

Effects of Feed and Operating Conditions on the Performance and Membrane Fouling of a Submerged Anaerobic Membrane Bioreactor

By

MENGNI HAN

A thesis submitted to the faculty of graduate studies

Lakehead University

in partial fulfillment of the requirements for the degree of

Master of Science in Engineering

Environmental Engineering

Lakehead University

Copyright © Mengni Han 2012

Lakehead

UNIVERSITY

OFFICE OF GRADUATE STUDIES

NAME OF STUDENT: Mengni Han


DEGREE AWARDED: Master of Science in Engineering

ACADEMIC UNIT: Faculty of Engineering

TITLE OF THESIS: Effects of Feed and Operating Conditions on the
Performance and Membrane Fouling of a Submerged
Anaerobic Membrane Bioreactor

This thesis has been prepared
under my supervision
and the candidate has complied
with the Master's regulations.


Signature of Supervisor


Date

Abstract

Anaerobic membrane bioreactors (AnMBRs) have been recognized as an effective method for enhanced wastewater treatment and re-use. However, the loss of the membrane performances due to membrane fouling remains a major obstacle in the extensive application of membrane bioreactors. In this study, a hollow fiber submerged anaerobic membrane bioreactor (SAnMBR) was developed for biorefining effluent and industrial wastewater treatment, and membrane fouling was controlled during the operation period. Subsequently, the effects of wastewater characteristics and mixed liquor properties on membrane fouling in an SAnMBR and a thermophilic submerged aerobic membrane bioreactor (TSAMBR) were studied with four different types of industrial wastewaters.

In the first part of this thesis, a laboratory-scale hollow fiber SAnMBR was operated for over 5 months to assess its performance for biorefining effluent treatment and the effect of organic loading rate (OLR) on the membrane performance, sludge properties and membrane fouling of the SAnMBR. The results showed that the SAnMBR is not ideally feasible for the treatment of the synthetic biorefining effluent due to the relatively low chemical oxygen demand (COD) removal efficiency (40-70%), the reduction in biogas production rate and the intolerability of the high OLR. A higher OLR resulted in a higher EPS concentration and smaller sludge particles, thus leading to faster membrane fouling. The study showed that too high OLR should be avoided for the operation of SAnMBR.

In the second part of this thesis, a laboratory-scale hollow fiber SAnMBR was operated for 160 days to assess its performance for thermo-mechanical pulping wastewater treatment and membrane fouling behaviour under different influent COD concentrations and biogas sparging

rates. A COD removal efficiency of 83 ± 4 % was achieved under all testing conditions, although the residual COD in permeate increased slightly with an increase in influent COD. The biogas yield slightly decreased with a higher feed concentration. The extracellular polymeric substances (EPS) production increased with an increase in OLR. Membrane performance was affected by both the influent COD concentration and biogas sparging rate. The fouling layer samples were characterized by conventional optical microscopy (COM), scanning electron microscopy (SEM)-energy-dispersive X-ray analyzer (EDX), and Fourier transform infrared (FTIR) spectroscopy. The results suggest that it is feasible and attractive to treat thermo-mechanical pulping wastewater by a hollow fiber SAnMBR. Non-uniform cake layer formation was the dominant mechanism of membrane fouling. An increase in biogas sparging rate actively mitigated the accumulation and deposition of sludge on/in membrane module, thus favored the enhancement of membrane flux and an efficient long-term operation.

In the third part of this thesis, characterization of the four different types of wastewaters and mixed liquors indicates that differences in particle size distribution (PSD), colloidal particle content, protein to polysaccharides ratio (PN/PS), and soluble compounds molecular weight distribution were studied. The differences in wastewater and mixed liquor characteristics were correlated to the changes in membrane filtration behaviour in both systems. The amount of colloidal particles in feed and mixed liquor plays a dominant role and is more important than the quantity of total suspended solids in controlling membrane fouling. The ratio of proteins to polysaccharides is more important than the total quantity of soluble organic substances in controlling membrane fouling. The results suggest that a full characterization of the feed and mixed liquor may be used as a tool to predict the membrane performance of membrane bioreactors.

Acknowledgements

I would like to express my deepest acknowledge to my supervisor, Dr. Baoqiang Liao, and co-supervisor, Dr. Charles C. B. Xu, for their inspiring guidance, experienced advice and endless encouragement throughout this thesis. Their guidance was very valuable to help me get through any difficulty during my studies. Many thanks also to my supervisory committee members Dr. Siamak Elyasi and Dr. Kam Leung for their valuable advice and guidance.

I must acknowledge Lakehead University for providing me the opportunity to study here. Financial support arranged by Dr. B. Liao and Dr. C. Xu through Natural Sciences and Engineering Research Council of Canada (NSERC) and GE Water & Process Technologies is highly appreciated. Special thanks go out to Abitibi-Bowater Inc. (Thunder Bay, Ontario) and Tembec Industries Inc. (Temiscaming, Quebec) whose generous contributions allowed me to carry out this thesis.

In addition, heartfelt thanks are extended to the professors and the graduate students in the Department of Chemical Engineering and the Program of the Environmental Engineering, particularly Dr. Lionel Catalan, Dr. Wa Gao and Dr. Bruce Kajartanson for their great lectures and help during my graduate study at Lakehead University. Their knowledgeable expertise was of great assistance to my studies. Special acknowledgements must be given to the members of Dr. Liao's team: Dr. Weijue Gao, Xiao Qu, Ram Bogita and Dr. Yi He.

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

List of Nomenclature and Abbreviations

AFM	Atomic Force Microscopy
AnMBR	Anaerobic Membrane Bioreactor
BAP	Biomass Associated Products
BOD	Biochemical Oxygen Demand
BSA	Bovine Serum Albumin
CER	Cation Exchange Resin
CSLM	Confocal Scanning Laser Microscopy
CSTR	Completely Stirred Tank Reactor
COD	Chemical Oxygen Demand
ED	Electrodialysis
EDX	Energy-dispersive X-ray spectroscopy
EEM	Excitation-emission Matrix
EPS	Extracellular Polymeric Substances
F	Full scale
F/M	Food/Microorganisms
FTIR	Fourier Transform Infrared
HRT	Hydraulic Retention Time
ICP	Inductively Coupled Plasma
L	Laboratory/bench scale
LB-EPS	Loosely Bound- Extracellular Polymeric Substances
LPM	Liters Per Minute
MBRs	Membrane Boireactors
MF	Microfiltration
MLSS	Mixed Liquor Suspended Solids
MW	Molecular Weight
MWCO	Molecular Weight Cutoff
NF	Nanofiltration

