38, 6.0 and 8.72 m3/ m2.h). Similarly, the PSD (results not shown) of MLTS at three other concentrations of 10.6 g/L, 7.7 g/L and 5.7 g/L were plotted as well. The results showed limited impact of biogas sparging rates on PSD at the same MLTS concentration. Fig. 3-3 illustrates PSDs of MLTS at various concentrations (15 g/L, 10.6 g/L, 7.7 g/L and 5.7 g/L) and the same biogas sparging rate of 8.72 m3/ m2.h. The PSDs of MLTS at various concentration and other two biogas sparging rates were also plotted (results not shown here). The results

suggested that PSDs of MLTS were similar at different MLTS concentrations. Overall, the results from Fig. 3-2 and 3-3 indicate that the PSD of MLTS had no any notable changes during the period of accelerated experimental study of critical flux determination; which supports our intent of the constant MLSS properties.
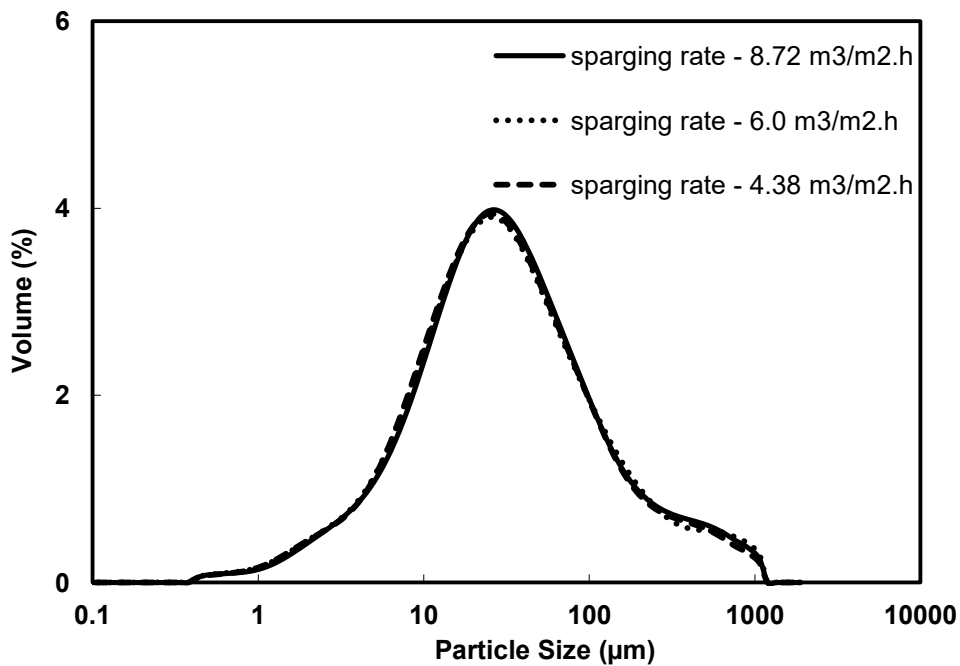
Figure 3-2: Particle size distributions for MLTS concentration of 15 g/L at various sparging rates
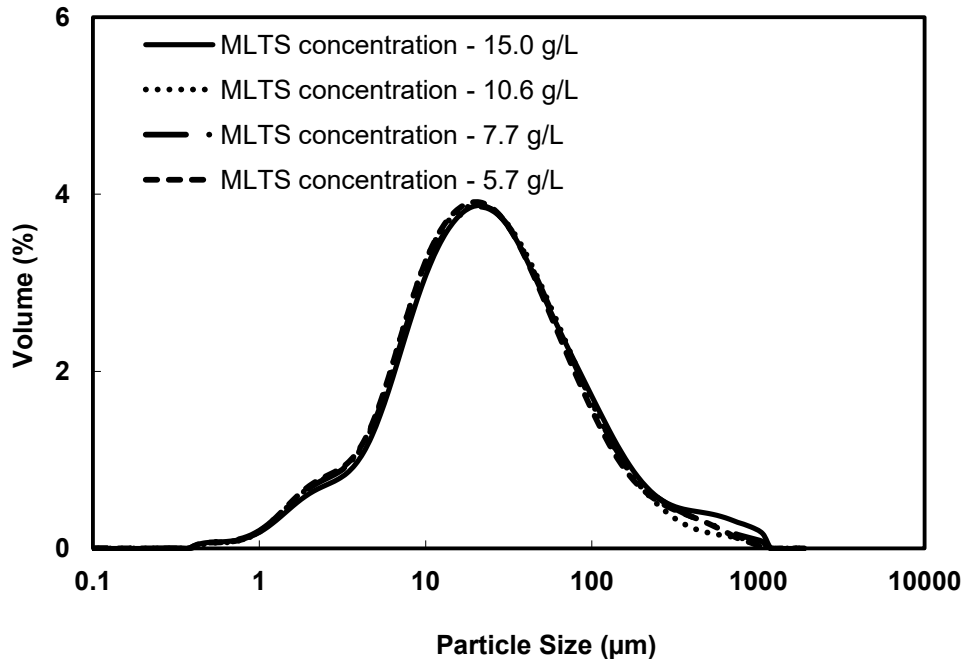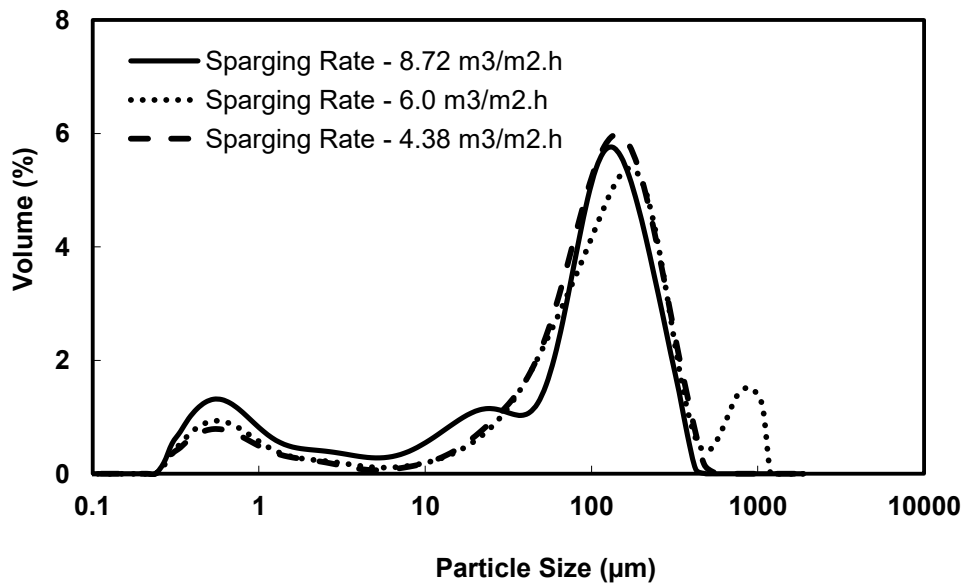
Figure 3-3: Particle size distributions of various MLTS concentrations at sparging rate of 8.72 m³/m².h

As the fraction of smaller particles (fine colloidal particles) is more important than the fraction of larger flocs in controlling membrane fouling (Lin et al., 2011; Lin et al., 2009) and would accumulate in the supernatant, the PSDs of supernatant were measured at the various conditions. Figs. 3-4 & 3-5 depict the plots of supernatant PSDs under various conditions. A close look at these plots reveals similar PSDs but some slight variations mainly at the peaks of smaller size particle distributions (< 1 μm). The appearance of the peaks of smaller particles (<1 um), as compared to the PSD of MLTS (Figs. 3-2 and 3-3), was due to the fact that smaller particles were concentrated in the supernatants after centrifugation and thus weight (or vol%) of smaller particles was increased in the spectrum of PSDs. The relative concentration of small and large

flocs was the same at different MLTS concentrations, but after concentration by centrifugation, the absolute amounts of small flocs accumulated in supernatants would be higher from a higher MLTS. Thus, some notable differences were observed in Figs. 3-4 and 3-5. Fig. 3-4 suggests that an increase in biogas sparging rate from 4.38 to 6.0 $m^3/m^{2\cdot}h$ had limited impact on the fraction (peak) of smaller particles (<1µm) but a further increase to 8.72 m3/ m2.h led to an increased fraction of smaller particles (<1 µm). The results suggest that there is a critical biogas sparging rate, after which its impact on the PSDs of supernatants is notable, due to increased shear force and break-up of flocs. The relatively higher peaks (or vol %) of smaller particles (<1 µm) at the higher MLTS concentrations (15 and 10.6 g/L) (Fig. 3-5) was due to the fact that a larger amount of smaller particles existed at the higher MLTS concentrations. This is consistent with the supernatant COD level under various MLTS concentrations as shown in Fig. 3-6. The higher level of supernatant CODs at a higher level of MLTS was related to a larger amount of smaller particles. This can be substantiated by the higher supernatant COD for the highest sparging rate in comparison to the lowest (Figure 3-5). The effect of intermediate sparging rate (6.0 $m^3/m^2.h$) was comparable to the highest sparging rate in this regard. Figure 3-5 represents the PSDs of the highest sparging rate on the several MLTS concentrations. The difference lies in the content of smaller size particles (< 1 µm); the general trend was that the smaller particles concentration decreased with the decrease in MLTS concentration; however, 15 & 10.6 g/L displayed comparable results and similarly 7.7 & 5.7 g/L. This observation can be supported by the supernatant CODs as shown in figure 3-6. Analogous results can be concluded from

the rest of the conditions not depicted here. We can conclude that the MLSS properties remained fairly constant with the exception of the slight variations as discussed above.

Figure 3-4: Particle size distributions of supernatant for MLTS concentration of 15 g/L at various sparging rates
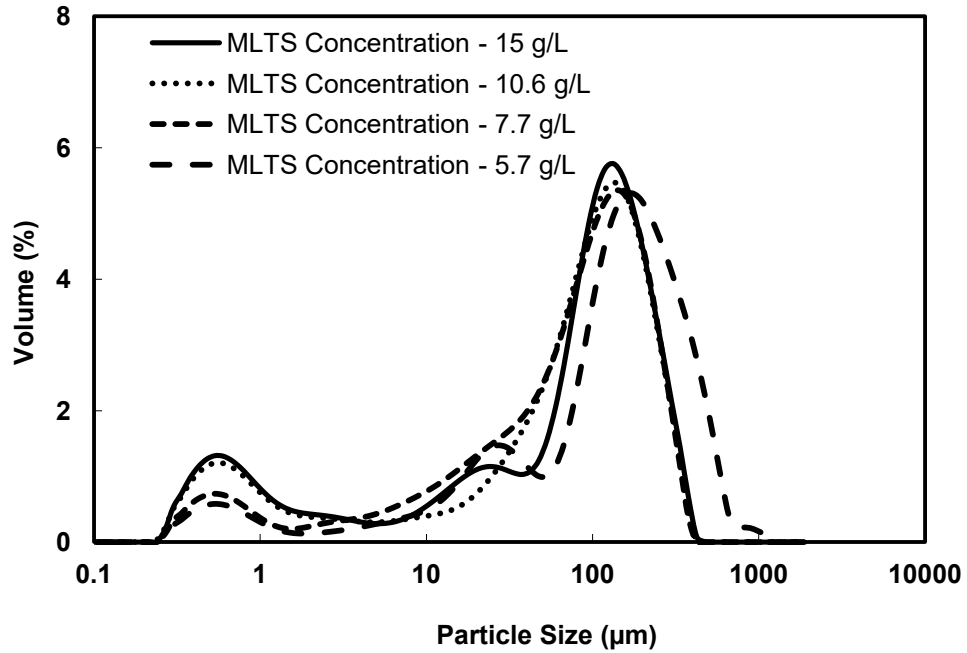
Figure 3-5: Particle size distributions of supernatant for various MLTS concentrations at sparging rate of 8.72 m^3/m^2.h
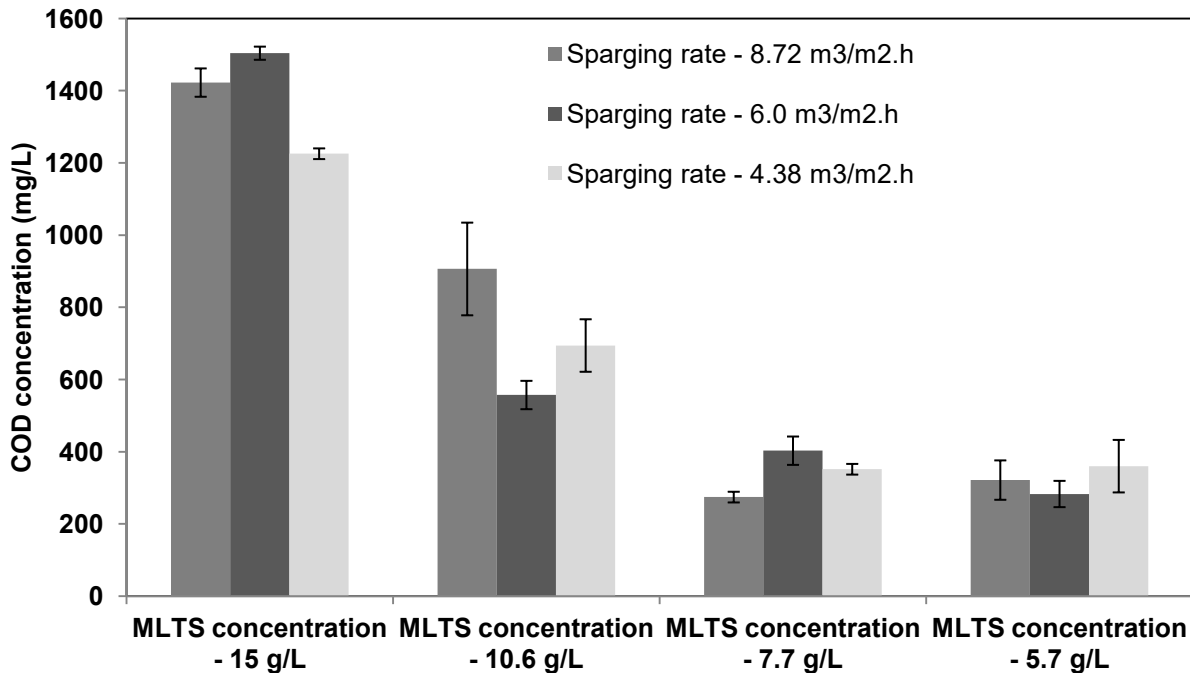

Figure 3-6: Supernatant COD of the various MLTS concentrations at the various sparging rates

### 3.3.1.3 Effect of MLSS concentrations & sparging rates on critical flux

Figure 3-7 depicts the effect of sparging rates on the critical flux at the various MLTS concentrations. The sparging rates were found to have significant effect on the critical flux under various MLTS concentrations (ANOVA, $P < 0.05$). At three MLTS concentrations (5.7, 10.6 and 15 g/L), an increase in the biogas sparging rate initially from 4.38 to 6.0 m^3/m^2.h led to an increase in the critical flux but no further improvement in critical flux was observed with a further increase of biogas sparging rate from 6.0 to 8.72 m^3/m^2.h (student t test, p>0.05). This can be explained by the change in shear forces and sludge properties. At the initial stage, an increase in the biogas sparging rate resulted in improved shear forces on membrane surfaces (i. e. more power to prevent particles deposition on the membrane) but the change in sludge properties were limited (as shown in Fig. 3-4) and thus led to improved critical flux. However, although a further increase in the biogas sparging rate (from 6.0 to 8.7 m^3/m^2.h) led to a further increased shear forces on membrane surface but simultaneously led to the break-up of large flocs into smaller flocs, as evidenced by the increase of the fraction of smaller flocs (<1 um) (Fig. 3-4). The positive impact of increasing biogas sparging rate on critical flux was compensated by the negative influence of increased smaller flocs and thus no further improvement in critical flux was observed. This is consistence with findings of other authors which state the existence of a maximum aeration rate beyond which there is no further increase in the flux can be gained (Fox and Stuckey., 2015). Monclus et al. (2010) proposed existence of a critical aeration rate for aerobic MBRs analogous to the critical flux concept. Similarly our results suggest the existence of the critical biogas sparging rate for SAnMBRs stressing the importance of optimising the sparging rate in

SAnMBRs. When MLTS concentration was lowered to 7.7 g/L, the critical flux increased consecutively with the increase of sparging rate from 4.38 m^3/m^2.h to 6.0 m^3/m^2.h and to 8.72 m^3/m^2.h (T-Test, $P < 0.05$). However, the increase in critical flux was only about 8.47% while the increase in sparging rate (from 6.0 m^3/m^2.h to 8.72 m^3/m^2.h) exceeded 45% which is economically unbalanced and we can fairly assume no flux increase above the intermediate sparging rate.

Figure 3-8 illustrates the effect of MLTS concentration on critical flux under the different sparging rates tested. The results indicate that MLTS concentration had a remarkable effect on the critical flux (ANOVA, $p<0.05$). The critical flux decreased with an increase in MLTS concentration from 5.7 to 10.6 g/L (ANOVA, $p <0.05$) but no further decrease in critical flux was observed when the MLTS concentration was increased from 10. 6 to 15 g/L under two (4.38 and 6.0 m^3/m^2.h) of the three biogas sparging rates tested (student t-test, $p>0.05$). The solids flux towards the membrane increased as MLTS concentration increased (Trussell et al., 2007), thus causing the decline in the critical flux. At MLTS concentration of 15.0 g/L, the effect of biogas sparging equated the transport of the particles towards the membrane and consequently the critical flux remained almost constant. At the highest biogas sparging rate (8.72 m^3/m^2.h) tested, no significant change in critical flux was observed when the MLTS was changed either from 5.7 to 7.7 or from 10.6 to 15 g/L (Student t-test, $p<0.05$). A significant decrease in critical flux was observed with an increase in MLTS from 7.7 to 10.6 g/L (Student t-test, $p<0.05$). This could be attributed to the increased smaller particle concentration induced by the high shear force of 8.72 m3/ m^2.h. A critical MLTS concentration range concept similar to the critical flux/aeration concept can be proposed here. Based on fig. 3-8,

there is a linear relationship between the critical flux and the MLTS concentrations (under the various sparging rate) up to a threshold value (10.6 g/L) beyond which no further decrease in the critical flux occurs. For example, as the flux remained comparable in the MLTS range 10.6 g/L – 15 g/L for each of the sparging rates tested; The SAnMBR could highly benefit from the higher limit of the MLTS concentration (i.e. 15 g/L) when treating higher strength wastewaters rather than using the lower limit of 10.6 g/L as both concentrations yielded same flux. These results are consistent with the current practise of limiting the MLSS concentration in the range 10 to 15 g/L (Schwarz et al., 2006). This demonstrates the importance of optimising the MLSS concentration in SAnMBRs and further studies could be conducted to further explore this area.

It is noteworthy to mention that all these critical flux measurements were carried out under an accelerated testing with minimum changes in other sludge properties other than MLSS concentration. An optimal biogas sparging rate at 6.0 m^3/m^2.h was identified to have high critical flux and save energy. The relationship between the critical flux and MLTS concentration in the range (5.7 to 10.6 g/L) under the several sparging rates tested could be approximated by a linear relationship. However, no remarkable loss in critical flux was observed at MLTS concentration of 15 g/L for the various sparging rates. This may also propose existence of critical MLSS concentration range. Further studies are needed to investigate this; as the SAnMBR could highly benefit from the increased MLSS concentration having no notable effect on the membrane flux.
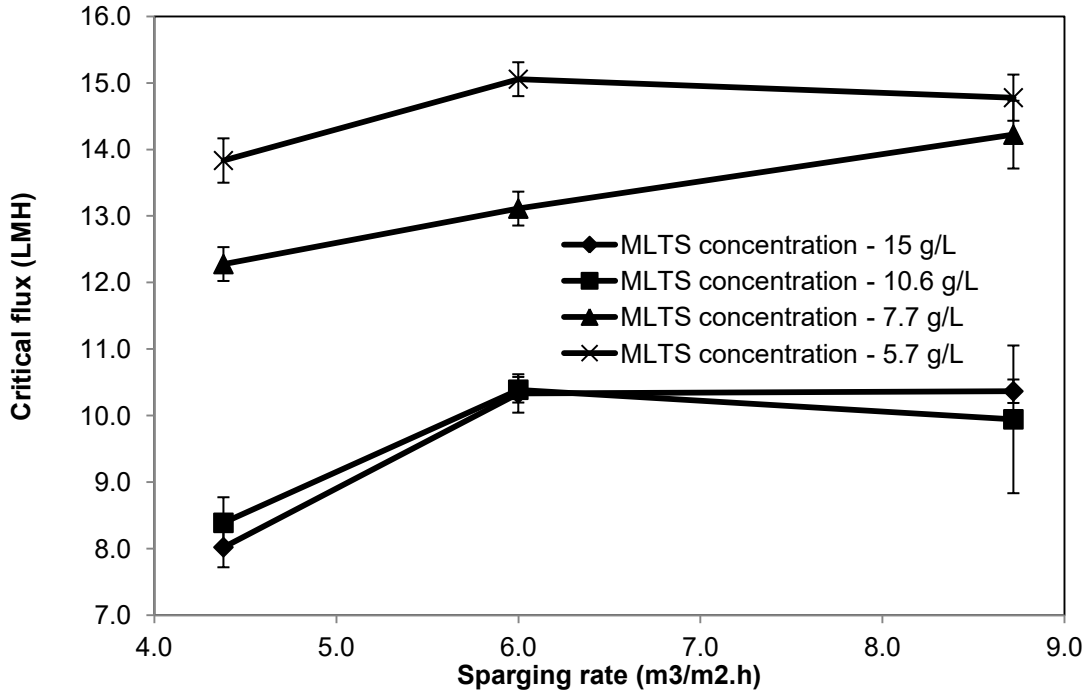
Figure 3-7: Critical flux versus sparging rates (4.38, 6.0 & 8.72 m^3/ m^2.h) for the various MLTS concentrations
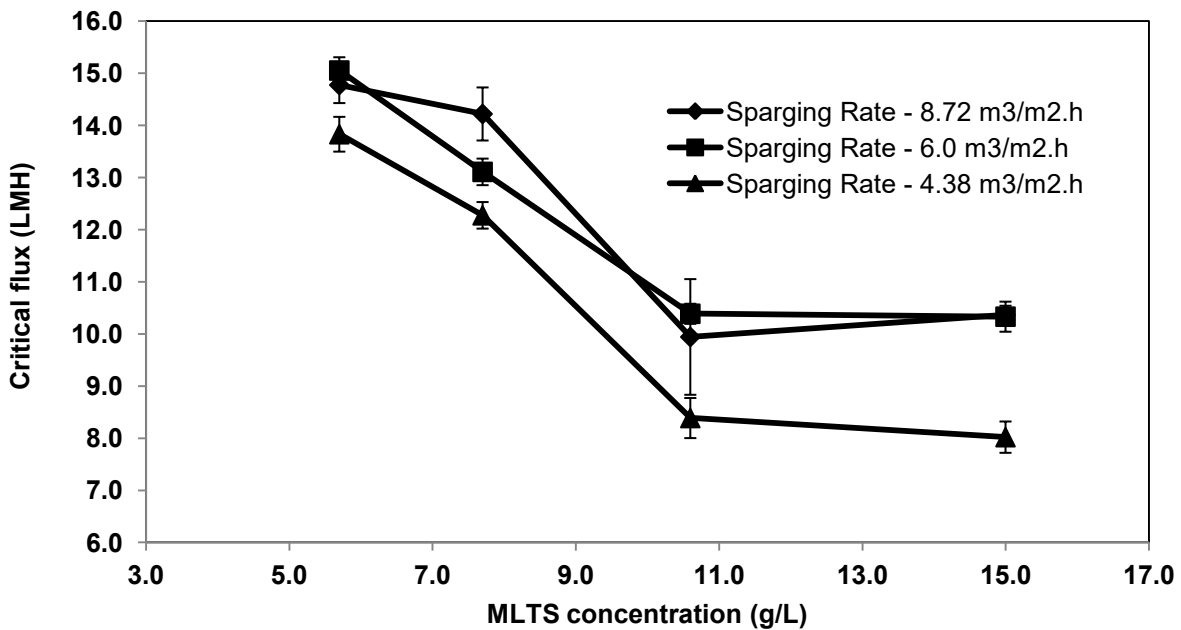
Figure 3-8: Critical flux versus the various MLTS concentrations at the various sparging rates (4.38, 6.0 & 8.72 m^3/m^2.h)

3.3. 2 Long term operation

3.3.2.1 SAnMBR performance

In the accelerated study it was found that the critical flux for MLTS concentrations of 10.6 & 15.0 g/L under a biogas sparging rate of 6.0 m^3/ m^2.h was 10.3 LMH. To verify the validity of the critical flux concept, a long-term study over 142 days at a sub-critical flux of 8.0 ±1 LMH was conducted under a MLTS concentration of 11.46 ± 0.92 g/L and the optimal biogas sparging rate of 6.0 m^3/m^2.h.

Figure 3-9 shows COD variation of influent, effluent and the supernatant with experimental time. Overall, excellent COD removal efficiency of 99.78 ± 0.0016% was achieved with a low effluent COD concentration of 37.95 ± 27.1 mg/L and supernatant COD was 462 ± 73 mg/L. Figures 3-10 and 3-11 show biogas production rate and composition with experimental time, respectively. The biogas production rate was 0.46 ± 0.1 L biogas/g COD consumed, which was composed of 78.73 ± 2.14% CH_4 , 19.00 ± 1.7 % CO_2 and 2.23 ± 0.8 N_2 . The biogas production rate and composition are similar to that reported by (Lin et al. (2010 and 2011)).

The PSDs of MLTS and supernatants are shown in figures 3-12 and 3-13. Similar PSDs of MLTS were observed in the three cyclic membrane operations. On the other hand, supernatant PSDs varied marginally.
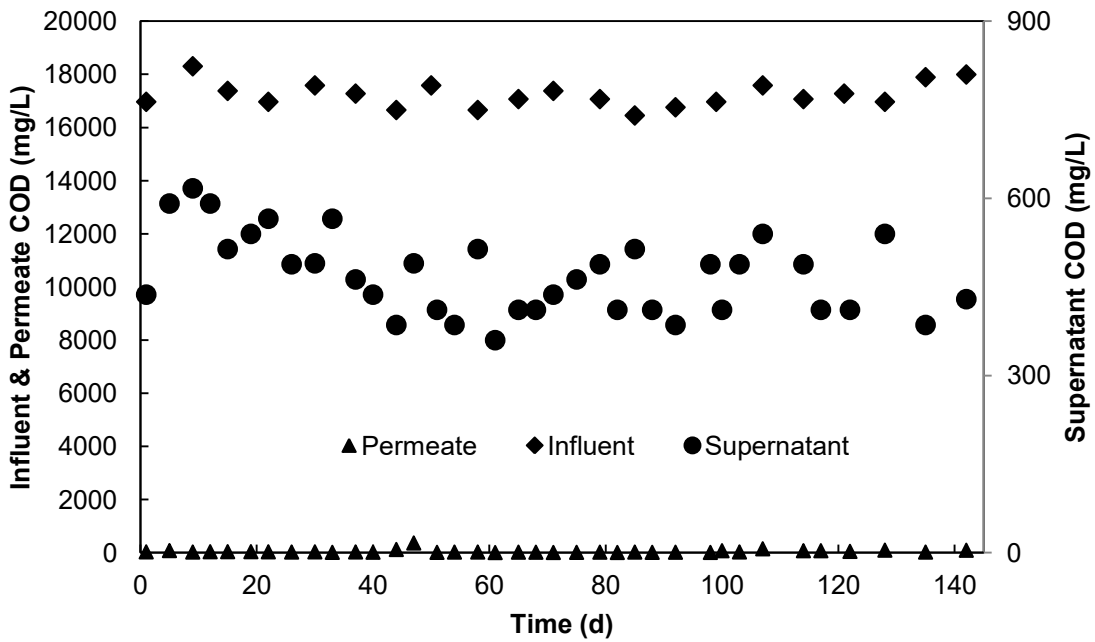
Figure 3-9: Influent, Supernatant & Permeate COD (mg/L) – Long term operation
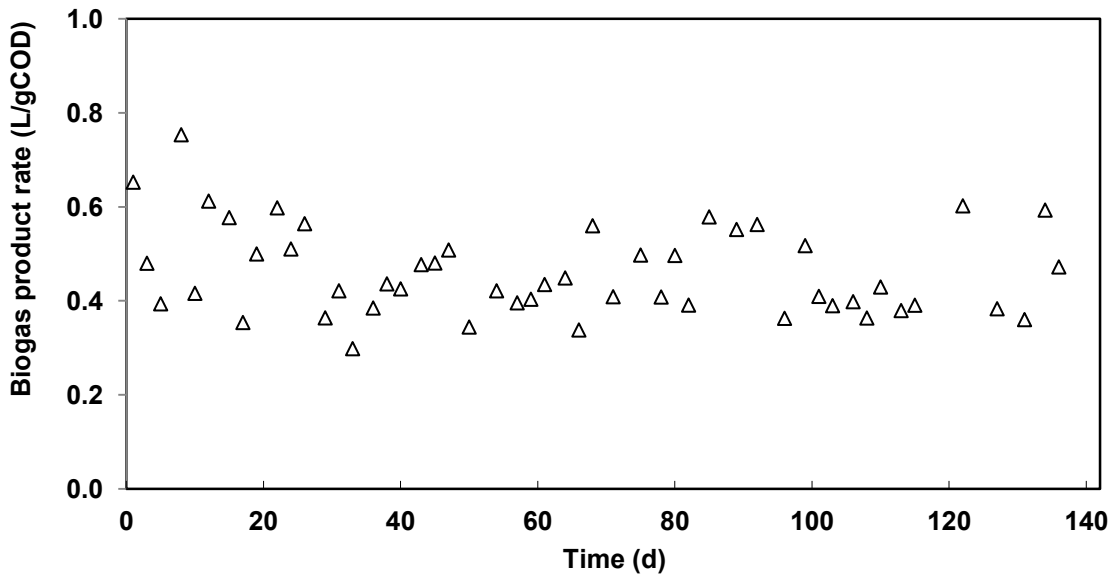

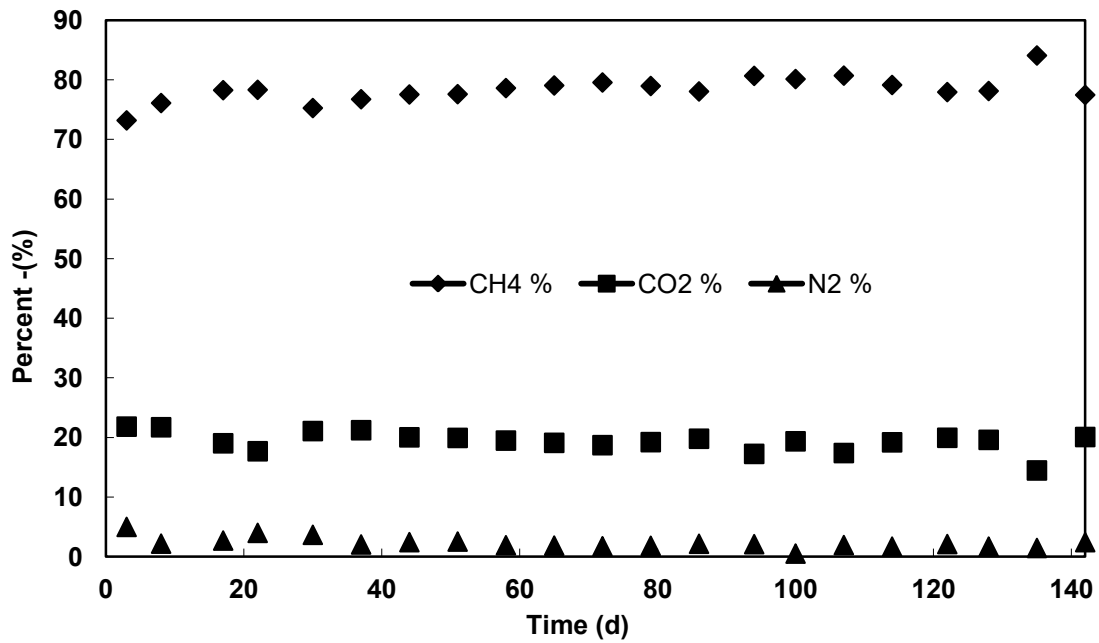**Figure 3-10: Biogas production rate versus time (Long term operation)**