NMR	Nuclear Magnetic Resonance
OLR	Organic Loading Rate
P	Pilot scale
PAC	Powered Activated Carbon
PE	Polyethylene
PN	Protein
PN/PS	Protein/ Polysaccharides
PS	Polysaccharides (Carbohydrates)
PSD	Particle Size Distribution
PSf	Polysulfone
PV	Pervaporation
PVC	Polyvinyl Chloride
PVDF	Polyvinylidene Fluoride
RO	Reverse Osmosis
R_t	Total Resistance
SAnMBR	Submerged Anaerobic Membrane Bioreactor
SEM	Scanning Electron Microscopy
SMP	Soluble Microbial Products
SRT	Solid Retention Time
SS	Suspended Solids
TB-EPS	Tightly Bound-Extracellular Polymeric Substances
TMP	Transmembrane Pressure/Thermo-mechanical Pulping Pressate
TSAMBR	Thermophilic Submerged Anaerobic Membrane Bioreactor
TSS	Total Suspended Solids
UAP	Utilization Associated Products
UASB	Upflow Anaerobic Sludge Blanket
UF	Ultrafiltration
UFAF	Upflow Anaerobic Filter
UV	Ultraviolet

VFAs

Volatile fatty acids

WWTP

Waste Water Treatment Plant

Table of Contents

Abstract.....	I
Acknowledgements.....	IV
List of Nomenclature and Abbreviations.....	V
Chapter 1.....	1
Introduction.....	1
1.1 Overview of the present study.....	1
1.2 Objectives.....	4
1.3 Outline of this thesis.....	4
Chapter 2.....	6
Literature Review.....	6
2.1 Anaerobic Membrane Bioreactor (AnMBR).....	6
2.2 Applications of AnMBR for industrial wastewater treatments.....	14
2.3 Membrane fouling.....	17
Chapter 3.....	31
Experimental Materials and Methods.....	31
3.1 SAnMBR Setup.....	31
3.2 Experimental Operations.....	33
Chapter 4.....	45
Results and Discussion.....	45
4.1 Performance and Membrane Fouling of SAnMBR for Biorefining Effluent Treatment....	45
4.2 Performance and Membrane Fouling of SAnMBR for TMP Wastewater Treatment.....	56
4.3 Wastewater and Mixed Liquor Characteristics and Their Role in Membrane Fouling.....	73
Chapter 5.....	89
Conclusions and Recommendations.....	89
5.1 Conclusions for the Performance and Membrane Fouling of SAnMBR for Biorefining Effluent Treatment.....	89
5.2 Conclusions for the Performance and Membrane Fouling of SAnMBR for TMP Wastewater Treatment.....	90
5.3 Conclusions for the Wastewater and Mixed Liquor Characteristics and Their Role in Membrane Fouling.....	90

5.4 Recommendations for Future Work.....	91
References.....	93
Appendix I Particle Size Distributions of Bulk Sludge under different Organic Loading Rates for Biorefining Effluent.....	107
Appendix II Particle Size Distributions of Bulk Sludge under different Organic Loading Rates for Thermo-mechanical Pulping Pressate.....	108

Chapter 1

Introduction

1.1 Overview of the present study

Membrane bioreactor (MBR) has received considerable attention in recent years. It has been well implemented in treating both municipal and industrial wastewaters (Visvanathan and Abeynayaka, 2012; Le-Clech, 2010). The MBR system has many advantages over the conventional activated sludge process in terms of its excellent effluent quality, high removal efficiency of chemical oxygen demand (COD), small footprint and integration of biological treatment and filtration (Jeison and van Lier, 2007; Akram and Stuke, 2008). In recent years, considerable attention has been paid to the use of membrane technologies in conjunction with anaerobic reactors, namely anaerobic membrane bioreactors (AnMBRs). With the incorporation of membrane technologies, complete biomass retention eliminates the impact of biomass separation problems and takes advantage of the biogas production in the anaerobic process for energy recovery. The methanogenic organisms and sulfate-reducing bacteria with slow growth rates in the anaerobic sludge can be retained to achieve a high biogas production and sulfate reduction rate (Vallero et al. 2005). However, the loss of the membrane performances due to membrane fouling remains a major obstacle in the extensive application of MBR. Membrane fouling results in a rapid reduction of permeation flux or an increase of trans-membrane pressure (TMP), energy consumption, frequent membrane cleaning and replacement, thus increasing the operation cost of the process. Because of the great

complexity and variability of the operational and the environmental conditions, current understanding of membrane fouling is still insufficient.

For the different configurations of AnMBRs, submerged anaerobic membrane bioreactor (SAnMBR) has gained great attention. As compared to side-stream AnMBR, SAnMBR can reduce energy costs and biomass stress associated with recirculation. In addition, such a configuration allows for the self-cleaning of the membrane surface by recirculating the biogas produced. Gas sparging is an important parameter in the design and operation of an MBR. For an aerobic MBR, air sparging achieves good mechanical mixing conditions and contributes to membrane fouling control and enhancement of filtration performance (Cui et al. 2003). Several strategies regarding air sparging, such as intermittent air sparging (McAdam et al. 2010), different aerator configurations (Park et al. 2010), bubble flow properties (Yamanoi et al. 2010) have been evaluated to enhance membrane performance and reduce energy cost. For AnMBRs, a reduction in biogas-sparging time caused an increase in TMP and a decrease in effluent quality (Vyrides et al. 2009). An increase in biogas sparging level also increased the critical flux (Jeison and van Lier, 2006). Higher flux without deteriorating wastewater treatment efficiency implies high productivity accompanied by low unit cost. Hence, pursuance of flux enhancement is always crucial for the broad application of SAnMBRs in the future. However, limited work has been done on the effect of biogas sparging rate on performance and membrane fouling behaviors for SAnMBRs.

Because of the variable nature of industrial wastewaters, seasonal variations in feed strength are often encountered for either short-term transient or a long-term operation. These variations can affect the performance of SAnMBRs by affecting the microbial

balance among the fast-growing acidogens and the slow-growing methanogens. A low feed concentration which may correlate to a low organic loading rate (OLR) will disfavor the reaction rate and cause serious membrane fouling, because a long-term starvation can lead to the loss of cell activity and even biomass decay releasing large amounts of biomass-associated products (BAPs). On the other hand, a high feed concentration may result in either metabolism inhibition or a great biological growth by providing more sufficient substrate to the biomass. Depending on the influent COD concentration (3800 - 15900 mg/L) and hydraulic retention time (HRT) applied, the COD removal efficiencies ranged from 64% to 85 % for the treatment of municipal landfill leachate using lab-scale anaerobic sequencing batch reactors (Timur et al. 1999). During practical operation, the reactor stability to feed strength is one of the most important considerations.

In the case of membrane fouling, it is directly or indirectly affected by a number of factors, such as wastewater characteristics, sludge properties, operating and environmental conditions as well as hydrodynamic conditions (Drews, 2010; Meng et al. 2009). Although extensive studies have been conducted on the effects of sludge properties (Choi et al. 2006; Satyawali and Balakrishnan, 2009) and operating and environmental conditions (Huang et al. 2011; Miyoshi et al. 2009) on membrane fouling, the factor of wastewater characteristics has not been well studied. There are only a few studies that addressed the effect of wastewater characteristics (Arabi and Nakhla, 2008; Park et al. 2006) on membrane fouling. Therefore, it is highly desirable to understand the importance of wastewater characteristics on membrane fouling in both submerged anaerobic membrane bioreactor (SAnMBR) and submerged aerobic membrane bioreactor (SAMBR) systems.