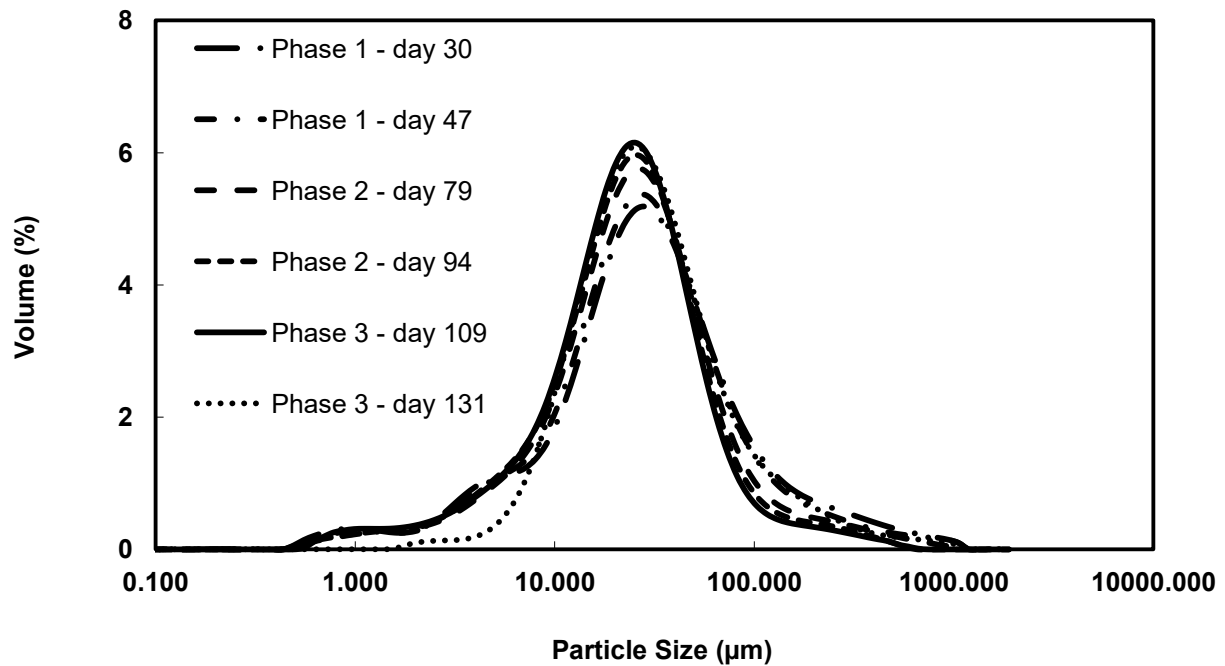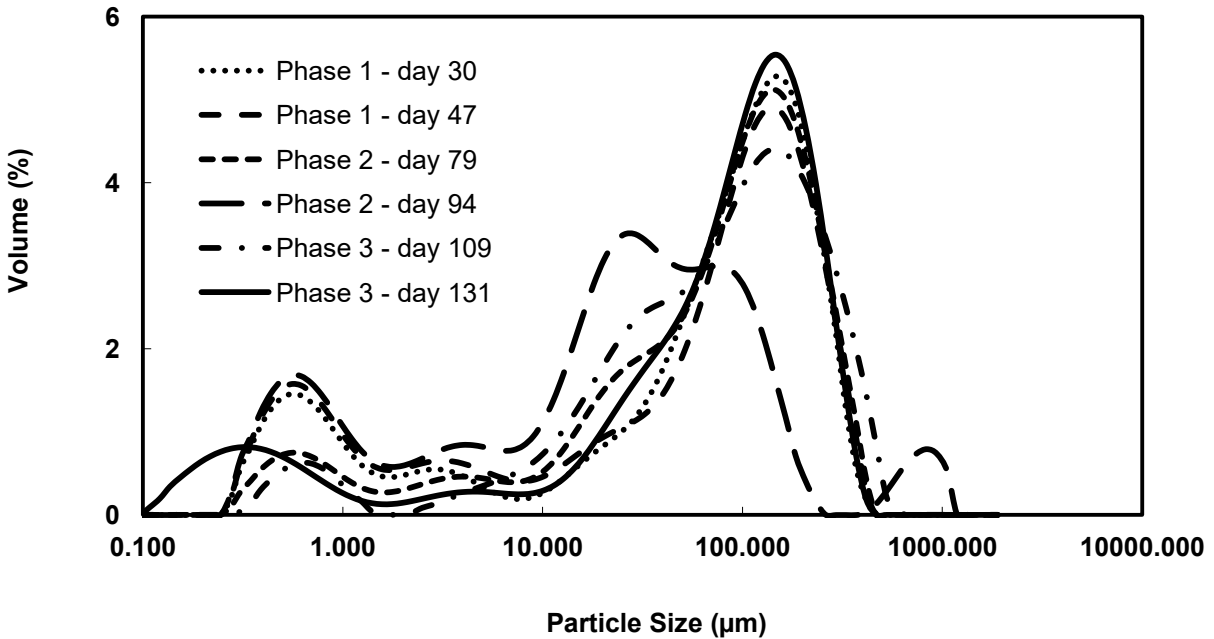**Figure 3-11: Variation of biogas composition (%) -Long term operation**

Figure 3-12: Particle size distributions of the mixed liquor (Long term operation)

Figure 3-13: Particle size distributions of the supernatant (Long term operation)

3.3.2.2 Permeate flux and TMP

Figures 3-14 and 3-15 show the variation of membrane flux and TMP with experimental time. Three cyclic membrane operations were performed: cycle 1 from day1 to day 55; cycle 2 from day 56 to day 101; and cycle 3 from day 102 to day 142. At the end of each cyclic operation, membrane inspection showed that a thin gel layer (yellow colour), but not cake layer (grey colour) was formed. Thus physical cleaning of the thin and sticky gel layer was performed using a wet sponge. The results of membrane flux as shown in Figure 3-14, indicates a sustainable membrane flux of 8.81

± 0.27 LMH (cycle 1), 7.7 ± 0.32 LMH (cycle 2), and 7.64 ± 0.33 (cycle 3) was achieved for approximately six weeks in each cyclic membrane operation. After that, membrane flux could not be maintained at the sustainable flux level and eventually led to membrane cleaning. The results of TMP changes, as shown in Figure 3-15, suggest a typical three-stage TMP profile: an initial increase stage from 5 kPa to 10 kPa in the first week; then a flat TMP stage for approximately four weeks and eventually TMP increase again in the first two cyclic membrane operations. Similar performance was observed by (Li et al., 2013).
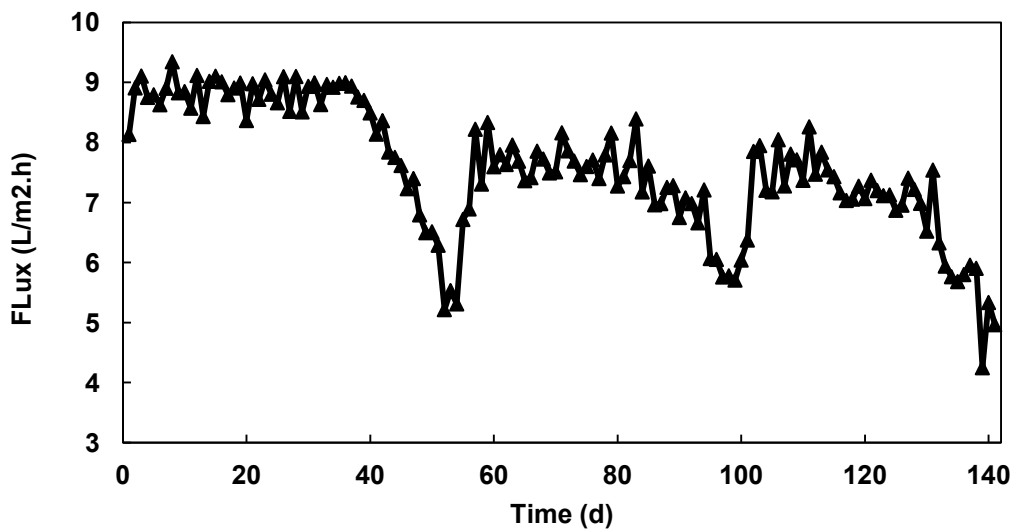
Figure 3-14: Variation of flux with time (Long term operation)
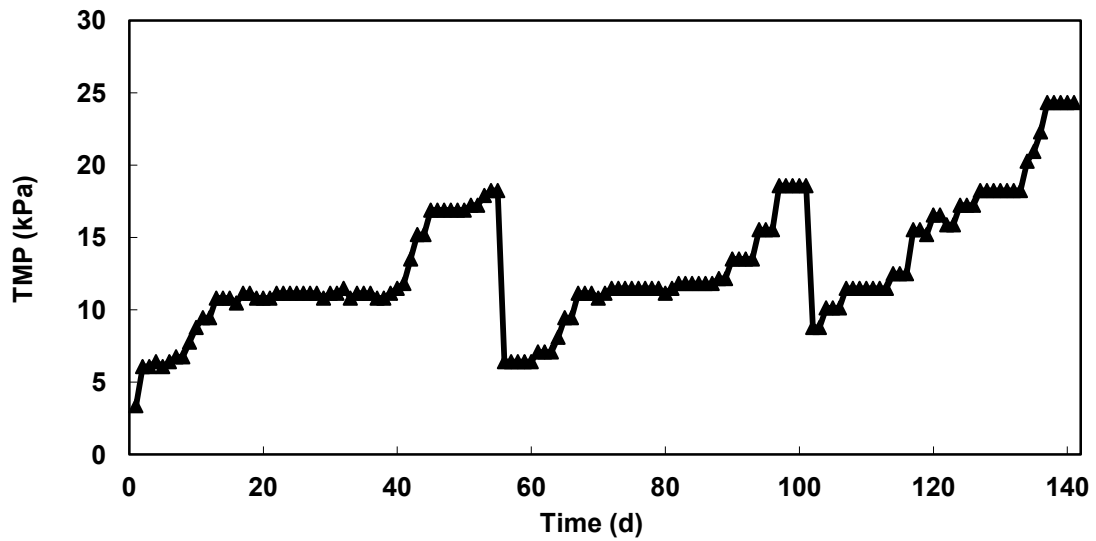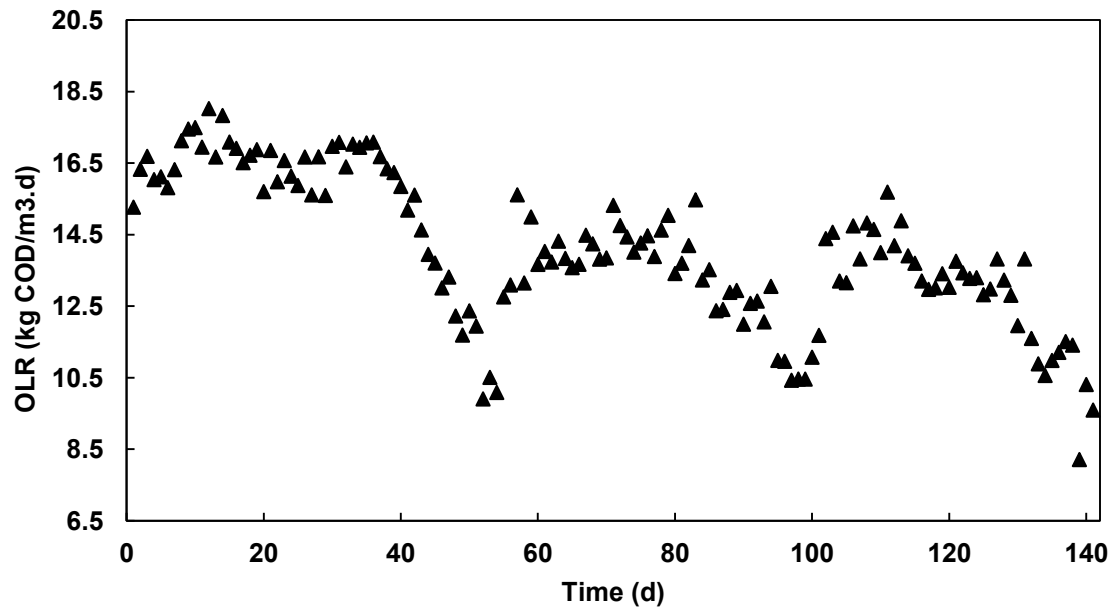
Figure 3-15: TMP versus time (Long term operation)

The OLR pattern throughout the long term operation obviously followed the flux pattern; figure 3-16 depicts the OLR variation. cycle 1 to 3 OLRs were 15.59 ± 2.0, 13.36 ± 1.34 and 12.89 ± 1.58 Kg COD/m^3.d respectively and the combined cycle 1 to 3 OLR was 14.07 ± 1.58 Kg COD/m^3.d.

Figure 3-16: Variation of organic loading rate (OLR) versus time

(Long term operation)

For both cycles one and two of the long term operation in this study, physical cleaning of the membrane to remove the gel layer coverage from the membrane surface was sufficient to restore the membrane permeability to (437 LMH) 91.6% and (399.7 LMH) 83.8% of the new membrane (477 LMH) respectively, indicating that gel layer formation was the dominant form of fouling. Interestingly, an increasing trend in fouling due to pore clogging (organic, inorganic and permanent) was observed from cycle 1 to 3 of the long term operation as the permeability loss due to pore clogging and/or biopolymer adsorption increased from 8.4% in cycle 1 to 16.2% in cycle 2 and 39.71%

in cycle 3. This drop in permeability (8.4%) at the end of cycle 1 and 16.2% at the end of cycle 2 caused the drop in flux in cycles 2 & 3 as can be seen in Figure 3-14 and clearly demonstrate the increasing importance of the pore clogging (organic, inorganic and permanent fouling) throughout the long term operation (cycles 1 to 3).

These results show that membrane fouling occurs even if the membrane is operated at subcritical flux, thus, forcing us to reject the critical flux concept. Similar findings were reported by (Li et al., 2013; Le Clech et al 2003a; Jeison and van Lier (2007)).

3.3.2.3 Membrane fouling characterization

At the end of the long term operation, membrane fouling cleaning and characterization was performed. The various resistances and corresponding permeability have been calculated and the results are illustrated in Fig 3-15 & 3-16. Table 3-2 also shows each resistance value and its percent contribution in R_t. R_c accounted for 94.88% of the total resistance indicating that the gel layer resistance is the dominant fouling mechanism influencing the permeate flux. R_p represented 2.05% of the total resistance which is subdivided to ($R_{organic}$ = 0.81%, $R_{inorganic}$ = 1.21% and R_{perm} = 0.02%). The ratio of Rc/ (Rc+Rp) was 97.89% clearly demonstrating the gel layer is the main factor influencing the membrane fouling. Although the inorganic fouling ($R_{inorganic}$) amounted to about 60% of the R_p it is very obvious that the R_p was not significant compared to R_c.
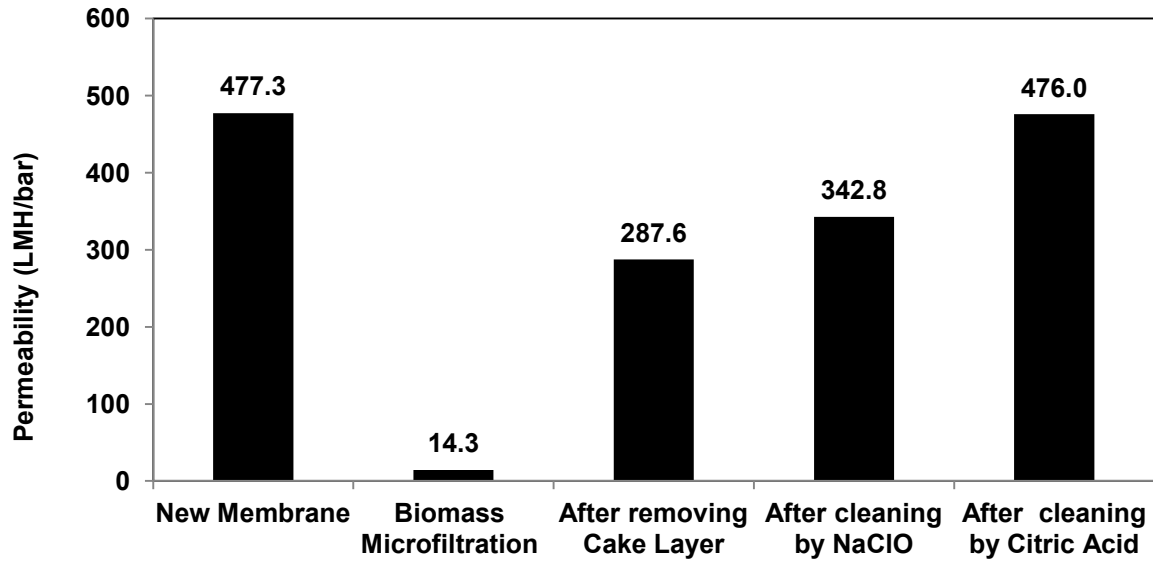
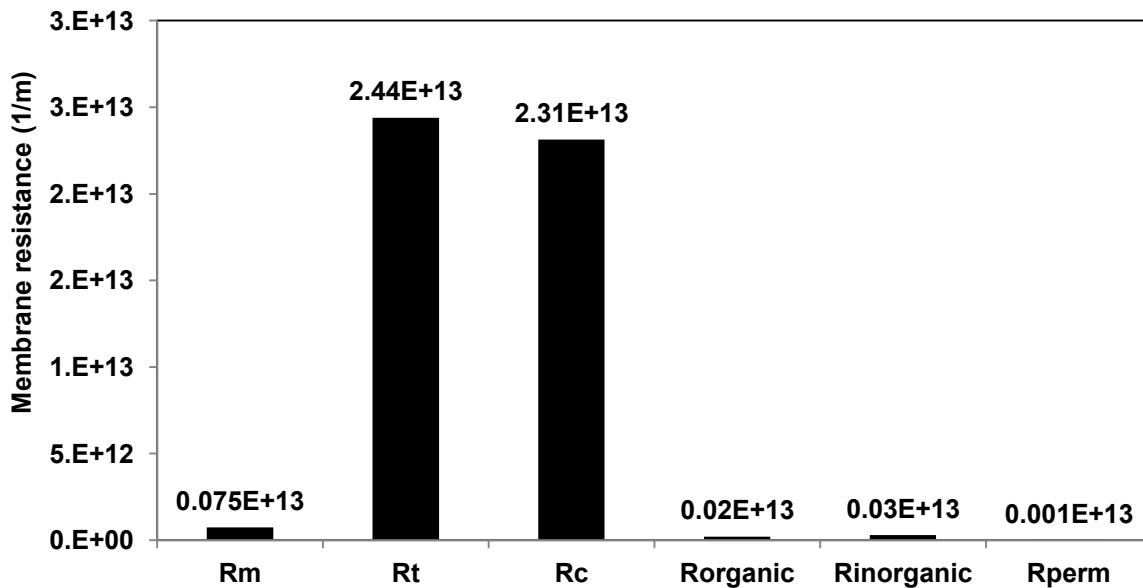**Figure 3-17: Permeability of the Membrane (LMH/bar) at various conditions.**

Figure 3-18: Membrane Resistance (m-1) at various conditions.

Note: (R_p = $R_{organic}$ + $R_{inorganic}$ + $P_{ermanent}$)

Similar results were reported by (Chang and Kim., 2005; Damayanti et al., 2011). The permeability for biomass filtration was about 3% of the new membrane and

increased to 60% after gel layer removal which supports the gel layer dominance of the membrane fouling. After cleaning the membrane by NaClO the permeability increased to about 71.83% and 99.73% of the permeability was recovered following the citric acid cleaning. These findings strongly support the less-significance of the pore fouling and the prevalence of the gel layer fouling over the other types. We can also conclude that the flux decline and TMP increase during the long term operation was mainly controlled by the gel layer (loss of 57% of permeability) and pore fouling which contributed to 40% loss in permeability and no permanent membrane fouling was developed.

Table 3-2: Membrane Resistance (m-1)

				R_p			
Resistance	R_t	R_m	R_c	$R_{organic}$	$R_{inorganic}$	R_{perm}	$R_c/(R_c+R_p)$
Value	2.44E+13	7.49E+11	2.31E+13	1.97E+11	2.96E+11	5.69E+09	97.89%
Percent %		3.07%	94.88%	0.81%	1.21%	0.02%	

3.4 Conclusions

3.4.1 Short term study

This short term study examined the effects of MLSS concentrations and sparging rates on the critical flux in SAnMBR. The study concluded that both MLSS concentration and sparging rate are key factors to be considered for optimisation and effective operation of the SAnMBR. The results can be summarized as follows:

- Mixed liquor PSDs remained constant under all sparging rates for all MLTS concentrations.

- Smaller size particles concentration in the supernatant increased with the increase in sparging rate for all MLTS concentrations but the impact was minimum in the range 10.6 g/L - 15.0 g/L and in the range of 5.7 g/L – 7.7 g/L. Similar trends were observed for the supernatant COD

- MLSS properties remained fairly constant with the exception of the slight variations in smaller particles concentration induced by the shear force of the sparging rate; however further studies are needed.

- Both the MLSS concentrations and sparging rates showed significant effect on the critical flux. Critical flux increased as the sparging rate increased for all MLSS concentrations, but no further increase was noted above (6.0 m^3/m^2.h)

- The relationship between the critical flux and MLTS concentration in the range 5.7 to 10.6 g/L can be approximated by a linear relationship for all the sparging intensities tested (the critical flux decreased as MLTS concentrations increased), but the critical flux stayed almost flat when MLTS concentration was increased to 15.0 g/L. This observation can be very beneficial when higher MLSS concentrations are desired above 10.6 g/L

- A critical MLSS concentration range concept similar to the critical flux/aeration concept can be proposed based on our results.

3.4.2 Long term operation

The long term operation demonstrated that FS-SAnMBR is a promising technology for industrial wastewater treatment. Excellent COD removal efficiency of 99.78 ± 0.0016% was achieved with low effluent COD concentration of 37.95 ± 27.1 mg/L at influent COD concentration of 17,235 ± 447 mg/L. However, membrane fouling still remains the main hurdle. The FS-SAnMBR was operated at sub-critical flux but significant fouling occurred (decreased flux and increased TMP) after six weeks operation mainly caused by gel layer formation. Membrane fouling characterization confirmed the gel layer formation was the main mechanism of fouling. Fouling due pore clogging increased with the operational time; by end of the long term operation it was responsible for 40% of permeability loss. Virtually complete recovery of the permeability could be obtained by removing cake layer then chemical cleaning for removal of organic and inorganic foulants, indicating that the permanent fouling was not important.

3.5 Acknowledgements

3.6 References

Andreottola, G., & Guglielmi, G. (2003). Critical flux determination in two MBRs for municipal wastewater treatment. Proc of IMSTEC, 3, 10-14.

APHA, 2005. Standard methods for the examination of water and wastewater, 21th ed.American Public Health Association (APHA)/American Water Works Association (AWWA)/Water Environment Federation (WEF), Washington, DC.

Bacchin, P., Aimar, P., & Field, R. W. (2006). Critical and sustainable fluxes: theory, experiments and applications. Journal of membrane science, 281(1), 42-69.

Bura, R., Cheung, M., Liao, B., Finlayson, J., Lee, B. C., Droppo, I. G., ... & Liss, S. N. (1998). Composition of extracellular polymeric substances in the activated sludge floc matrix. Water Science and Technology, 37(4), 325-333.

Chang, S. (2014) Anaerobic Membrane Bioreactors (AnMBR) for Wastewater Treatment. Advances in Chemical Engineering and Science, **4**, 56-61.

Chang, I. S., & Kim, S. N. (2005). Wastewater treatment using membrane filtration—effect of biosolids concentration on cake resistance. Process Biochemistry, 40(3), 1307-1314.

Damayanti A, Ujang Z, Salim M R, Olsson G. The effect of mixed liquor suspended solids (MLSS) on biofouling in a hybrid membrane bioreactor for the treatment of high concentration organic wastewater. Water science and technology 2011;63(8):1701-6.

Espinasse, B., Bacchin, P., & Aimar, P. (2002). On an experimental method to measure critical flux in ultrafiltration. Desalination, 146(1), 91-96.

Estrada-Arriaga, E. B., Mijaylova Nacheva, P., & García-Sánchez, L. (2015). Effect of Mixed Liquor Volatile Suspended Solids on Membrane Fouling During Short and long-term Operation of Membrane Bioreactor. Ingeniería y Ciencia,11(21), 137-155.

Field, R.W., Wu, D., Howell, J.A., Gupta, B.B., 1995. Critical flux concept for microfiltration fouling. J. Membr. Sci. 100, 259–272.

Fox, R. A., & Stuckey, D. C. (2015). The effect of sparging rate on transmembrane pressure and critical flux in an AnMBR. Journal of environmental management, 151, 280-285.

Huang, Z., Ong, S. L., & Ng, H. Y. (2011). Submerged anaerobic membrane bioreactor for low-strength wastewater treatment: effect of HRT and SRT on treatment performance and membrane fouling. Water research, 45(2), 705-713.

Jeison, D., & van Lier, J. B. (2007). Cake formation and consolidation: main factors governing the applicable flux in anaerobic submerged membrane bioreactors (AnSMBR) treating acidified wastewaters. Separation and Purification Technology, 56(1), 71-78

Kim, J., & DiGiano, F. A. (2006). Defining critical flux in submerged membranes: influence of length-distributed flux. Journal of membrane science,280(1), 752-761.

Le Clech, P., Jefferson, B., Chang, I. S., & Judd, S. J. (2003a). Critical flux determination by the flux-step method in a submerged membrane bioreactor.Journal of Membrane Science, 227(1), 81-93.

Le-Clech, P., Jefferson, B., & Judd, S. J. (2003b). Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of a membrane bioreactor. Journal of Membrane Science, 218(1), 117-129.

Li, J., Zhang, X., Cheng, F., & Liu, Y. (2013). New insights into membrane fouling in submerged MBR under sub-critical flux condition. Bioresource technology, 137, 404-408.

Liao, B.Q., Kraemer, J.T. and Bagley, D.M. (2006) Anaerobic membrane bioreactors: Applications and research directions. Critical Reviews in Environmental Science and Technology 36(6), 489-530.

Liao, B. Q., Allen, D. G., Droppo, I. G., Leppard, G. G., & Liss, S. N. (2001). Surface properties of sludge and their role in bioflocculation and settleability.Water Research, 35(2), 339-350.

Lin, H., Gao, W., Meng, F., Liao, B. Q., Leung, K. T., Zhao, L., ... & Hong, H. (2012). Membrane bioreactors for industrial wastewater treatment: a critical review. Critical Reviews in Environmental Science and Technology, 42(7), 677-740.

Lin, H., Liao, B. Q., Chen, J., Gao, W., Wang, L., Wang, F., & Lu, X. (2011). New insights into membrane fouling in a submerged anaerobic membrane bioreactor based on characterization of cake sludge and bulk sludge.Bioresource technology, 102(3), 2373-2379.

Lin, H. J., Xie, K., Mahendran, B., Bagley, D. M., Leung, K. T., Liss, S. N., & Liao, B. Q. (2010). Factors affecting sludge cake formation in a submerged anaerobic membrane bioreactor. Journal of Membrane Science, 361(1), 126-134.

Lin, H. J., Xie, K., Mahendran, B., Bagley, D. M., Leung, K. T., Liss, S. N., & Liao, B. Q. (2009). Sludge properties and their effects on membrane fouling in submerged anaerobic membrane bioreactors (SAnMBRs). Water Research,43(15), 3827-3837.

Monclus, H., Zacharias, S., Santos, A., Pidou, M., & Judd, S. (2010). Criticality of flux and aeration for a hollow fiber membrane bioreactor.Separation Science and Technology, 45(7), 956-961.

Nielsen, P. H., Frølund, B., & Keiding, K. (1996). Changes in the composition of extracellular polymeric substances in activated sludge during anaerobic storage. Applied microbiology and biotechnology, 44(6), 823-830.

Pollice, A., Brookes, A., Jefferson, B., & Judd, S. (2005). Sub-critical flux fouling in membrane bioreactors—a review of recent literature. Desalination,174(3), 221-230.

Robles A, Ruano M V, Garcia Usach F, Ferrer J, García Usach F. Sub-critical filtration conditions of commercial hollow-fibre membranes in a submerged anaerobic MBR (HF-SAnMBR) system: The effect of gas sparging intensity. Bioresource technology 2012;114:247-254.

Schwarz, A. O., Rittmann, B. E., Crawford, G. V., Klein, A. M., & Daigger, G. T. (2006). Critical review on the effects of mixed liquor suspended solids on membrane bioreactor operation. Separation science and technology, 41(7), 1489-1511.

Trussell, R. S., Merlo, R. P., Hermanowicz, S. W., & Jenkins, D. (2007). Influence of mixed liquor properties and aeration intensity on membrane fouling in a

submerged membrane bioreactor at high mixed liquor suspended solids concentrations. Water research, 41(5), 947-958.

Vogelaar, J. C. T., Bouwhuis, E., Klapwijk, A., Spanjers, H.,van Lier, J. B., 2002. Mesophilic and thermophilic activated sludge post-treatment of paper mill process water. Water Research 36, 1869-1879.

Welander, T., Morin, R.,Nylén, B., 1999. Biological removal of methanol from kraft mill condensate. In: TAPPI Proceedings International Environmental Conference.

Wu Z, Wang Z, Huang S, Mai S, Yang C, Wang X, Zhou Z. Effects of various factors on critical flux in submerged membrane bioreactors for municipal wastewater treatment. Separation and purification technology 2008;62(1):56-63.

Xie, K., Lin, H. J., Mahendran, B., Bagley, D. M., Leung, K. T., Liss, S. N., & Liao, B. Q. (2010). Performance and fouling characteristics of a submerged anaerobic membrane bioreactor for kraft evaporator condensate treatment.Environmental technology, 31(5), 511-521.

Yu, K., Wen, X., Bu, Q., & Xia, H. (2003). Critical flux enhancements with air sparging in axial hollow fibers cross-flow microfiltration of biologically treated wastewater. Journal of Membrane Science, 224(1), 69-79.

Chapter 4 : Development of a high-rate submerged anaerobic membrane bioreactor (SAnMBR)

4.1 Introduction

Due to the global attention to reduce green-house gas emissions and recover energy from waste, anaerobic treatment of industrial wastewater has become very appealing compared to aerobic wastewater treatment and has been growing rapidly (Visvanathan and Abeynayaka (2012); Chong et al., 2012). Conventional high rate anaerobic technology for industrial wastewaters treatment, like up-flow anaerobic sludge blanket (UASB) and expanded granular sludge bed (EGSB), is a well-established technology that has many benefits such as high organic loading rates (OLRs), recovery of energy (by production of biogas), low sludge yield and smaller bioreactor volume (Dereli et al., 2012). Due to the combination of simple construction and a high volumetric treatment capacity, UASB is the most dominant high rate anaerobic reactor. In full-scale plants worldwide, the UASB constitutes more than 50% of the market (i.e. 852 out of 1599 plants) (Kleerebezem and Macarie, 2003; Dereli et al., 2012; Gomec, 2010; Chong et al., 2012). Full-scale UASB reactors are operated at high influent chemical oxygen demand (COD) concentration ranges of 1,000 to 20,000 mg/L, hydraulic retention times (HRTs) of 2.4 hours to 8 days, COD removal rate of more than 60% and very high organic loading rates (OLRs) of 3 - 40 kg COD/m^3.day (Visvanathan and Abeynayaka, 2012; Kleerebezem and Macarie, 2003; Ahn et al., 2001). The current commercial high rate anaerobic bioreactor systems include BIOPAQ®UASB (OLR of 10-15 kgCOD/m^3.day at influent COD of 1000-20000 mg/L)

("BIOPAQ®UASB," 2015), ADI-UASB (OLR of 8-10 kgCOD/m^3.day), ADI-ECSB (external circulation sludge bed) (OLR of 16~24 kgCOD/m^3.day) (Wilson (2014)) and BIOBED® ADVANCED (OLR ~20 kgCOD/m^3.day) ("Veolia Water Technologies," 2015).

Although granular sludge based processes (e.g. UASB) are successfully applied for the anaerobic treatment of a wide range of wastewaters, certain limitations exist. They have performed poorly in treating industrial wastewaters at extreme conditions, such as high organic content (i.e wastewater with > 60 g COD/L), high salinity, high or low temperatures, high FOG (fat, oil and grease) content, high concentrations of suspended solids (SS), OLR and HRT shocks, calcium scaling and toxicity. These characteristics impede the granulation process and biomass retention or deteriorate the biological activity of treatment systems (Dereli et al., 2012; Mockaitis et al 2006; Visvanathan and Abeynayaka, 2012). The major problems associated with the conventional UASB reactor in treating wastewaters at normal conditions include: long duration for start-up period, requirement for sufficient amount of granular sludge, biomass wash-out, requirement for effluent polishing (e.g. aerobic post treatment for UASB effluent), failure to remove pathogens and poor effluent quality that cannot be re-used or recycled in the industrial processes (Martinez-Sosa et al., 2011; An et al., 2009; Najafpour et al., 2008; Khan et al 2014; Mockaitis et al., 2006). Therefore, it is highly desirable to develop novel technologies that have the advantages of the UASB but can overcome the disadvantages of UASB.

In recent years, anaerobic membrane bioreactors (AnMBRs) have emerged as a competitive technology as it offers superior effluent quality (free of solids and pathogens) and complete retention of biomass, irrespective of its settling and/or

granulation characteristics (Fox and Stuckey, 2015; Lin et al., 2011; Dereli et al., 2012; Xie et al., 2010; Liao et al., 2006). Most importantly, the AnMBRs are able to overcome some of the challenges of UASB as discussed above (Bornare et al., 2014) and produce high quality of effluent for water reuse or system closure. In lab-scale studies of industrial wastewater treatment, AnMBRs have performed very promisingly. They have successfully treated high strength wastewaters of more than 80,000 mg COD/L at high OLRs up to 25 kgCOD/m^3.day, COD removal efficiency of 92->99%, biogas yield of 0.24 – 0.38 L CH_4/g COD removed and composition of 63-90% (Bornare et al., 2014; Xie at al., 2010; Visvanathan and Abeynayaka, 2012; Fakhru'l-Razi and Noor,1999; Dereli et al., 2012; Lin et al., 2013). Pilot-scale studies reported OLRs of 0.14 ~ 10 kgCOD/m^3.d at influent CODs up to 56,900 mg/L and COD removal rates of ≥ 98% (Watanabe et al., 2014; Dereli et al., 2012). Full-scale applications are at much lower OLRs of ~ 3 kg COD/m^3.d and high feed COD up to 101 g/L with an excellent COD removal of 72->99% (Dereli et al., 2012). ADI's commercial AnMBR (ADI-AnMBR) can operate in the OLR ranges of 2-8 kgCOD/m^3.day (Wilson (2014)).

Although the AnMBR has much potential, it has not been utilized fully, due to the competition of the conventional high-rate UASB and EGSB. Low OLRs have been synonymous with AnMBRs. Therefore, it is desirable to develop high-rate AnMBR technology to compete with the established UASB and EGSB technologies. The objectives of this study were to develop a high rate SAnMBR (OLR > 40 kgCOD/m^3.d) to pave the way for high rate OLR AnMBR (OLR > 20 kgCOD/m^3.d) in pilot- and full-scale applications and thus AnMBRs can compete with the conventional anaerobic reactors such as UASB, to investigate the membrane fouling and its control, and to

characterize membrane fouling and foulants at higher OLRs that were not achieved in previous studies.

4.2 Material and Methods

4.2.1 The laboratory scale HF-SAnMBR setup and operation

Figure 4-1 depicts the hollow fibre SAnMBR (HF-SAnMBR) used in this study. The HF-SAnMBR has a total working volume of 10 L and is composed of a bottom sludge blanket zone (4 L) and a top filtration zone (6 L). The purpose of the bottom zone was to form sludge granules' acting as the sludge blanket, hence, the HF-SAnMBR was designed to simulate the performance of the UASB reactor and benefit from the membrane separation. A hollow-fibre (HF) membrane module made of polyvinylidene fluoride (PVDF) material and with effective filtration area of 0.03 m^2 and pore size of 0.04 μm was submerged in the top zone of the HF-SAnMBR. The HF membrane module was used for approximately two years in a previous study of AnMBR (Gao et al., 2014; Gao et al., 2013) prior to this study and was supplied by GE Water & Process Technologies, Oakville, Ontario, Canada.