1.2 Objectives

The objectives of this thesis are: (1) to study the feasibility of using a hollow fiber SAnMBR for biorefining effluent and thermo-mechanical pulping pressate treatment; (2) to evaluate the effects of the organic loading rate (OLR) on the performance and membrane fouling behavior of the SAnMBR treating biorefining effluent; (3) to evaluate the effects of biogas sparging rate and influent COD concentration on the performance and membrane fouling behavior of the SAnMBR treating thermo-mechanical pulping wastewater, in terms of COD removal, biogas production, particle size distributions (PSDs), trans-membrane pressure (TMP) rise and fouling layer characterization.

On the other hand, to gain more insight into the optimization of MBRs design, another objective of this thesis is to provide a comprehensive characterization of four types of industrial wastewaters and the mixed liquors, to correlate the wastewater characteristics and mixed liquor properties to the observed differences in membrane fouling in both the SAnMBR and the SAMBR system (each system treating two types of wastewaters).

1.3 Outline of this thesis

The general introduction including the motivation and the objectives of this research is presented in Chapter 1. Chapter 2 provides a comprehensive literature review of previous studies on AnMBR, including its configuration, operation, application and membrane fouling issue. Chapter 3 presents the materials and methods used in this study. Chapter 4 discusses the performance and membrane fouling of the hollow fiber SAnMBR for biorefining effluent and thermo-mechanical pulping pressate treatment, respectively. The wastewater and mixed liquor characteristics and their role in membrane fouling were

discussed in this chapter as well. The general conclusions from this study and recommendations for future research are summarized in Chapter 5.

Chapter 2

Literature Review

2.1 Anaerobic Membrane Bioreactor (AnMBR)

The concept of anaerobic membrane bioreactor (AnMBR) was introduced in the 1970s (Grethlein, 1978). It can be simply defined as the integration of anaerobically biological treatment process and membrane filtration in the absence of oxygen. With the retaining of the solids within the reactor, the effluent contains no suspended BOD. Thus the effluent quality is improved.

2.1.1 Anaerobic treatment process

Anaerobic wastewater treatment includes a series of processes in which microorganisms break down biodegradable materials in an oxygen free environment. Anaerobic processes have been successfully used to treat pulp and paper, food processing, and agricultural wastewaters for more than a century (Liao et al. 2006). In anaerobic treatment process, the initial feedstock would be finally converted to biogas that is mainly composed of methane and carbon dioxide.

However, the anaerobic digestion process is occurred in 4 stages (Figure 2.1): hydrolysis, acidogenesis (fermentation), acetogenesis and methanogenesis (Buhr and Andrews, 1977). Hydrolysis is the chemical and biological reactions where complex organic matters (e.g. carbohydrates, proteins, fats) are broken down into soluble simple

organic molecules (e.g. sugars, amino acids, fatty acids). Acidogenesis is the biological reactions where simple monomers are converted into volatile fatty acids (VFAs) by acidogenic (fermentative) bacteria. Besides VFAs, other byproducts (alcohols, ammonia, carbon dioxide, and hydrogen sulfide) were made as well. Acetogenesis is the biological process where the VFAs produced through acidogenesis process are further converted to largely acetic acids, as well as carbon dioxide and hydrogen by the microorganism known as acetogenic bacteria. Methanogenesis is the biological reaction where the methanogens convert the intermediate products into biogas (methane, carbon dioxide) and water (Buhr and Andrews, 1977).

In AnMBR, the stability of anaerobic digestion process is very important. The anaerobic microorganisms can cause the reactor instability by any disturbances. For example, the acetogenesis and methanogenesis are less robust than the hydrolysis and acidogenesis. The optimal pH range for methanogens is 6.8-7.2 (Rajeshwari et al. 2000). A higher pH results in negative impacts on biogas production, chemical oxygen demand (COD) removal and the performance of the membrane filtration (Gao et al. 2010). Gao et al. 2010 studied the effect of elevated pH shock on an SAnMBR. The study showed that pH 9.1 and 10.0 shocks exerted significant long-lasting negative impacts on the performance of the AnMBR. It took 6 and 30 days for the SAnMBR to recover from pH 9.1 and 10.0 shock respectively (Gao et al. 2010). Adjustment of the operational conditions to provide a stable and proper environment for the biological metabolism is always necessary.

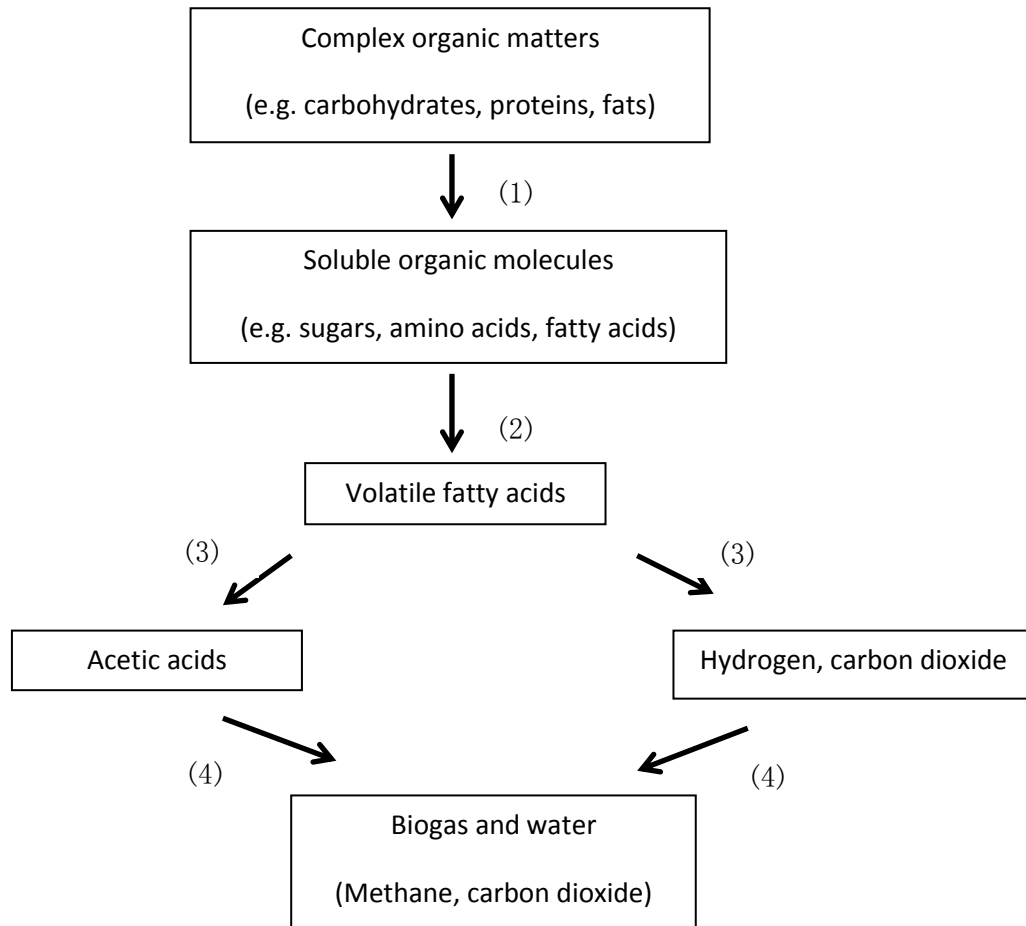


Figure 2.1 the four-stage anaerobic digestion process: (1) Hydrolysis; (2) Acidogenesis (Fermentation); (3) Acetogenesis; (4) Methanogenesis.

2.1.2 Membrane process

Membrane is defined as a barrier separating two fluids. The membrane filtration process is regarded as the essential part of a membrane bioreactor. It has been successfully incorporated into biological processes (Liao et al. 2006). The existence of membrane in membrane bioreactors is not only to retain all biomass in the reactor, but also to complement decreased biological removal efficiency by rejecting soluble organics (Ho and Sung, 2009). What's more, the membrane process will decouple the solid retention time (SRT) from the hydraulic retention time (HRT), eliminate the suspended solids in the permeate for completely biomass retention and allow higher biomass concentration and higher organic loading rates (OLRs).

Types of membrane processes can be classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), dialysis and pervaporation (PV) (Beerlange et al. 2001), whereas the first four types produce permeate. Table 2.1 shows the characteristics of different membrane processes.

Table 2.1 Characteristics of different membrane processes (Melamane, 2003)

Parameters	MF	UF	NF	RO
Operating Pressure (bar)	1-4	2-7	10-40	15-100
Pore size (µm)	0.1-1.5	0.01-0.05	0.001-0.01	< 0.0002
MWCO range (Dalton)	>300000	300000-100000	200000-20000	< 500
Size-cut-off-range (µm)	0.1-20	0.005-0.1	0.001-0.01	<0.001

There are two main types of membrane operations in anaerobic membrane bioreactor. It is commonly called an external cross-flow membrane operation and submerged membrane operation when the membrane is operated under pressure and vacuum, respectively (Liao et al. 2006) (Figure 2.2 (a) (b)). Lin et al. (2010) indicated that external cross-flow membrane operation usually employs high cross-flow velocity along the membrane surface to provide membrane driving force and control membrane fouling. For submerged membrane operation, the vacuum force across the membrane is achieved by creating negative pressure on the permeate side. The distinct advantages of submerged membrane operation are lower energy cost and less cleaning procedures (Judd, 2004). A new membrane operation, air-lift side-stream (Figure 2.2 (c)), has been developed in recent years (Shariati et al. 2010, Lin et al. 2011). The concept of air-lift side-stream membrane operation incorporated the side-stream operation and the low energy requirement of submerged operation. Heran et al. (2006) confirmed the interest of air-lift side-stream membrane operation by injecting the air at the bottom of the membrane module to induce an important suspension circulation and the local turbulence closed to the membrane surface in a side-stream membrane module.

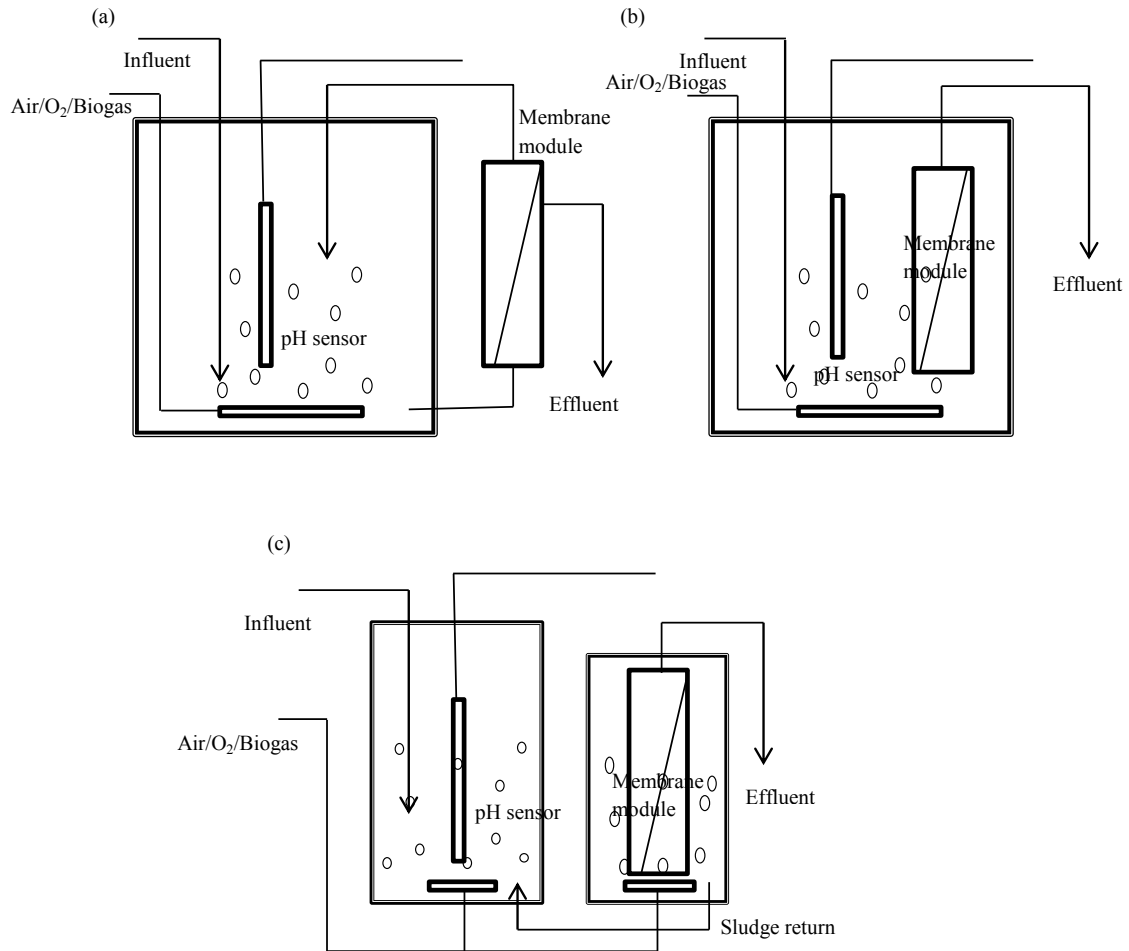


Figure 2.2 Membrane operation process: (a) external operation, (b) submerged operation, (c) air-lift side-stream operation.

Basically, two types of membrane module, hollow fiber and flat sheet, are used in membrane bioreactors. Most MBRs use hollow fiber membranes due to its low cost and high packing density. Flat sheet membranes are believed to be more expensive than hollow fiber membranes. Both membrane modules can be operated in pilot plant for several months without external cleaning. For example, the hollow fiber membrane module was operated for 4 months for a domestic wastewater treatment aerobically without external cleaning with a flux of 20-45 LMH in a waste water treatment plant

(WWTP) (Bodik et al. 2009). The operation of flat sheet membrane was conducted for the same domestic wastewater without external cleaning for 6 months with flux of 20-60 LMH (Bodik et al. 2009). For fouling modes, the hollow fiber membrane exhibited fouling with a cake layer. However, under the similar conditions, the flat sheet membrane suffered from fouling of pore blocking easily (Hai et al. 2005).