The HF membrane module was fabricated as a complete module with a built-in hardware to facilitate biogas sparging. The biogas in the headspace was recirculated by a gas recycle pump (Masterflex Console Drive, Model 7520-40, Thermo Fisher Scientific, USA) to furnish mixing of the mixed liquor in the top filtration zone and to control solids deposition on the HF membrane fibres by scouring the surface by the produced bubbles. The biogas sparging rate was fixed at 6.0 $m^3.m^{-2}.h^{-1}$ during the entire experimental period.

The seeded sludge used in this study was obtained from a full-scale UASB treating pulping wastewater at Tembec Industries Inc. (Timiskaming, Quebec). The temperature of the mixed liquor of the HF-SAnMBR was maintained constant at 37 ± 1 °C by continuously circulating warm water through the water jacket of the bioreactor and was supplemented by preheating the feed wastewater (which was stored in 4 °C in a refrigerator) to 37 ± 1 °C prior to entering the HF-SAnMBR through the water bath.
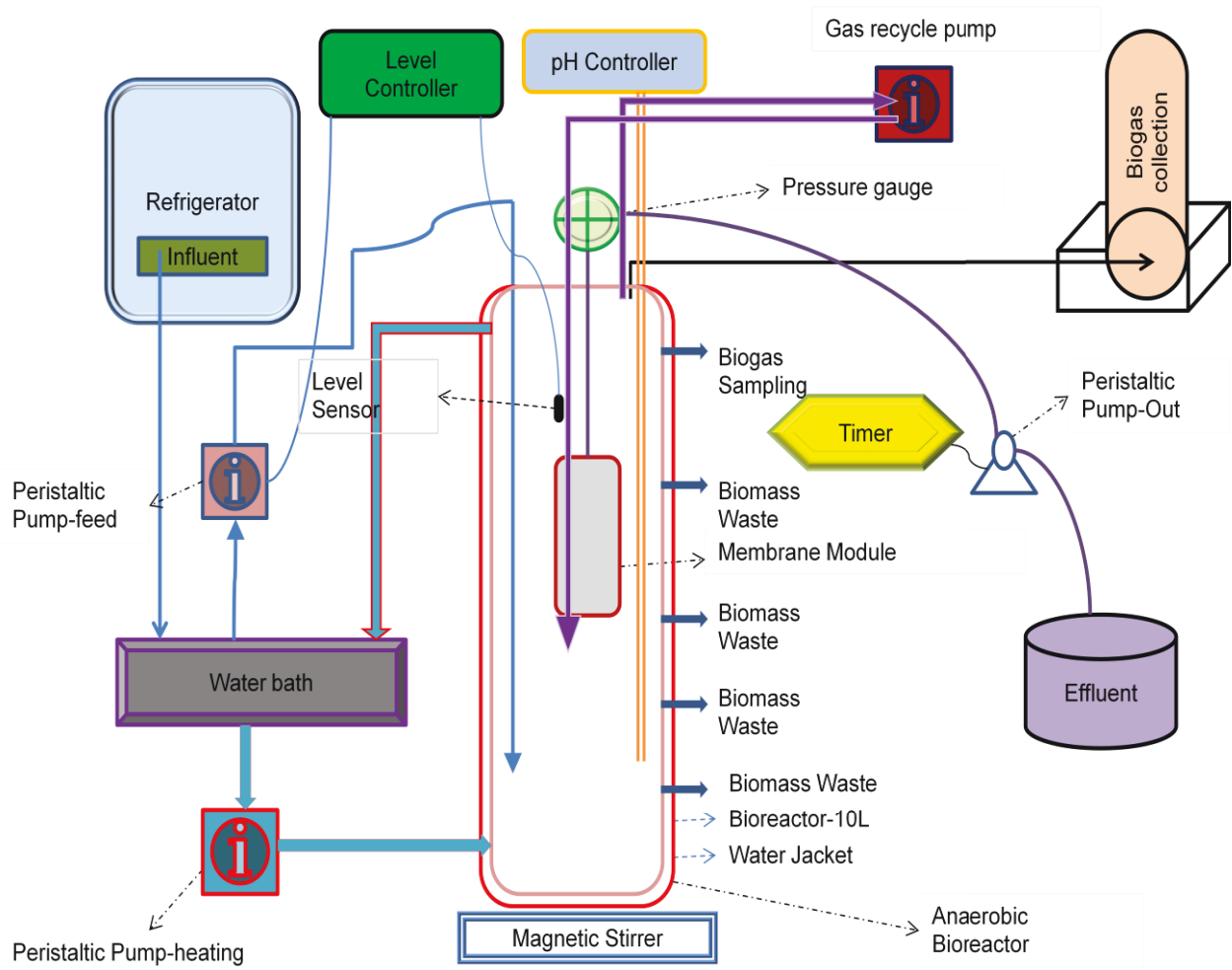
Figure 4-1: Schematic of the laboratory scale submerged anaerobic membrane bioreactor (SAnMBR).

The pH of the mixed liquor in the SAnMBR was monitored regularly and was adjusted manually by controlling the feed pH. NaOH solution was used to raise the feed pH which was typically < 3. The mixed liquor sludge pH was maintained at 7.0 ± 0.2. The HF-SAnMBR pH was reasonably stable during the steady-state operation and was easily controlled by adding the required amount of the NaOH solution at each phase of operation. The influent (wastewater) was pumped automatically into the bottom zone of the HF-SAnMBR by a feeding pump (Masterflex Model 7520-50, Barnant Co., USA). The feed pump was controlled by a water level sensor (Madison Co., USA), and controller (Flowline, USA) to constantly maintain the liquid level in the HF-SAnMBR.

The effluent was intermittently obtained by a peristaltic pump (Masterflex, C/L, Model 77120-70, Barnant Co., USA), which was operated in a three minutes permeation and two minutes relaxation mode. A timer connected to the permeate pump was used to control the operation mode. To manage the membrane flux, the permeate pump speed was adjusted and calibrated whenever necessary. The trans-membrane pressure (TMP) was measured by a vacuum pressure gauge that was connected to the HF membrane module in the bioreactor and the permeation pump. Nitrogen gas (99.998 %) was introduced to the HF-SAnMBR to remove the oxygen from the bioreactor whenever the HF-SAnMBR system was opened to remove or clean the membrane

The operation of the HF-SAnMBR system was arranged into three phases: Phase 1 (day 1 to 78); Phase 2 (day 79 to 193); Phase 3 (day 194 to 338); SRT ranged from 25 to 50 days while HRT was in the range of 2.35 to 2.7 days during the steady state operation.

4.2.2 Synthetic Wastewater

In the petrochemical industry of manufacturing dimethyl terephthalate (DMT), the generated wastewater is mainly composed of high concentrations of methanol and acetic acid (Ramakrishna and Desai., 1997; Sharma et al., 1994). Synthetic wastewater composed of methanol and acetic acid was used for this experimental study (methanol to acetic acid COD ratio of 2.66:1). As the synthetic wastewater was lacking macro-nutrients, nitrogen (NH_4Cl) and phosphorus (KH_2PO_4) were added to the synthetic wastewater at a ratio of COD: N: P of 100:2.6:0.4 to sustain the nutrient concentrations requirement for biomass growth and maintenance in an anaerobic environment (VogelaLiar et al., 2002; Lin et al., 2010). A trace element solution was also supplemented to the synthetic wastewater to prevent trace metal limitations of the methanogens as per the recommendations found in literature (Rittmann & McCarty (2012); Badshah et al., 2012; Welander et al., 1999; Huang et al., 2011). Table 4-1 shows the list of micronutrients and concentrations used in this study (Rittmann & McCarty (2012)). Furthermore, Mg^{2+} ion was added to the influent wastewater to provide sufficient hardness for the biomass growth and granulation. The concentration of Mg^{2+} was maintained at 0.1 mM added in the form of $MgCl_2$ (Xie et al., 2010). The required amount of methanol, acetic acid, macro-nutrients, micro-nutrients, Mg^{2+} ion and NaOH were mixed in tap water in 8 L containers and stored in 4 °C during usage.

Table 4-1: List of micronutrients and concentrations used in this study (Adapted from Rittmann & McCarty (2012))

Micronutrient	Concentration in feed (mg/g COD)	Chemical form of addition
Iron	0.03	$FeCl_2 \cdot 4 \, H_2O$
Cobalt	0.003	$CoCl_2.6H_2O$
Nickel	0.004	$NiCl_2.6H_2O$
Zinc	0.02	$ZnCl_2$
Copper	0.004	$CuCl_2.2 \, H_2O$
Manganese	0.004	$MnCl_2.4H2O$
Molybdenum	0.004	$NaMoO_4.2H_2O$
Selenium	0.004	Na_2SeO_4
Tungsten	0.004	$NaWO_4$
Boron	0.004	H_3BO_3

4.2.3 Analytical methods

4.2.3.1 Water Quality Measurements

CODs of influent, permeate and supernatant, mixed liquor suspended solids (MLSS) and mixed liquor total solids (MLTS) were measured according to the standard protocols (APHA, 2005). MLSS / MLTS ratio was 0.9623. The mixed liquor supernatant was obtained by centrifuging a sample at 18000g of gravitational acceleration for 20 minutes. The samples were taken from the top zone of the HF-SAnMBR and the end supernatant was used for chemical oxygen demand (COD) and particle size distributions (PSDs) measurement. The permeate COD was measured without further treatment by taking samples directly from the HF-SAnMBR. Samples were measured

two to three times per week and additional measurements were conducted whenever the situation dictated.

4.2.3.2 Measurements of the biogas production rate and composition

Biogas samples were taken from the headspace of the HF-SAnMBR using a syringe. The biogas produced in the HF-SAnMBR was mainly composed of methane, nitrogen, and carbon dioxide. The biogas composition was measured by a gas chromatography (Shimazu, GC-2014) which is equipped with a thermal conductivity detector (TCD) and a silica gel packed column (5,486 × 3.18 mm). Helium gas was used as the carrier for the equipment at a flow rate of 30 mL/min. Biogas composition was monitored throughout the study period and was normally measured once per week. Biogas yield or production rate was measured using a water displacement method.

4.2.3.3 Particle size distributions

The particle size distributions (PSDs) of the mixed liquor and supernatant samples of the HF-SAnMBR were determined by Malvern Mastersizer 2000 instrument (Worcestershire, UK) that has a detection range of 0.02-2000 μm. The Mastersizer 2000 instrument detects the scattered light by means of a detector that converts the signal to a size distribution based on number or volume. Each sample was automatically measured (by the built-in software) three times with a standard deviation of 0.1-4.5%. The average of the three measurements was automatically provided by the instrument and the average was used for data analysis of this study. Samples of the mixed liquor were taken from three different zones of the HF-SAnMBR and the supernatant for the top zone mixed liquor was obtained as described in section 4.2.3.1. The PSDs were regularly monitored throughout the experimental period.

4.2.3.4 Analysis of membrane flux, resistance and permeability

The resistance-in-series model ($R_t = R_m + R_f = R_m + R_c + R_p$) was used to evaluate the membrane filtration characteristics. Membrane resistance was analyzed using Darcy's law as follows:

$$R_t = R_m + R_f = R_m + R_c + R_p = \frac{\Delta P_T}{\eta x J} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where R_t represents the membrane total resistance (1/m), R_m is the new membrane resistance (1/m), R_f (1/m) is the total fouling resistance ($R_c + R_p$), R_p is the resistance due to the pore blocking(1/m), R_c is the cake layer resistance caused by the cake layer deposition over the membrane surface during filtration (1/m), ΔP_T is the trans-membrane pressure(Pa), η is the dynamic viscosity of the effluent (Pa.s) and J is the measured membrane flux (m^3/m^2.s). Each resistance value was determined using the exact HF membrane module used in the laboratory-scale SAnMBR for this study.

The experimental protocol used to measure each resistance value was as follows:(a) R_m was assessed by measuring the clean water flux of tap water; (b) R_t was calculated from equation (2) using the final flux of the biomass ultra-filtration (at the end of the operation of the HF-SAnMBR) and the corresponding trans-membrane pressure. (c) The HF membrane surface (or fibres) was then gently washed with tap water and cleaned with a sponge to remove the cake layer formed during filtration on the HF-SAnMBR. After that, the pure water flux was measured again to find the resistance of the membrane equating to ($R_m + R_{p)}$. From steps (a) to (c), R_t, R_m, R_f, R_p and R_c were calculated. R_t & R_m were directly calculated using equation (2) above; then from step (c)

and equation (2), R_f, R_c & R_p were calculated. This method of evaluating R_t, R_m, R_p and R_c was used by (Jeison et al., 2009; Lin et al., 2009; Chang and Kim (2005)).

The organic fouling resistance, inorganic fouling resistance and permanent (irremovable fouling) resistance were determined using the following equation:

$$R_p = R_{organic} + R_{inorganic} + P_{permanent} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

Where, $R_{organic}$ represents the organic fouling resistance (1/m), $R_{inorganic}$ represents the inorganic fouling resistance (1/m) and $P_{permanent}$ represents the permanent fouling resistance (1/m).

After step (c) above, the chemical cleaning of the HF membrane was performed by submerging the HF module in 200 ppm sodium hypochlorite (NaClO) solution at pH 10 for two hours to remove the organic foulants (Andreottola and Guglielmi (2003)). (d) The resistance (R_m + ($R_{inorganic}$ + $P_{permanent}$)) was estimated by carrying out a clean water flux test. Subsequently $R_{organic}$ and ($R_{inorganic}$ + $P_{permanent}$) were calculated. Lastly, after step (d), the HF membrane module was chemically cleaned by submerging it in a 2000 ppm citric acid solution at pH 2.5 for two hours to remove the inorganic foulants (Wang et al., 2014; Liao et al., 2006). Then (e) clean water flux test was done to measure the resistance (R_m + $P_{permanent}$) so $R_{inorganic}$ & $P_{permanent}$ could be obtained from these steps and equation (3) above.

4.3 Results and discussions

4.3.1 Biological performance (COD removal, Biogas, OLR)

Figure 4-2 shows variations of influent, effluent and supernatant COD with the operational time in phases 1-3. An excellent COD removal efficiency was achieved throughout the operational time. The COD Removal efficiency was 99.63% ± 0.10%, 99.71% ± 0.35% and 99.85% ± 0.12% for phases 1-3, respectively, with effluent COD concentrations of 76 ± 19, 57 ± 19, 42 ± 17 mg/L for phases 1-3, correspondingly. A decreasing trend was observed in the effluent COD concentration in phase 1-3 from 76 ± 19 to 42 ± 17 mg/L. The high COD removal efficiency is consistent with that of previous studies (Xie et al., 2010) and was probably due to the fact that both methanol and acetic acids are easily biodegradable compounds. At the beginning of each phase, the feed COD was increased to increase OLR, a corresponding slight increase (~100 mg/L) in the effluent COD concentration was observed, but the system was able to recover and adapt to the new conditions within a short period of time (approximately one week). A high supernatant COD (4,936 mg/L) at the start-up period of phase 1 was observed and then it decreased to a low level (874 mg/L) after 10 weeks. At the end of phase 3 the feed COD was gradually increased again but the system was not able to recover, the removal efficacy dropped rapidly marking the end of the operational time and the system was shut down.
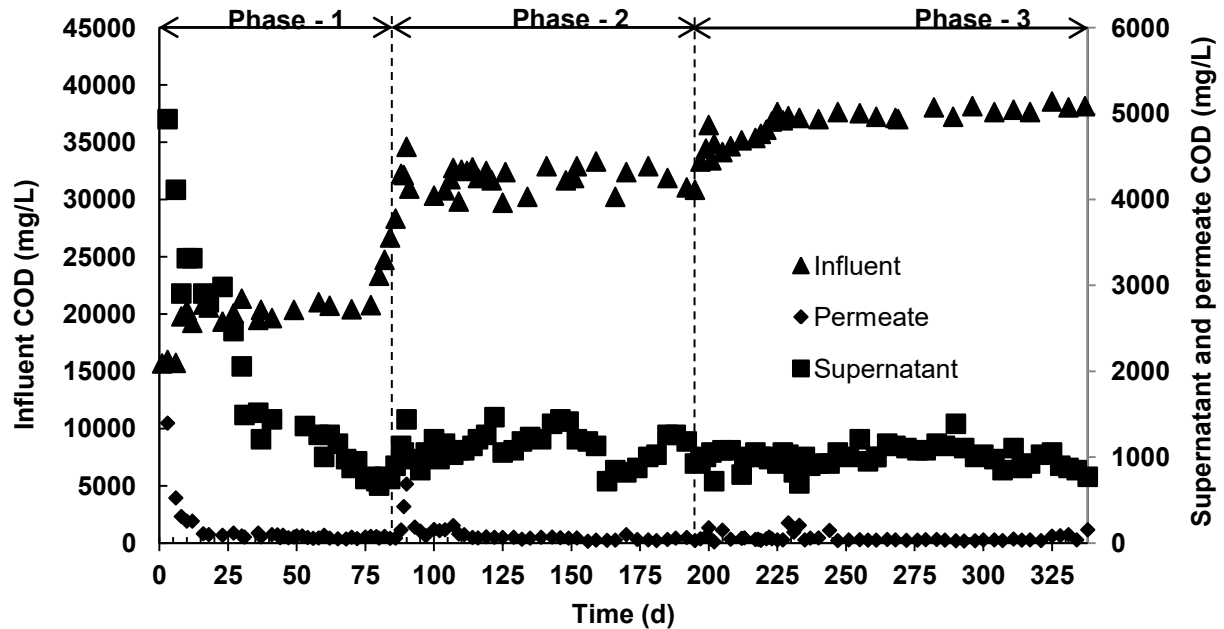
Figure 4-2: Variation of Influent, effluent and supernatant COD with operational time - (Phase 1-3).

Figure 4-3 illustrates the variation of OLRs with operational time. In phase 1(days 1-78), the OLR was increased by gradually increasing the feed concentration. The initial feed COD was 15,681 mg/L then gradually increased to 20,341 ± 593 mg/L by day 10 and kept constant throughout phase 1. The starting OLR was 12.28 Kg COD/m^3.d and exceeded 20 Kg COD/m^3.d at the end of phase 1 due to increased feed concentration and improved flux. In phase 2 (days 79-193), the SAnMBR was operated for more than 100 days at an OLR of 32.86 ± 1.5 Kg COD/m^3.d at feed COD of 31,928 ± 1021 mg/L and removal efficiency exceeding 99%. The overall system performance was excellent and stable throughout the phase except the transient decrease due to the feed shock at the beginning of each phase. In Phase 3 which represents days 194-338, the feed was

increased several gradual steps then was dropped one step due to the sudden flux improvement causing the OLR to reach 45.6 Kg COD/m^3.d at permeate COD of 177 mg/L and feed COD of 36,504 mg/L at days 199. To avoid system disturbance, the influent COD was immediately decreased to 33,419 mg/L and the system was able to recover within few days and the OLR increase was resumed. By day 227 the feed was increased again to 37561 ± 442 mg/L and remained constant till day 336. During this period of the more than 100 days, the SAnMBR maintained an OLR of 39.85 ± 1.14 Kg COD/m^3.d at removal efficiency of more than 99.7%. At end of phase 3, on day 336, the feed COD was increased again to increase OLR; however, the system was not able to tolerate further increase, system failure was observed and the reactor was shut down on day 338. The maximum safe OLR was 41.65 Kg COD/m^3.d at influent COD of 38150 mg/L, effluent COD of 36 mg/L and removal efficiency of 99.91%.
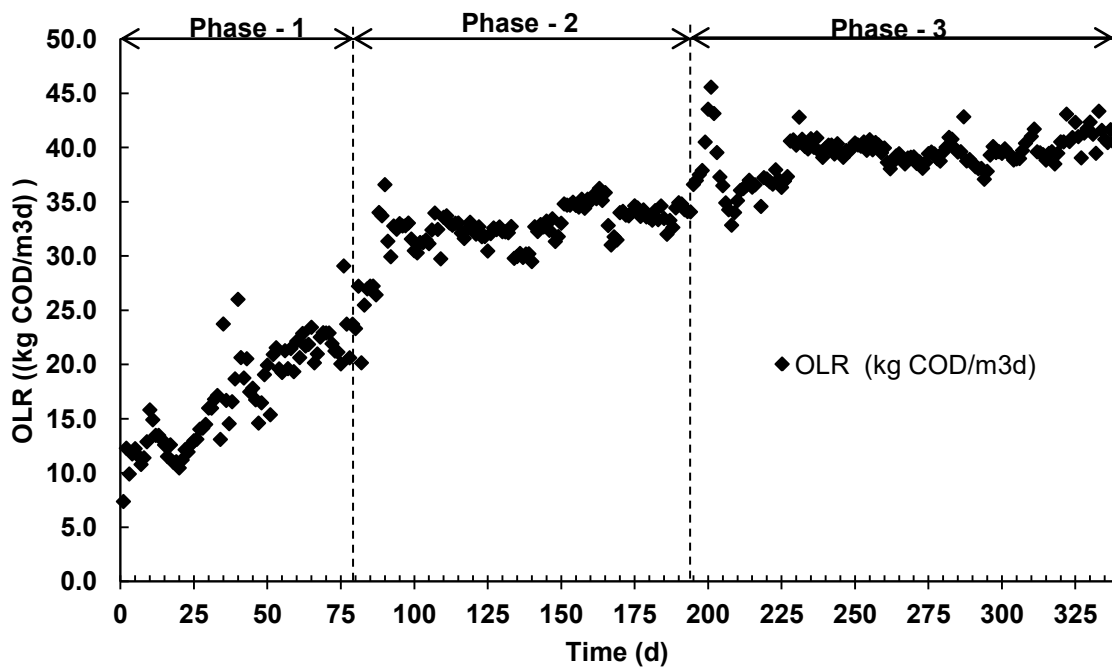

Figure 4-3: Variation of OLR with time (phase 1-3).

Methane (Biogas) production rates of the HF-SAnMBR under the various OLRs are shown in figure 4-4. The wide spread of data in phases 1 and 2(from 0.21-0.70) L CH_4 /g COD removed can be attributed to biogas collection method and feeding pattern (semi-continuous) used. Due to the experimental set up restrains, only 2 litres of biogas could be collected at a time. If the biogas collection time was coincidently with the feeding time, some of the biogas in the bioreactor would be pushed out of the bioreactor to the biogas collector and thus a higher biogas production rate was observed. On the other hand, if biogas collection started right after feeding, some biogas will be accumulated in the bioreactor due to the decrease in liquid level of the bioreactor and thus a lower biogas production rate would be observed. Therefore, the biogas production throughout the day varied significantly in phases 1 and 2 as the feed was not pumped in continuously (controlled by a sensor). In phase 3, a large volume of biogas would be produced in a short period of time, due to the higher OLRs. Therefore, the impact of feeding pattern was minimized and a more stable biogas production rate was observed. However, the average biogas production rates are similar in each phase. The overall biogas yield was 0.44 ± 0.12, 0.39 ± 0.13 and 0.39 ± 0.07 L CH_4 /g COD removed for phase 1 to 3 respectively. The biogas yield results of this study are similar to the theoretical value (0.397 L CH_4 / g COD removed at 37 ˚C (Hu and Stuckey 2006)) and indicate that the high rate SAnMBRs can indeed readily convert the waste to methane with an excellent biogas yield. Phase 2 & 3 were the most stable periods and yielded typical production rates, showing no correlation to the OLR increase.
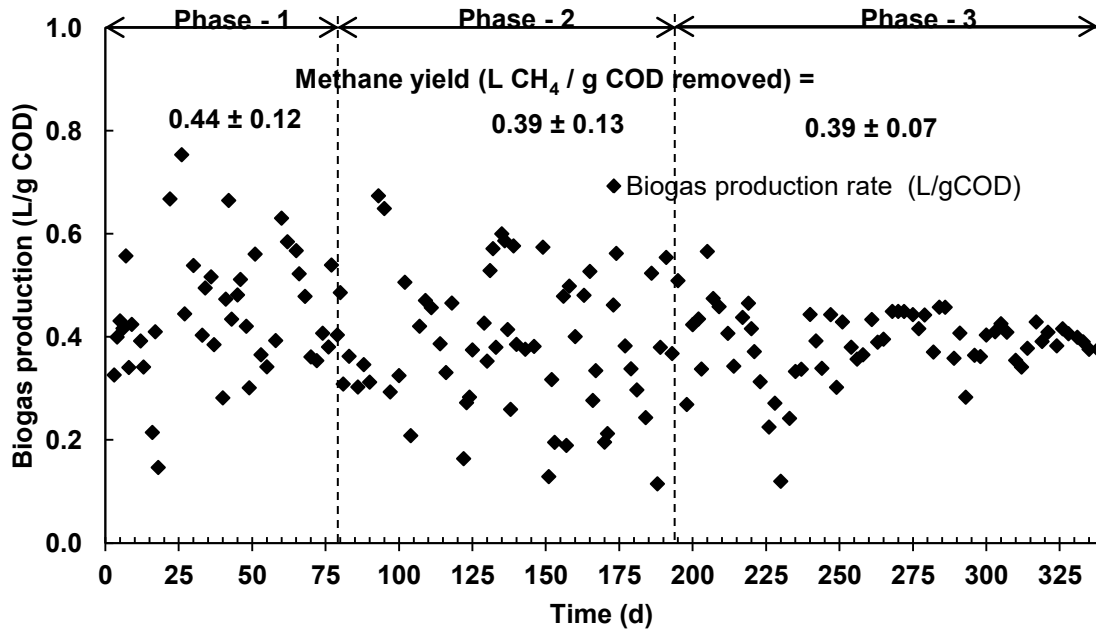
Figure 4-4: Variation of biogas production (phase 1-3).

The biogas composition (CH_4, CO_2 and N_2) of the HF-SAnMBR is illustrated in Figure 4-5. The percentage of methane content was 74.28 ± 0.63, 70.04 ± 2.45 and 66.89 ± 1.52 for phase 1-3 respectively. The CO_2 composition varied between 23.54 ± 0.34 and 31.41 ± 1.51 while the N_2 composition ranged from 1.69 ± 0.67 to 2.24 ± 1.55. The biogas yield and composition results of this study are in agreement with the results of previous studies (Rico et al., 2015; Diamantis et al., 2014; Rittmann and McCarty (2012); Huang et al., 2011; Xie et al., 2009). It is interesting to note that the methane content in the biogas decreased continuously with the increase of OLR from phase 1 to 3. A similar trend was observed in previous studies (Rico et al., 2015; Babaee and Shayegan (2011); Spagni et al., 2010; Lindorfer et al., 2008; Najafpour et al., 2006;

Fakhru'l-Razi and Noor (1999)). According to Rico et al. (2015), this phenomenon can be attributed to the increased carbon dioxide production per unit volume of the liquid phase as the OLR increases, saturating the liquid phase with CO_2. As a consequence, most of the produced CO_2 is released in the gas phase which in turn decreases the methane percentage in the biogas. Higher OLRs are perfect for the growth of acidogenic bacteria which produce more CO_2 and reduce the CH_4 content (Fakhru'l-Razi and Noor (1999)).
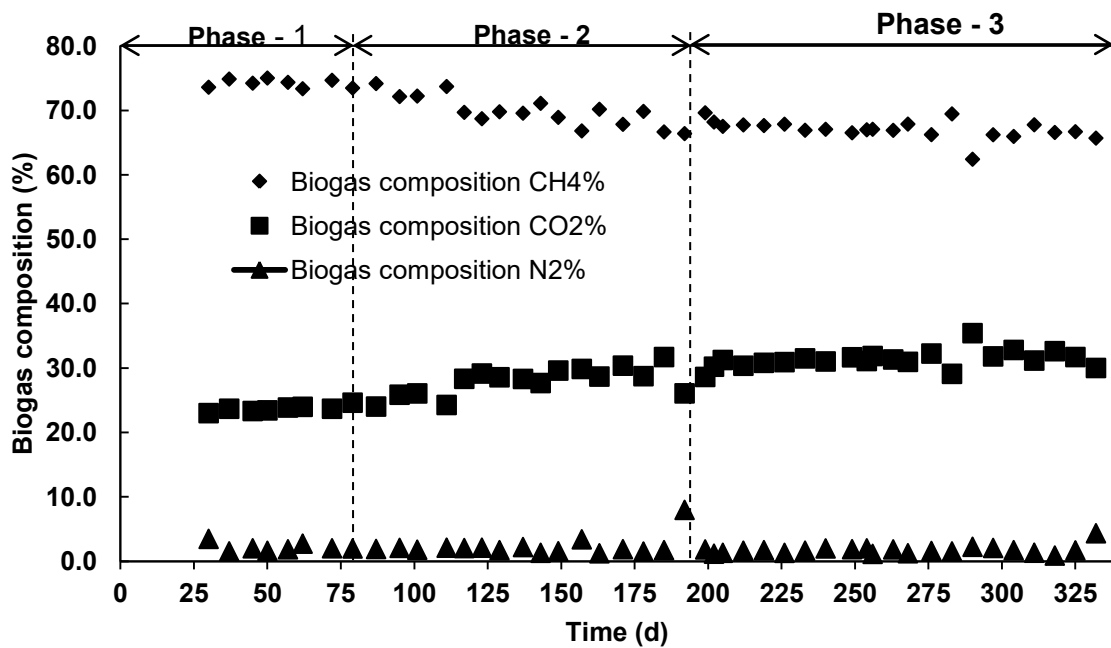
Figure 4-5: Variation of biogas composition in phase 1-3

4.3.2 Membrane performance

4.3.2.1 Flux and TMP

Figures 4-6 & 4-7 represent instant membrane flux and TMP profiles respectively. The variation in trans-membrane pressure (TMP) is an important parameter used to evaluate the membrane performance in SAnMBR as TMP is directly related to the rate of membrane fouling when operated at constant permeate flow rate (Lin et al., 2009). There was a significant fluctuation in TMP & Flux in phase 1. The lower instant membrane flux was caused by higher membrane fouling rates (e. g. high TMP jumps (Figure 4-7)) during the transition of seed anaerobic sludge adapted to the new substrates (methanol and acetic acid), which caused sludge deflocculation and pin-point floc formation and thus a larger amount of fine colloidal flocs (Figure 4-12) and a higher level of supernatant COD (Figure 1-2). The level of supernatant COD and the amount of fine colloidal flocs decreased with time, due to wasting of mixed liquor in the filtration zone and thus the TMP decreased (after day 36), as it is well-known that the amount of fine colloidal flocs and supernatant COD are positively correlated to membrane fouling rate (Lin et al., 2011; Lin et al., 2010). The instant membrane flux was improved with time in phase 1, due to reduced membrane fouling and TMP. The improvement in TMP and membrane fouling was related to the decrease in supernatant COD level (Figure 1-2) and decrease in the amount of fine colloidal particles (<1 um) (Figure 4-12). Under stable operation in Phases 1-3, a stable instant membrane flux was maintained. In phase 2, the average flux was 9.52 ± 0.38 LMH and the corresponding TMP was 5.51 ± 0.54 kPa while in phase 3 the flux was slightly higher at 9.84 ± 0.47 LMH slightly higher TMP of 5.99 ± 0.48 kPa. The results suggest that

excellent membrane performance was achieved for a long-term operation (over 10 months) under tested conditions.

It is worth noting that the HF-SAnMBR was operated without any membrane cleaning and the only fouling control techniques used were the biogas sparging (6.0 m^3/m^2.h) and intermittent permeation (3 minutes on and 2 minutes off). These results may suggest that the biogas sparging combined with relaxation is very efficient in controlling membrane fouling of the high rate-SAnMBR for long term operation as demonstrated in this study.
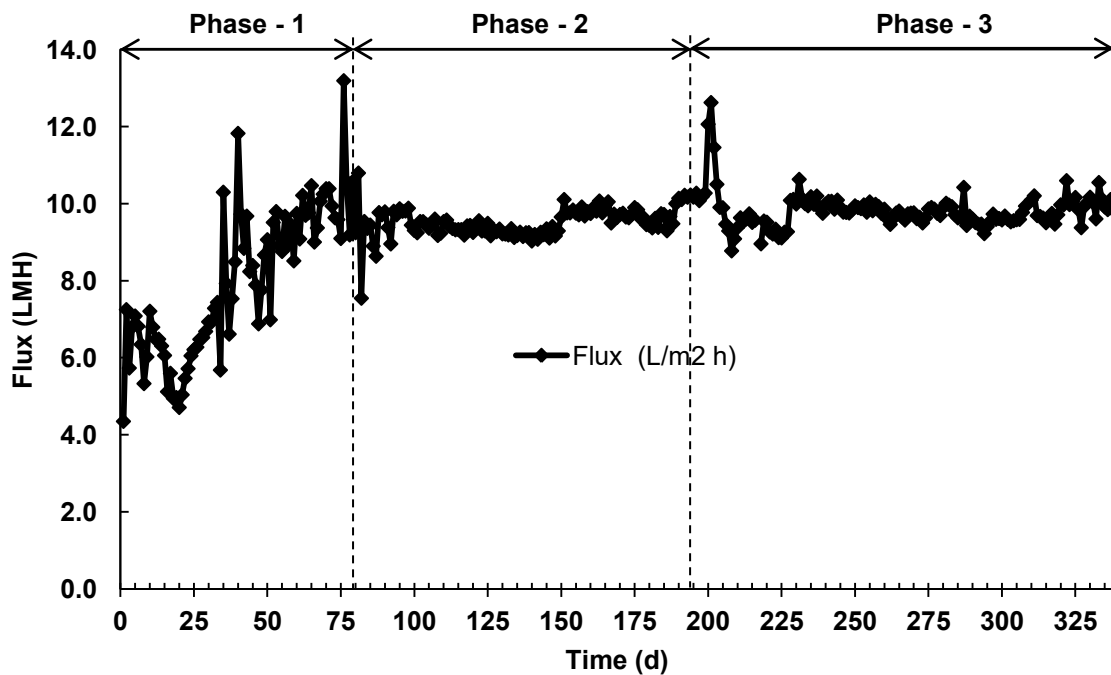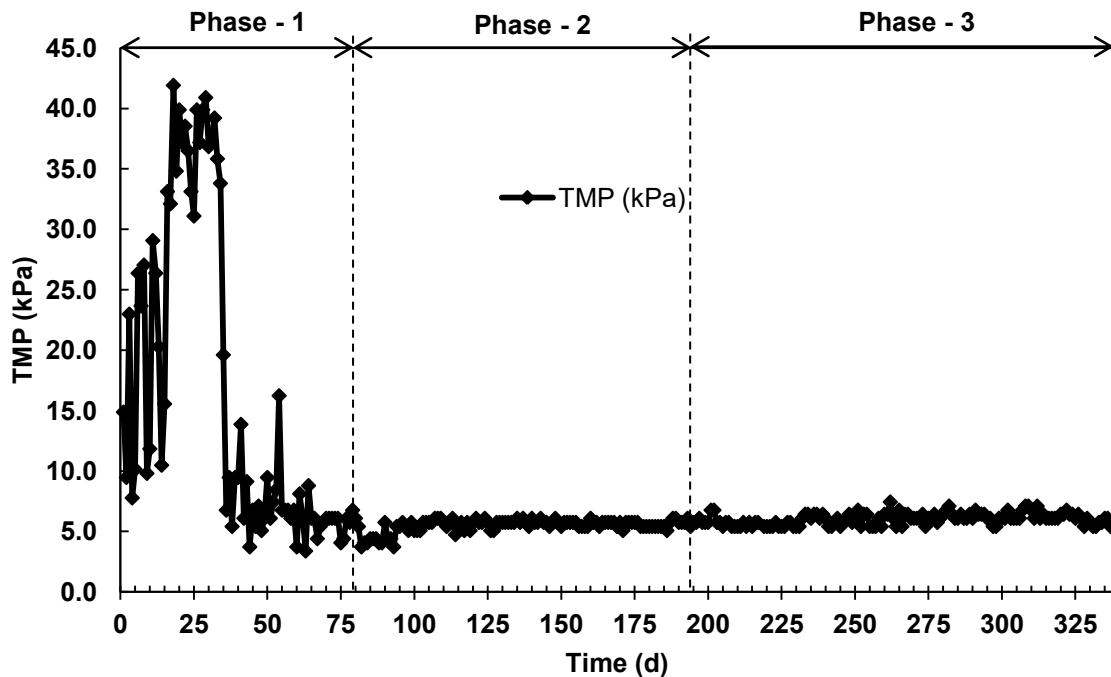