2.1.3 Operational parameters in AnMBR

The operational parameters that affect effluent flux in an external membrane system are transmembrane pressure (TMP) and cross-flow velocity. The operational parameters that affect effluent flux in a submerged membrane system are TMP, sparging intensity, and the duration of the relaxation period (Berube et al. 2006). Some parameters, including TMP, cross-flow velocity, operating temperature, are introduced in this section. Other operational parameters such as organic loading rate (OLR), SRT, HRT, especially their influences on membrane fouling, are discussed later section (section 2.3.2.2).

Compared to the TMP in the external membrane system, submerged membrane system has a relatively low TMP. The TMP has impacts on the flux in an AnMBR. Ahmad et al. (2005) reported that the increase in TMP led to an increase in both the initial and final flux values for different types of membranes (ceramic and PVDF). However, a higher TMP may result in an increase in the fouling layer thickness, coupled with a decrease in the fouling layer voidage (Thomassen et al. 2005). Thomassen et al. (2005) studied the effect of varying TMP and cross-flow velocity on the microfiltration fouling of a model beer. They indicated that under a constant cross-flow velocity an increase in TMP led to a reduction in transmission of components in the model beer

while an increase in the cross-flow velocity resulted in an increased transmission of components through membrane at a given TMP.

Cross-flow velocity operation is applied in external membrane system as a means to provide high shear conditions at the membrane surface. Much in the same manner as the cross-flow velocity, gas sparging is extensively used in submerged membrane systems to provide high shear conditions at the membrane surface. Increasing the cross-flow velocity or the gas sparging would increase the shear force on the biomass in the AnMBR (Berube et al. 2006). High shear forces can reduce the size of the biomass or flocs in the mixed liquor and increase the release of soluble microbial products. However, Beaubien et al. (1996) reported that the performance of the biological part of an MBR system depended mainly on the mass loading while the separative component was impacted only by operating parameters such as cross-flow velocity, pressure and suspended solids concentration. It was possible to maintain a relatively high permeate flux in an AnMBR by sparging the submerged membrane system with air (Lee et al. 2001). However, sparging the anaerobic system with air for long duration resulted in non-anaerobic conditions that significantly reduced the activity of the microorganisms in the system. Stuckey et al. (2003) effectively used biogas in the headspace in an AnMBR as a source of relatively inert gas for continuously sparging a submerged membrane system. Similarly, Liao's group developed an SAnMBR system using the produced biogas as recirculated gas to minimize membrane fouling by scouring the membrane surface (Gao et al. 2010, Lin et al. 2010, Liao et al. 2010, Xie et al. 2010).

It was earlier reported that a higher temperature could be maintained in an AnMBR (32°C) compared to the aerobic counterparts (29°C) (Baek and Pagilla, 2003). Lin et al.

(2010) operated a thermophilic AnMBR at high temperature of 55 °C. In all microbial systems, temperature increase leads to increased microbial activity. Higher operating temperatures have beneficial effects on permeate flux by reducing the viscosity of the permeate. In conclusion, the three common temperatures ranges at which AnMBR operates are thermophilic (50-65°C), mesophilic (20-45°C) and psychrophilic (<20°C).

2.2 Applications of AnMBR for industrial wastewater treatments

The membrane biological reactor (MBR) configuration has proven to be optimal for treatment of many industrial wastewaters when treatment efficiency is an important consideration (Lin et al. 2011). Early in 1982, Dorr Oliver introduced an AnMBR system for treatment of industrial wastewater. Many studies have indicated that the AnMBR technology held great promise for treatment of high strength wastewaters (e.g. industrial wastewater). Since that time, a number of AnMBR research and development studies have been completed (Sutton et al. 2002). Table 2.2 shows the AnMBR performance for treatment of food processing and non-food processing industry wastewater (Lin et al. 2011).

The characteristics of industrial wastewaters are sector specific, although, in general, they have the potential to have a high organic strength and contain synthetic and natural chemicals that may be slowly degradable or non-biodegradable anaerobically or toxic. Industrial wastewater may also have extreme physicochemical nature, such as pH, temperature, and salinity. Compared to municipal wastewater whose organic strength range is around 250-800 mg COD/L, the industrial wastewater is usually the strong or extremely strong wastewater (>1000 mg COD/L) (Lin et al. 2011). Industrial wastewaters

may contain a large variety of potentially inhibiting or toxic compounds, such as heavy metal, phenols, chlorinated and biocides (Sipma et al. 2010). Some of the toxic compounds may be mostly inert to biodegradation and may require additional physicochemical treatment.

For food processing wastewater treatment, SAnMBR can be a key technology because the wastewaters from the food industry are generally biodegradable and nontoxic. He et al. (2005) successfully used an AnMBR to treat high-concentration food wastewater containing starch and fat. The COD removal in their study was as high as 81-94%. They also reported that the control of operating parameters in the AnMBR was very important. For example, pH control by addition of an alkali solution was needed to maintain the total buffering capacity during the AnMBR operation; a relatively high temperature could slightly enhance organic degradation rate of the food wastewater and significantly increase water flux. It should be mentioned that due to the high suspended solids (SS) in the food industry wastewater, pre-treatment of the feedwater to remove the SS before the treatment of AnMBR should be conducted.

Non-food processing industrial wastewaters include effluents from the pulp and paper, chemical, pharmaceutical, petroleum, and textile industries. For non-food processing wastewater, the pulp and paper industry is responsible for large discharges of highly polluted wastewaters. The sources of different wastewaters in the pulp and paper industry are from various processes: wood preparation, pulping, pulp washing, screening, washing, bleaching, paper machine and coating operations (Pokhrel and Viraraghavan, 2004). A number of treatment technologies have been used to treat and reuse the pulp and paper industry wastewater, such as physical process (steam stripping) and traditional biological

treatment (Pokhrel and Viraraghavan, 2004). Since the operational costs of the steam stripping process are proportional to the volume of the liquid to be treated and the discharges of the pulp and paper wastewater keeps increasing these days, biological treatment process has become the dominating treatment technology. Although pulp and paper wastewater can be both aerobically and anaerobically treated, anaerobic processes are considered more suitable to treat high concentration organic effluent with pollution decreasing and energy production (Lin et al. 2011, Wijekoon et al. 2011). Minami et al. (1991, 1994) successfully investigated an external AnMBR for pulp and paper wastewater treatment with excellent permeate quality. However, external AnMBRs may consume large energy due to the high cross-flow velocity. To overcome the drawbacks of external AnMBR, a promising technology of SAnMBR was mentioned in the work of Lin et al. (2009). What's more, to save energy in a further step, Lin studied a thermophilic submerged AnMBR to treat pulp and paper wastewater which is usually discharged at a high temperature of 50-70°C. Although Lin's results showed that thermophilic SAnMBR provided adorable permeate quality, a serious membrane fouling was a challenge and needed further investigations (Lin et al. 2009, Lin et al. 2010).