Figure 4-6: Flux profile

Figure 4-7: TMP profile

4.3.2.2 Membrane fouling characterization

At the end of this study (shortly after the system failed at an OLR of 48 kg COD/m^3.d after phase-3) membrane fouling characterization was conducted. Figure 4-8 shows membrane resistances at various conditions while Figure 4-9 shows the various types of membrane resistance. R_c accounted for 96.68% of the total resistance indicating that the cake layer resistance is the dominant fouling mechanism influencing the membrane fouling. Similar results were obtained by (Lin et al., 2011; Lin et al., 2009; Chang and Kim., 2005; Damayanti et al., 2011). R_m represented 1.33% while R_p represented 1.99% of the total resistance (R_t). R_p was composed of $R_{organic}$ = 0.21%, $R_{inorganic}$ = 0.80% and R_{perm} = 0.99%. Unfortunately, it is not possible to predict when the

inorganic fouling and permanent pore plugging occurred. The ratio of Rc/ (Rc+Rp) was 97.98% and clearly demonstrates that the cake layer is the main factor affecting the membrane fouling. Rp was insignificant, and among its subcategories Rperm was slightly dominant than Rinorganic (50% and 40% of Rp respectively). It is worthy of noting that the Rperm value was obtained for a HF membrane module used for approximately three years in SAnMBR. The results suggest that permanent membrane fouling is not important in the SAnMBR. The results also suggest that inorganic fouling is more important than organic fouling, after cake layer formation. Therefore, strategies for cake layer formation should be developed to control membrane fouling. For chemical cleaning, more attention should be paid to inorganic foulants removal.
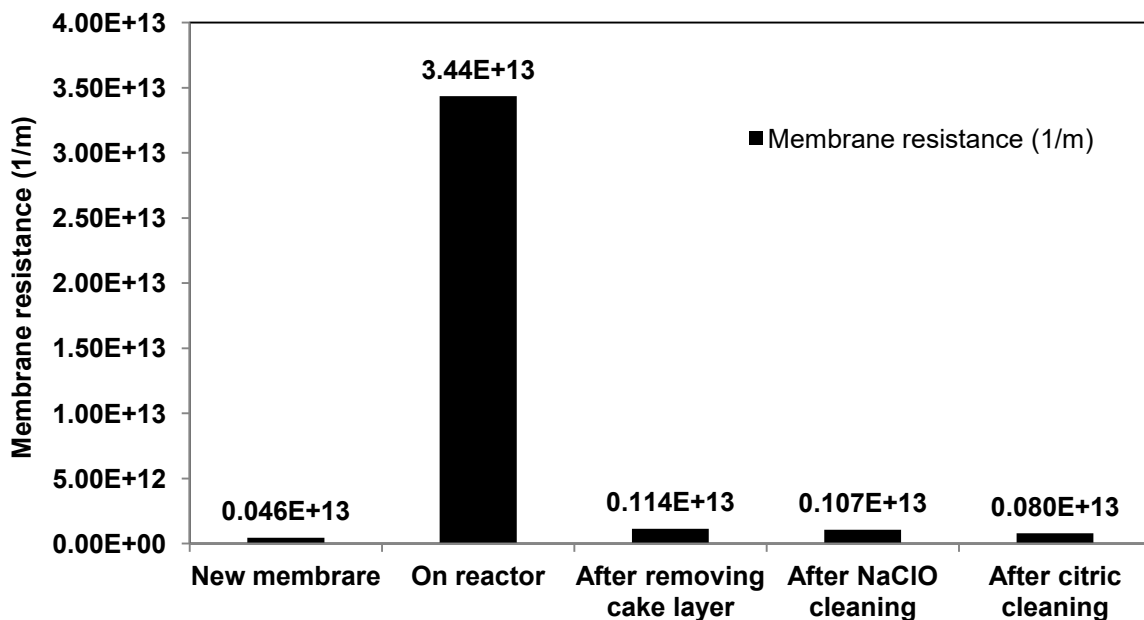
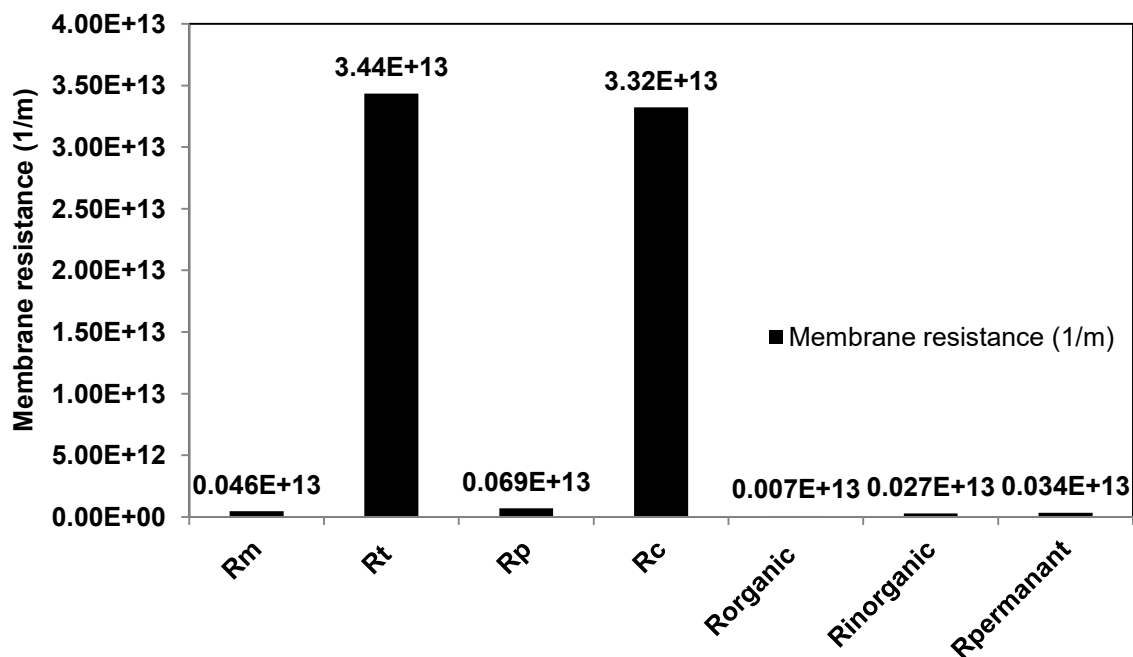**Figure 4-8: Membrane resistance at various conditions**

Figure 4-9: Various types of membrane resistance

4.3.3 Sludge properties role in membrane fouling

The MLTS concentration of the top filtration zone in each phase is tabulated in Table 4-1. MLTS concentration was initially about 22 g/L and then gradually decreased to about 15 g/L to minimize fouling at the early stage of operation. Although MLTS concentration increased with the increased OLR, it did not influence the membrane fouling rate in phase 2 & 3, as shown in Figure 1-7.

**Table 4-2: MLTS concentration of the top filtration zone in each phase**

Phase	Phase – 1 (Day 1-78)	Phase – 2 (Day 79-193)	Phase – 3 (Day 194-338)
MLTS (g/L)	17.29 ± 2.82	17.73 ± 2.28	19.95 ± 1.7

It is interesting to note that the formation of sludge granular at the bottom zone of the reactor was successful, thus, validating our intent of simulating UASB reactor. Figure 4-10 shows a sample (taken on day 327 in phase 3) of sludge granular measured using a ruler, the length was approximately 3-5 mm and granular biomass concentration was 71 g/L. Kleerebezem and Macarie (2003) documented that the granular sludge has a diameter of 0.5-3.0 mm and biomass concentration of approximately 100 g/L.

Supernatant COD (figure 4-4) was initially very high (4,936 mg /L) and gradually decreased to about 800 mg/L at the end of phase 1. The original seed sludge might have contained a substantial amount of insoluble material such as fine solids, and cell debris or biodegradable fine particles which may have caused the high supernatant COD and, thus, high TMP and low flux. These particles might be wasted or gradually digested by anaerobic sludge by the end of phase 1; resulting in the low supernatant COD of about 800 mg/L. Membrane fouling was clearly demonstrated by the high TMP in phas-1 due to the high supernatant COD. A significant fluctuation in TMP/flux was noted in phase 1, ranging from 28.12 ± 11 kPa during days 1-34 to 6.82 ± 2.43 kPa during days 35-78 and this was matched by supernatant COD concentrations of 4936 - 1500 mg/L and 1500 – 771 mg/L respectively. The TMP fluctuation can mostly be attributed to the faulty permeation pump which was replaced upon observation. However, a sudden significant improvement in TMP and flux was noted on day 35 which may be credited to the power shut-down for approx 8 hours, thus, causing starvation of bacteria and digestion of much of the remaining smaller particles within the reactor. Nevertheless, the supernatant COD was gradually dropping from day 1 to 78. It has

been reported that the supernatant COD contributes to the flux reduction; actually, it is the most important parameter governing the flux at solid concentration below 20 g TSS/L. The drop in flux is partially reversible once the supernatant COD is degraded within the bioreactor (Martinez-Sosa et al, 2011). These phenomena were clearly observed throughout this study. Phase 2 & 3 supernatant COD were 1,083 ± 210 and 989 ± 128 mg/L receptively, demonstrating that supernatant COD continuously improved from phase 1 to 3. No membrane fouling was observed in phase 2 & 3, thus, constant flux and TMP was recorded. The supernatant COD was found to be constantly higher than the effluent COD (more than 15 times) in all phases. The higher reactor supernatant COD is due to the retention of organic matter by the membrane ultra-filtration and the cake layer. Some of the COD may have been degraded by a bio-film when passing through the membrane. Similar observations were noted by (Martinez-Sosa et al, 2011; Gao et al., 2010; Mahendran et al., 2010; Hu and Stuckey (2006)). Based on our observations, supernatant COD is directly related to membrane fouling; a typical pattern of increasing and decreasing TMP along with the supernatant COD was observed. This can be clearly seen in the TMP and supernatant COD profiles in phase 1-3.
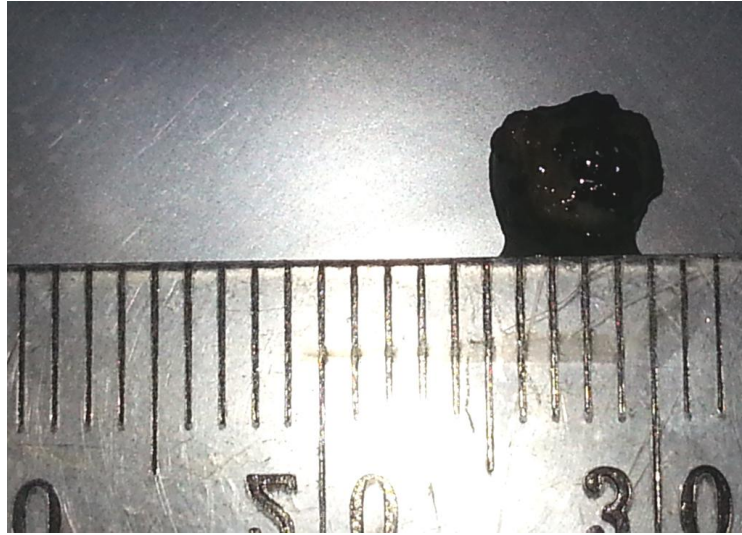
Figure 4-10: A sample of granular sludge size taken from the bottom zone of the HF-SAnMBR

A reprehensive particle size distribution (PSD) of the top zone mixed liquor for phase 1-3 is shown in figure 4-11. Phase 1 had the highest concentration of smaller particles (less than 10 µm) while phase 2 showed the lowest concentration of smaller particles. Smaller particles concentration in phase 3 was slightly higher than phase 2 and this may be attributed to the slightly higher MLTS concentration in phase 3. Particle size distribution of the supernatant COD for Phase 1-3 are illustrated in figure 4-12. In phase 1, the concentration of smaller particles (less than 10 µm) was significantly high while phase 2 & 3 were low and comparable with phase 3 being slightly higher than phase 2. The results of the PSDs for mixed liquor and supernatant CODs are consistent. However, comparison of supernatant CODs with PSDs in each phase provides much better picture of the membrane fouling and performance behaviour throughout the study. Interestingly, the high peak for smaller particles concentration

seen on phase -1 graph (figure 4-12) for supernatant PSDs decreased (became smaller) with time from the beginning of phase-1. This is consistent with the supernatant COD behaviour discussed above. Particle size of the anaerobic mixed liquor is directly affiliated with the fouling behaviour, since smaller particles have more tendencies to deposit on the membrane surface. In fact, a steady increase in the critical flux was observed with the increase in particle size (Martinez-Sosa et al, 2011).
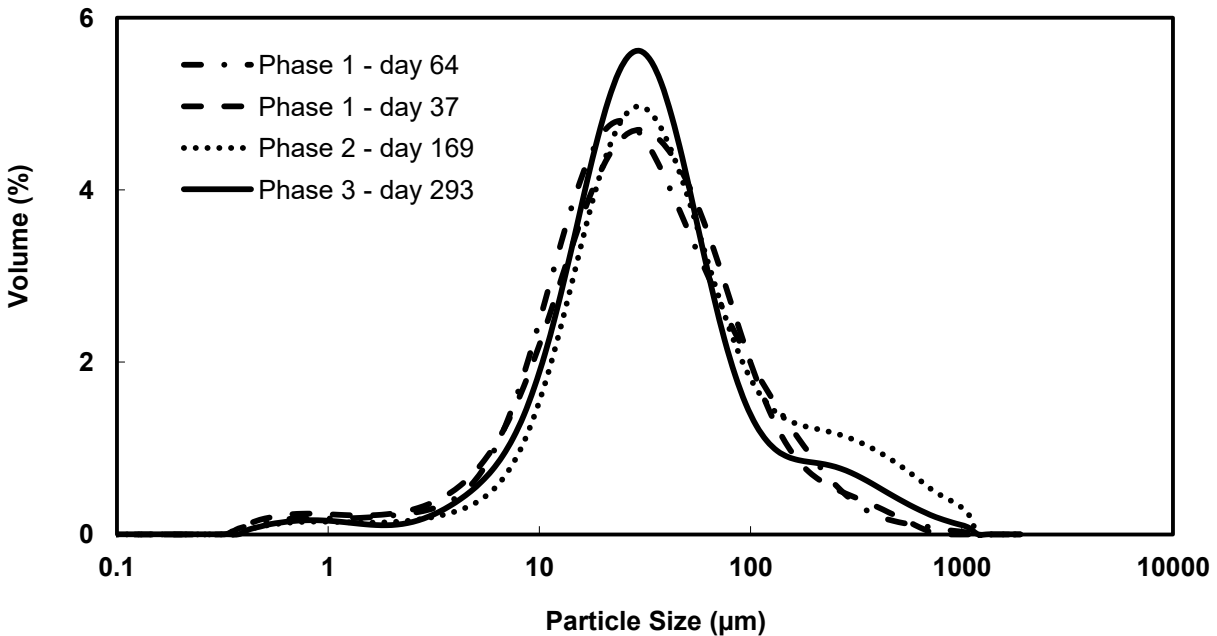
Figure 4-11: Particle size distribution of the mixed liquor (Phase 1-3)
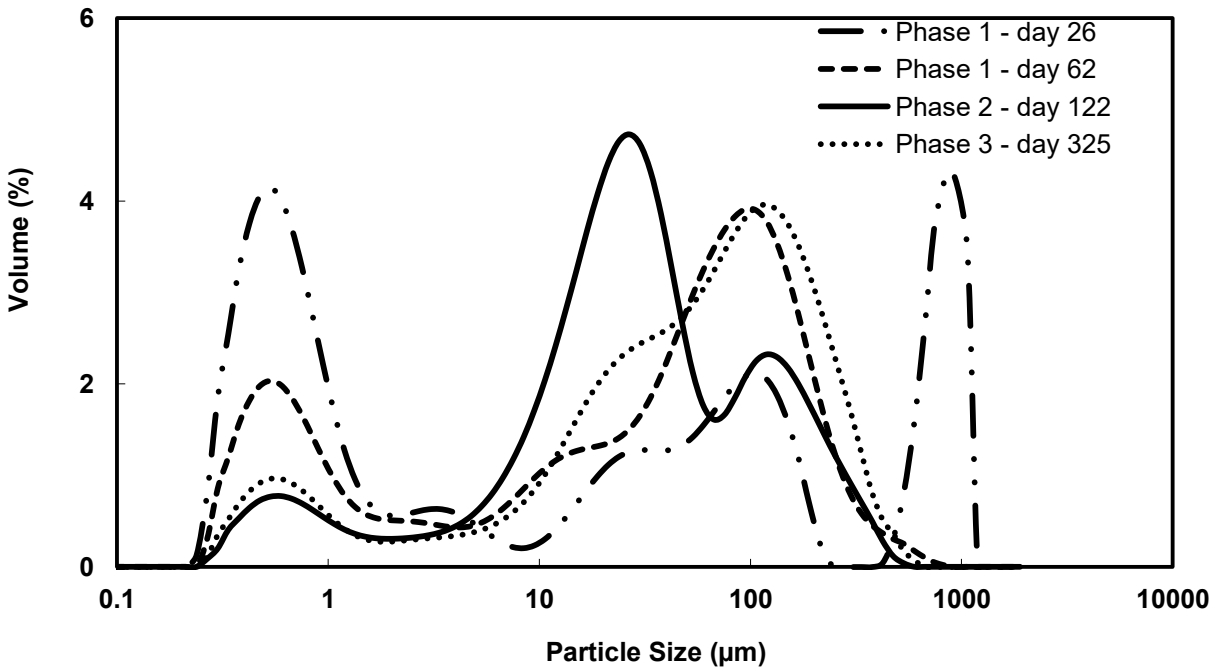
Figure 4-12: Particle size distribution of the supernatant COD (Phase 1-3)

4.4 Conclusions

- An high-rate HF SAnMBR up to an OLR of 41 kg/m^3.d was successfully operated for nearly one year with excellent COD removal efficiency of more than 99.7% (with low effluent COD concentration of 42 ± 17 mg/L) and excellent biogas production (0.39 ± 0.07 L CH$_4$ /g COD removed) and methane composition (66.89% ± 1.52).

- Granular sludge was successfully maintained or developed in the bottom zone to simulate the performance of a UASB-AnMBR.

- An excellent membrane performance was observed under stable operation. Biogas sparging and membrane relaxation were sufficient to maintain a low TMP (5-6 kPa) and no chemical cleaning was needed for nearly one year.

- .Under steady-state operation, no cake layer formation was observed and inorganic fouling was the dominant mechanism of membrane fouling.

4.5 Acknowledgements

4.6 References

Ahn, Y. H., Min, K. S., & Speece, R. E. (2001). Full scale UASB reactor performance in the brewery industry. Environmental technology, 22(4), 463-476.

An, Y., Yang, F., Bucciali, B., & Wong, F. (2009). Municipal wastewater treatment using a UASB coupled with cross-flow membrane filtration. Journal of Environmental Engineering, 135(2), 86-91.

Andreottola, G., & Guglielmi, G. (2003). Critical flux determination in two MBRs for municipal wastewater treatment. Proc of IMSTEC, 3, 10-14.

APHA, 2005. Standard methods for the examination of water and wastewater, 21th ed.American Public Health Association (APHA)/American Water Works Association (AWWA)/Water Environment Federation (WEF), Washington, DC.

Babaee, A., & Shayegan, J. (2011, May). Effects of Organic Loading Rates (OLR) on production of methane from anaerobic digestion of vegetable waste. In Proceedings of the World Renewable Energy Congress, Linköping, Sweden(pp. 8-13).

Badshah, M., Parawira, W., & Mattiasson, B. (2012). Anaerobic treatment of methanol condensate from pulp mill compared with anaerobic treatment of methanol using mesophilic UASB reactors. Bioresource technology, 125, 318-327.

BIOPAQ®UASB. (n.d.). Retrieved September 24, 2015, from http://en.paques.nl/products/featured/biopaq/biopaquasb

Bornare, J. B., Raman, V. K., Sapkal, V. S., Sapkal, R. S., Minde, G., & Sapkal, P. V. (2014). An Overview of Membrane Bioreactors for Anaerobic Treatment of Wastewaters.

Chang, I. S., & Kim, S. N. (2005). Wastewater treatment using membrane filtration—effect of biosolids concentration on cake resistance. Process Biochemistry, 40(3), 1307-1314.

Chong, S., Sen, T. K., Kayaalp, A., & Ang, H. M. (2012). The performance enhancements of upflow anaerobic sludge blanket (UASB) reactors for domestic sludge treatment–A State-of-the-art review. Water research, 46(11), 3434-3470.

Damayanti A, Ujang Z, Salim M R, Olsson G. The effect of mixed liquor suspended solids (MLSS) on biofouling in a hybrid membrane bioreactor for the treatment of high concentration organic wastewater. Water science and technology 2011;63(8):1701-6.

Dereli, R. K., Ersahin, M. E., Ozgun, H., Ozturk, I., Jeison, D., van der Zee, F., & van Lier, J. B. (2012). Potentials of anaerobic membrane bioreactors to overcome treatment limitations induced by industrial wastewaters. Bioresource technology, 122, 160-170.

Diamantis, V. I., Kapagiannidis, A. G., Ntougias, S., Tataki, V., Melidis, P., & Aivasidis, A. (2014). Two-stage CSTR–UASB digestion enables superior and alkali addition-free cheese whey treatment. Biochemical Engineering Journal,84, 45-52.

Estrada-Arriaga, E. B., Mijaylova Nacheva, P., & García-Sánchez, L. (2015). Effect of Mixed Liquor Volatile Suspended Solids on Membrane Fouling During Short and long-term Operation of Membrane Bioreactor. Ingeniería y Ciencia,11(21), 137-155.

Fakhru'l-Razi, A., Noor, M.J.M.M. (1999). Treatment of palm oil mill effluent (POME) with the membrane anaerobic system (MAS). Water Sci. Technol., 39(10-11), 159-163.

Fox, R. A., & Stuckey, D. C. (2015). The effect of sparging rate on transmembrane pressure and critical flux in an AnMBR. Journal of environmental management, 151, 280-285.

Gao, W. J., Mahmoud, I., Liao, B. Q., Cumin, J., Dagnew, M., & Hong, Y. (2014). A high-rate submerged anaerobic membrane bioreactor. Proceedings of the Water Environment Federation, 2014(13), 2048-2055.

Gao, W. J., Liao, B. Q., Dagnew, M., & Cumin, J. (2013). Comparison of performance between flat-sheet and hollow-fibre submerged anaerobic membrane bioreactors for the treatment of synthetic petrochemical wastewater.Proceedings of the Water Environment Federation, 2013(10), 5242-5246.

Gao, W. J., Lin, H. J., Leung, K. T., & Liao, B. Q. (2010). Influence of elevated pH shocks on the performance of a submerged anaerobic membrane bioreactor. Process Biochemistry, 45(8), 1279-1287.

Gomec, C. Y. (2010). High-rate anaerobic treatment of domestic wastewater at ambient operating temperatures: A review on benefits and drawbacks. Journal of Environmental Science and Health Part A, 45(10), 1169-1184.

Hu, A. Y., & Stuckey, D. C. (2006). Treatment of dilute wastewaters using a novel submerged anaerobic membrane bioreactor. Journal of environmental engineering, 132(2), 190-198.

Huang, Z., Ong, S. L., & Ng, H. Y. (2011). Submerged anaerobic membrane bioreactor for low-strength wastewater treatment: effect of HRT and SRT on treatment performance and membrane fouling. Water research, 45(2), 705-713.

Jeison, D., Plugge, C. M., Pereira, A., & Van Lier, J. B. (2009). Effects of the acidogenic biomass on the performance of an anaerobic membrane bioreactor for wastewater treatment. Bioresource technology, 100(6), 1951-1956.

Khan, A. A., Gaur, R. Z., Mehrotra, I., Diamantis, V., Lew, B., & Kazmi, A. A. (2014). Performance assessment of different STPs based on UASB followed by aerobic post treatment systems. Journal of Environmental Health Science and Engineering, 12(1), 43.

Kleerebezem, R., & Macarie, H. (2003). Treating industrial wastewater: anaerobic digestion comes of age. Chemical engineering, 110(4), 56-64.

Liao, B.Q., Kraemer, J.T. and Bagley, D.M. (2006) Anaerobic membrane bioreactors: Applications and research directions. Critical Reviews in Environmental Science and Technology 36(6), 489-530.

Lin, H., Peng, W., Zhang, M., Chen, J., Hong, H., & Zhang, Y. (2013). A review on anaerobic membrane bioreactors: applications, membrane fouling and future perspectives. Desalination, 314, 169-188.

Lin, H., Gao, W., Meng, F., Liao, B. Q., Leung, K. T., Zhao, L., ... & Hong, H. (2012). Membrane bioreactors for industrial wastewater treatment: a critical review. Critical reviews in environmental science and technology, 42(7), 677-740.

Lin, H., Liao, B. Q., Chen, J., Gao, W., Wang, L., Wang, F., & Lu, X. (2011). New insights into membrane fouling in a submerged anaerobic membrane bioreactor based on characterization of cake sludge and bulk sludge.Bioresource technology, 102(3), 2373-2379.

Lin, H. J., Xie, K., Mahendran, B., Bagley, D. M., Leung, K. T., Liss, S. N., & Liao, B. Q. (2010). Factors affecting sludge cake formation in a submerged anaerobic membrane bioreactor. Journal of Membrane Science, 361(1), 126-134.

Lin, H. J., Xie, K., Mahendran, B., Bagley, D. M., Leung, K. T., Liss, S. N., & Liao, B. Q. (2009). Sludge properties and their effects on membrane fouling in submerged anaerobic membrane bioreactors (SAnMBRs). Water Research,43(15), 3827-3837.

Lin, Y., He, Y., Meng, Z., & Yang, S. (2008). Anaerobic treatment of wastewater containing methanol in upflow anaerobic sludge bed (UASB) reactor. Frontiers of Environmental Science & Engineering in China, 2(2), 241-246.

Lindorfer, H., Corcoba, A., Vasilieva, V., Braun, R., & Kirchmayr, R. (2008). Doubling the organic loading rate in the co-digestion of energy crops and manure–a full scale case study. Bioresource technology, 99(5), 1148-1156.

Mahendran, B., Lin, H., Liao, B., & Liss, S. N. (2010). Surface properties of biofouled membranes from a submerged anaerobic membrane bioreactor after cleaning. Journal of Environmental Engineering, 137(6), 504-513.

Martinez-Sosa, D., Helmreich, B., Netter, T., Paris, S., Bischof, F., & Horn, H. (2011). Anaerobic submerged membrane bioreactor (AnSMBR) for municipal wastewater treatment under mesophilic and psychrophilic temperature conditions. Bioresource technology, 102(22), 10377-10385.

Mockaitis, G., Ratusznei, S. M., Rodrigues, J. A., Zaiat, M., & Foresti, E. (2006). Anaerobic whey treatment by a stirred sequencing batch reactor (ASBR): effects of organic loading and supplemented alkalinity. Journal of Environmental Management, 79(2), 198-206.

Najafpour, G. D., Zinatizadeh, A. A. L., Mohamed, A. R., Isa, M. H., & Nasrollahzadeh, H. (2006). High-rate anaerobic digestion of palm oil mill effluent in an upflow anaerobic sludge-fixed film bioreactor. Process Biochemistry,41(2), 370-379.

Najafpour, G. D., Hashemiyeh, B. A., Asadi, M., & Ghasemi, M. B. (2008). Biological treatment of dairy wastewater in an upflow anaerobic sludge-fixed film bioreactor. Am. Eurasian J. Agric. Environ. Sci, 4, 251-257.

Ramakrishna, C., & Desai, J. D. (1997). High rate anaerobic digestion of a petrochemical wastewater using biomass support particles. World Journal of Microbiology and Biotechnology, 13(3), 329-334.

Rico, C., Muñoz, N., Fernández, J., & Rico, J. L. (2015). High-load anaerobic co-digestion of cheese whey and liquid fraction of dairy manure in a one-stage UASB process: Limits in co-substrates ratio and organic loading rate. Chemical Engineering Journal, 262, 794-802.

Rittmann, B. E., & McCarty, P. L. (2012). Environmental biotechnology: principles and applications. Tata McGraw-Hill Education.

Robles, A., Ruano, M. V., Ribes, J., & Ferrer, J. (2013). Advanced control system for optimal filtration in submerged anaerobic MBRs (SAnMBRs).Journal of Membrane Science, 430, 330-341.

Sharma S.; Ramakrishna C.; Desai J. and Bhatt N. (1994) Anaerobic biodegradation of a petrochemical waste-water using biomass support particles. Appl. Microbiol. Biotechnol.40 (5), 768-771.

Spagni, A., Casu, S., & Farina, R. (2010). Effect of the organic loading rate on biogas composition in continuous fermentative hydrogen production. Journal of Environmental Science and Health Part A, 45(12), 1475-1481

Trussell, R. S., Merlo, R. P., Hermanowicz, S. W., & Jenkins, D. (2007). Influence of mixed liquor properties and aeration intensity on membrane fouling in a

submerged membrane bioreactor at high mixed liquor suspended solids concentrations. Water research, 41(5), 947-958.

Veolia Water Technologies | Features and Benefits of the Biobed® Advanced system. (n.d.). Retrieved September 24, 2015, from http://technomaps.veoliawatertechnologies.com/biobed_advanced/Biobed-Advanced-en/features_benefits.htm

Visvanathan, C., & Abeynayaka, A. (2012). Developments and future potentials of anaerobic membrane bioreactors (AnMBRs). Membr Water Treat, 3, 31-23.

Vogelaar, J. C. T., Bouwhuis, E., Klapwijk, A., Spanjers, H.,van Lier, J. B., 2002. Mesophilic and thermophilic activated sludge post-treatment of paper mill process water. Water Research 36, 1869-1879.

Wang, Z., Ma, J., Tang, C. Y., Kimura, K., Wang, Q., & Han, X. (2014). Membrane cleaning in membrane bioreactors: a review. Journal of Membrane Science, 468, 276-307.

Watanabea, R., Qiaoa, W., Nortond, M., Wakaharae, S., & Lia, Y. Y. (2014). Recent Developments in Municipal Wastewater Treatment Using Anaerobic Membrane Bioreactor: A Review. Journal of Water Sustainability, 4(2), 101-122.

Welander, T., Morin, R.,Nylén, B., 1999. Biological removal of methanol from kraft mill condensate. In: TAPPI Proceedings International Environmental Conference.

Wilson, Dwain R. (2014, October 08). Sustainable Energy Authority of Ireland. Waste to Energy - Anaerobic digestion for large industry, ADI Systems Inc. Retrieved

September 24, 2015, from:
http://www.seai.ie/Your_Business/Large_Energy_Users/LIEN/LIEN_Events/Even
ts-2014/Waste-to-Energy-%E2%80%93-Anaerobic-digestion-for-large-
industry.pdf

Xie, K., Lin, H. J., Mahendran, B., Bagley, D. M., Leung, K. T., Liss, S. N., & Liao, B. Q.
(2010). Performance and fouling characteristics of a submerged anaerobic
membrane bioreactor for kraft evaporator condensate treatment. Environmental
technology, 31(5), 511-521.

Chapter 5 : Recommendations

5.1 Recommendations for Future Work

The following studies are recommended for the future research and application of SAnMBR in treatment of industrial wastewater.

- This study used synthetic wastewater composed of methanol and acetic acid to test the limits of AnMBR in terms of OLR, real wastewater containing methanol and acetic acid can be used to further strengthen our results.

- Biogas sparging and permeate relaxation proved to be very effective fouling control measures. Optimization of the relaxation is necessary in the future developments.

- A sudden flux improvement was observed each time the feed COD concentration was increased. Further studies are needed to confirm and utilize this observation.

- Biogas production for the entire day should be measured to determine accurate biogas yield.

- Hybrid AnMBR reactor simulating UASB and attached growth media along with the submerged membrane can be tested

- More studies should be conducted to investigate the concept of the critical sparging rate and critical MLSS concentrations as these could highly benefit the AnMBR technology.

- Membrane fouling is a complex phenomenon and needs further studies.