For other non-food process industrial wastewater, the potential role of AnMBR needs to be further studied. A COD removal of 50% at an OLR of 15 kg/m³/day was achieved in an AnMBR system treating a type of textile wastewater (Hogetsu et al. 1992). You et al. (2009) combined anaerobic and aerobic membrane bioreactor to treat azo dye wastewater. The COD removal achieved 92%. Due to the color presented in the textile wastewater, a combined AnMBR and aerobic MBR process would be a promising technology for the textile wastewater treatment. The AnMBR system is used for energy

recovery and the subsequent use of aerobic MBR can achieve color removal to produce an effluent for subsequent reuse. Zayen et al. (2009) proved that landfill leachate can be treated by AnMBR without any physical or chemical pre-treatment. At stable conditions, the treatment efficiency was high with an average COD reduction of 90% and biogas yield of 0.46 L biogas/g COD removed.

As mentioned above, AnMBR can be applied for a number types of industrial wastewaters including both food processing wastewater and non-food processing wastewater. It is anticipated that more full-scale AnMBR systems will be in operation in the near future.

2.3 Membrane fouling

2.3.1 Mechanisms of membrane fouling

Membrane fouling is regarded as a major obstacle that limits the performance of membrane bioreactors. The definition of membrane fouling can be described as permeate flux decline because of accumulation of substances within membrane pores and/or onto membrane surface (Hong et al. 2002). Membrane fouling mechanisms are firstly observed as the adsorption and accumulation of solutes and colloids on the membrane surface or within the membrane pore (pore blocking). The sizes of the solutes and colloids in this mechanism should be smaller or comparable to the membrane pore size. At the same time, the sludge particles larger than the pore size will deposit onto the membrane surface to form cake layer, as shown in Figure 2.3. But the shear force will cause the detachment of the sludge particles to the membrane. In a long-time operation, the spatial and temporal changes of foulants composition occur (Meng et al. 2009).

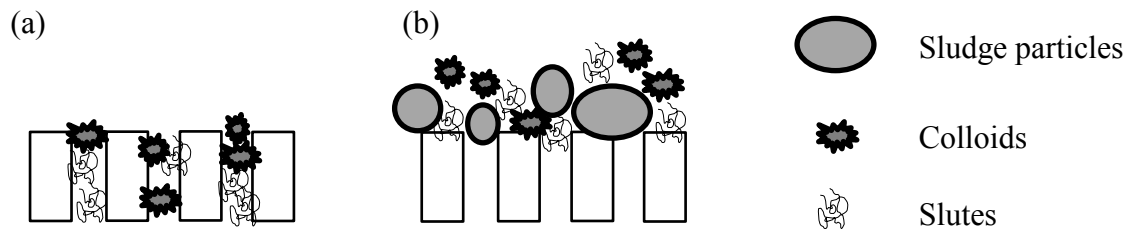


Figure 2.3 Membrane fouling process in MBRs: (a) pore blocking; (b) cake layer.

According to the components of fouling, membrane fouling can be classified into biofouling, organic fouling and inorganic fouling (Liao et al. 2006, Meng et al. 2009). Biofouling is caused by the accumulation and deposition of sludge flocs on the membranes or the metabolism and growth of bacteria cells on the membranes (Peng and Escobar, 2005). Liao et al. (2006) indicated that the adsorption of extracellular polymeric substances (EPS) and soluble microbial products (SMP) lead to biofouling on membrane and pore surfaces as well. Organic fouling refers to the accumulation of biopolymers onto the membranes. Zhou et al. (2007) reported that the major components of the biopolymers were proteins and polysaccharides. In general, these two biopolymers are generated during biological activity. Inorganic fouling is due to the chemical and biological precipitation of a large number of cations (i.e., Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+}) and anions (i.e., CO_3^{2-} , SO_4^{2-} , PO_4^{3-} and OH^-) presented in the membrane bioreactors. Generally, inorganic fouling happens in anaerobic MBRs. The most common inorganic foulant is struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Other inorganic foulants include CaCO_3 and $\text{K}_2\text{NH}_4\text{PO}_4$ (Liao et al. 2006).

Membrane fouling can also be classified into removable fouling, irremovable fouling and irreversible fouling (permanent fouling), according to the removability of the foulants

on the membrane (Meng et al. 2009). The removable fouling can be easily removed by physical cleaning (i.e. aeration, backwashing) due to its loosely attached foulants. For irremovable fouling, chemical cleaning (i.e. acidic cleaning, alkaline cleaning) is needed to eliminate the strongly attached foulants. However, irreversible fouling is defined as the fouling cannot be removed by any methods so that the membrane cannot be recovered to its original state. It can be readily understood that removable fouling may lead to cake layer formation, while pore blocking is caused by irremovable fouling and irreversible fouling (Meng et al. 2009).

2.3.2 Factors affecting membrane fouling

Membrane fouling can be reflected by the decrease in the permeate flux or the increase in transmembrane pressure (TMP) during a membrane process. All the parameters involved in the design and operation processes have impacts on membrane fouling. The major factors affecting the membrane fouling can be divided into five categories: membrane characteristics, operating conditions, biomass properties, environmental conditions, and hydrodynamic conditions.

2.3.2.1 Membrane characteristics

Membrane characteristics (i.e. membrane material, pore size, porosity, roughness, surface charge, hydrophilicity/hydrophobicity, module structure) have direct impacts on membrane fouling (Meng et al. 2009). Membrane materials can be categorized into two types: organic and inorganic. Organic polymer materials include: polyolefin, polyethylene (PE), polyvinylidene fluoride (PVDF) and polyvinyl chloride (PVC), etc. Inorganic materials are metals, ceramic and porous glass, etc. Compared to inorganic

membrane material, organic membrane material is applied in most cases due to its low cost and convenience of control. Yamato et al. (2006) found out that PVDF membrane was better than PE membrane in the aspect of reducing irreversible fouling. In terms of the pore size of membrane, it was suggested that a narrow pore size is preferred to control the membrane fouling of the pore blocking in membrane filtration process. Therefore, it is assumed that membrane with large pore size (i.e. MF) would present higher fouling than small pore size membranes (i.e. UF). As for the hydrophilicity and hydrophobicity property of the membrane, membrane fouling on hydrophobic membranes is more severe because of the hydrophobic interaction between foulants and membranes (Meng et al. 2009).

2.3.2.2 Operating conditions

In an MBR, the biological system design and operation parameters, e.g. SRT, HRT, or OLR (Zhang et al. 2010), F/M ratio, nutrient conditions, etc., play significant roles in the membrane filtration performance. The operating conditions (i.e. permeate flux, TMP, aeration intensity (Menniti and Morgenrith, 2010) exert direct shear stress on the membrane surfaces and sludge itself.

Flux selection provides the most important factor in determining fouling rate. At high flux, rapid membrane fouling due to colloidal aggregation and heterogeneous deposits takes place. On the other hand, the fouling rate can be reduced with some specific value of flux which is called critical flux. The critical flux concept was introduced by Field et al. (1995) more than 15 years ago and was defined as the flux below which fouling does not occur. However, because of the complexity of the MBR system and the inevitability of

membrane fouling even without flux operation, Jeison (2007) redefined the concept of critical flux as the flux above which the relation between flux and TMP becomes non-linear. In order to maintain a certain flux for a long term operation, the sub-critical flux is used to gain low and moderate level of fouling.

Aeration or gas sparging applied in MBR has a complicated influence on membrane fouling. In aerobic MBRs, aeration carries out three functions: providing oxygen to the biomass, maintaining the solids in suspension and scouring the membrane surface to suppress fouling (Bouhabila et al. 1998, Cui et al. 2003, Dufresne et al. 1997). In anaerobic MBRs, biogas can be recirculated to achieve similar effects (Liao et al. 2006). It has been reported that increasing the aeration intensity in MBRs will reduce the fouling rate and achieve a better hydrodynamic conditions. However, increasing the aeration intensity could increase energy cost and disrupt sludge flocs, producing small size particles and releasing more EPS which negatively impact membrane fouling (Khan and Visvanathan, 2008).

Organic loading rate (OLR) is determined by the influent organic concentration and hydraulic retention time (HRT). Visvanathan et al. (1997) noted that reduced fouling (no TMP increase) at higher HRT values. On the contrary, a low HRT or high OLR as food to microorganism (F/M) ratio increased membrane fouling rates (Trussell et al. 2006). This could be explained by the relation of HRT to the mixed liquor suspended solids (MLSS): a shorter HRT provides more nutrients to the biomass, and leads to a greater biological growth and so a higher MLSS (Dufresne et al. 1996). Solid retention time (SRT) can also influence membrane fouling by altering sludge composition and MLSS concentration (Bouhabila et al. 2001, Patsios and Karabelas 2011, Urbain et al. 1998).

Either a too short SRT or a too long SRT was found to result in extensive membrane fouling (Huang et al. 2008, Ng et al. 2006). There is an optimum SRT determined by different operating conditions for each MBR (Meng et al. 2009).

2.3.2.3 Biomass properties

As AnMBR is a complex and enclosed system that concentrates the foulants in the sludge suspension, biomass properties such as the mixed liquor suspended solids (MLSS) concentration, colloids (Wang and Tarabara, 2008), particle size distribution (PSD), extracellular polymeric substances (EPS) (Wang et al. 2009), soluble microbial products (SMP) (Meng et al. 2007) can contribute to the overall performance of an AnMBR. The relative contributions of suspended solids (SS), colloids, and dissolved molecule on membrane fouling were 24%, 50%, and 26%, respectively (Bouhabila et al. 2001).

Membrane filtration performance in MBRs was proven to depend on the concentration of MLSS. MLSS concentration is defined as the concentration of suspended solids in the sludge suspension. Chiemchaisri and Yamamoto (1994) reported that the flux decreased abruptly if the MLSS concentration exceeded 40,000 mg/L in a submerged membrane bioreactor. Also, Chang and Kim (2005) confirmed that the membrane fouling took place more rapidly at higher MLSS concentrations. Membrane fouling resistance was considered to increase exponentially with an increase of MLSS concentration (Meng et al. 2007). The reason of the effect of MLSS concentration on membrane fouling can be explained by the filtration process. During the filtration process, water in the mixed liquor passed through the membrane, while the suspended solids in the mixed liquor were retained on the membrane surface, which could induce the

membrane fouling. On the other hand, some studies showed that MLSS concentration did not have the impacts on membrane permeability. Hong et al. (2002) reported that the MLSS exhibited very little influence on permeate flux for the range of 3600-8400 mg/L. Lee et al. (2001) even suggested the improvement of membrane permeability with increasing in MLSS concentration.

It has been observed that colloidal particles in the mixed liquor have particularly impacts on membrane fouling. Due to any turbulence in the bioreactor caused by system operation, weak flocs in biomass can be easily broken into smaller particles. The relative contribution of colloids to the membrane fouling resistance was found to be 30% by Defrance et al. (2000). Bai and Leow (2002) found that the smaller particles such as colloidal ones played a more important role in membrane fouling. The specific resistance of the colloids and solutes fraction was about ten times as high as the specific resistance of the total sludge including the suspended solids, colloids and solutes (Bouhabila et al. 2001).

Many studies showed that the particle size distribution of sludge was an important factor that affects membrane fouling: the membrane fouling resistance increased as sludge particle size decreased. The Carman-Kozney equation establishes the impacts of particle size distribution on the cake layer resistance: the smaller particles deposited on the membrane surface would generate greater specific resistance. This conclusion was proven by Bai and Leow (2002). They studied the effect of operation parameters on membrane fouling in a cross-flow microfiltration system and observed that particles smaller than 50 μm create greater specific resistance and lead to greater cake resistance.

Meanwhile, the filtration rate was determined by the smallest particles in the suspension (Kromkamp et al. 2006).

EPS and SMP have been regarded as the most significant factors affecting membrane fouling. EPS, including proteins, carbohydrates, lipids, and nucleic acids, is the polymeric substances extracted from sludge flocs, while SMP, mainly consisting of macromolecule organisms, is the soluble microbial products which is produced during biological reactions (Meng et al. 2009). SMP can be seen as soluble EPS.

The total amount of EPS showed a significant positive effect on the membrane fouling resistance. The macromolecules (proteins, DNA, carbohydrates, lipids, and nucleic acids) are retained in the suspension sludge by the membrane in the MBR process. Nagaoka et al. (1996) indicated that the accumulation of EPS can cause an increase of viscosity of the mixed liquor and thus an increase in the filtration resistance. Cho et al. (2005) found that the specific cake resistance became higher as the amount of bound EPS increased. Most of EPS components are either tightly bound to cells (TB-EPS) or loosely bound to cells (LB-EPS) (Li and Yang, 2007). TB-EPS and LB-EPS can be separated by a modified heat extraction at temperature of 50 °C. Wang et al. (2009) found in their study that compared to TB-EPS, LB-EPS showed more significant positive correlations with membrane fouling. It is reported that both the quantity and composition of bound EPS in sludge suspension or on the membrane surface influenced membrane fouling (Ji and Zhou, 2006). Although protein and carbohydrates are typically characterized in the solution containing EPS, Dvorak et al. (2011) reported that more than 34% of the EPS components in the activated sludge are humic substances.

SMP, representing the soluble EPS, have been found to be released into solution during substrate metabolism, biomass growth, and biomass decay (Barker and Stuckey, 1999). SMP have been classified into two groups: substrate utilization associated products (UAP) and biomass associated products (BAP). UAP are associated with substrate metabolism and biomass growth and are produced at a rate proportional to the rate of substrate utilisation, while BAP are associated with biomass decay and are produced at a rate proportional to the concentration of biomass. SMP are produced across a wide range of molecular weight (MW): < 0.5 to > 50 kDa (Barker and Stuckey, 1999). The SMP of larger MW (> 30 kDa) was the most abundant fraction in the MBR (Pan et al. 2009). Jarusutthirak and Amy (2006) also indicated that the SMP with high molecular weight play an important role in creating high resistance of the membrane, leading to a reduction of permeate flux. SMP can block membrane pores, absorb on membrane surface, form a gel layer, and/or build up on cake layer through physical and chemical adsorption, leading to smaller filtration areas, greater hydraulic resistance (Rosenberger et al. 2005) and finally a decrease in filtration flux (Liao et al. 2004).

2.3.3 Membrane fouling characterization

The development of techniques for membrane fouling characterization has advanced the knowledge of mechanisms involved in membrane fouling. Scanning electron microscopy (SEM) is one of the most common instruments providing high resolution images at nano/micro-meter scale. SEM was used to characterize the bacteria clusters deposited on the membrane surface (Meng et al. 2007). Recently, by analyzing the SEM images, Pendashteh et al. (2011) reported that rod-shape bacteria clusters were one of the contributors to cake layer. Unlike the SEM which provides a two-dimensional image of a

sample, the atomic force microscopy (AFM) provides a three-dimensional surface profile. Observed by SEM and AFM, the gel layer caused by soluble microbial products and the cake layer caused by flocs showed great differences in morphology (Yu et al. 2006). Confocal scanning laser microscopy (CSLM) is an optical microscopic technique that was commercially developed in the early nineties. CSLM has better resolution through the observation axis than conventional optical microscopy, and at the same time it provides high resolution images obtained at different depths of a three-dimensional (3D) object.

Many other methods have been utilized to characterize membrane fouling. Fourier transform infrared (FTIR) spectrometer can be used to characterize the major functional groups of biopolymers in membrane foulants. The SEM coupled with an energy-dispersive X-ray spectroscopy (EDX) was used to determine the chemical components of the cake layer (Meng et al. 2007). SEM-EDX analysis showed that inorganic precipitate in an AnMBR consist of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), calcite, and clay which was the result of ammonium and phosphate ions production during anaerobic decomposition of organics (Berube et al. 2006). Three-dimensional excitation–emission matrix (EEM) fluorescence spectroscopy was proven to be an appropriate and effective method to characterize the extracellular polymeric substances (EPS) from various origins in wastewater treatment systems (Sheng and Yu, 2006). FTIR spectroscopy and solid-state ^{13}C -nuclear magnetic resonance (NMR) spectroscopy are powerful analytical tools for investigation of the characteristics of organic substances. Kimura et al. (2005) subjected the organic substances that were desorbed from fouled membrane of pilot-scale MBRs to

the FTIR/NMR analyses, which showed that the carbohydrate was a dominant component in the foulants.

2.3.4 Membrane fouling control

As the widespread application of the MBR process is constrained by membrane fouling, many researches have been done on membrane fouling control since 1990s. Fouling control techniques which have been investigated include chemical cleaning of membrane, low-flux operation, high-shear slug flow aeration in submerged configuration, periodical air or permeate backflushing, intermittent suction operation or addition of powdered activated carbon (PAC) (Ng et al. 2006, Hu and Stuckey 2007).

Chemical cleaning is considered to be an efficient way to recover the permeate flux. It has been widely applied for cleaning membrane in MBRs either in situ (Wei et al. 2011) or ex situ. Chemical cleaning can be classified into caustic solution (e.g. NaOCl, NaOH, H₂O₂, Cl₂) and acidic solution (e.g. citric acid). Caustic agents has been found to be effective at removing organic or biological fouling while acidic solutions are considered to be effective at removing inorganic fouling (Al-Amoudi and Lovitt 2007). A low concentration of chemical agents can be added to the backflush water to produce chemically enhanced backflush. Backflushing is a very effective in situ chemical cleaning way. The permeate flux can be recovered by backflushing the membrane with a caustic solution followed by an acidic solution (Lee et al. 2001).

On the other hand, another strategy for membrane fouling control is to reduce the fouling rate which can prolong the length of time between the cleanings. The fouling rate can be controlled by operating a membrane below the critical flux. It can be easily

understand the severe membrane fouling occurs if the permeate flux is too high. The relation between the flux and TMP becomes non-linear when the flux is above the critical flux (Jeison, 2007). That means to some extent fouling can be removed when the permeate flux is reduced back to the sub-critical level.

In addition, Mishima and Nakajima (2009) reported that coagulant addition is an effective way to reduce the membrane fouling. They found out that Fe coagulant can reduce the cleaning times by lowering the protein and carbohydrate concentrations of the SMP in the bioreactors. Other coagulants that have been tested in MBRs with positive results include: alum, chitosan, filter acids, polymeric aluminum chloride and polymeric ferric sulphate (Iversen et al. 2008, Ji et al. 2008, Song et al. 2008, Tian et al. 2008, Zhang et al. 2008). Periodic relaxation is typically used to encourage diffusive back transport of foulants away from the membrane surface. The sustainable operation periods can be prolonged by the combinations of membrane relaxation and the ultraviolet (UV) inactivation (Phattaranawik and Leiknes, 2011). Ultrasound has been suggested as an effective cleaning technology to enhance the membrane filtration (Chai et al. 1999, Latt et al. 2006, Muthukunaran et al. 2004). Moreover, this technology was advanced in an anaerobic membrane bioreactor by Xu et al (2010). The optimal ultrasound power intensity of 0.18 W/cm^2 and timing of 3 min/h were estimated, and under the observation of scanning electron microscope (SEM), the cake layer could be controlled more effectively by ultrasound.

Table 2.2 AnMBR performance for treatment of food processing and non-food processing industry wastewater (modified from Lin et al. 2011)

Wastewater	Type of reactor ^a	Configuration, scale ^b and volume	Characteristics of Membrane ^c	Temp (°C)	HRT (d)	SRT (d)	OLR (kg COD/m ³ d)	MLSS (g/L)	Feed COD (mg/L)	COD removal efficiency
<i>Food processing wastewater</i>										
Wheat starch waste (Butcher, 1989)	Anaerobic, CSTR	External, F (2000 m ³)	--	40	-- ^d	--	2.1	10	--	78%
Soybean processing wastewater (Kataoka et al. 1992)	Anaerobic, UFAF	External, P (3.0 m ³)	PSf, capillary type, UF, MWCO = 15k Da	30	0.4	--	3.2	2	1.4	78%
Maize processing effluent (Ross et al. 1992)	Anaerobic, CSTR	External, F (2610 m ³)	--	35	5.2	--	2.9	21	15	97%
Wheat starch and gluten wastewater (Yanagi et al. 1994)	2 phase, Anaerobic, UFAF+M/USAB	External, P (24 m ³)	PE, hollow fiber, pore size = 0.2 µm	37	0.6/0.4	--/--	32/27	18/--	19/10	98%
Palm oil mill effluent (Fakhru'l-Razi et al. 1999)	Anaerobic, CSTR	External, L (0.05 m ³)	UF, MWCO = 200k Da	35	3.2	77	21.7	57	68	92%
Sauerkraut brine (Fuchs et al. 2003)	Anaerobic, CSTR	External, L (0.007 m ³)	Ceramic, pore size = 0.2 µm	30	6.1	--	8.6	55	52.7	99%
Cheese whey (Saddoud et al. 2007)	2 phase, Anaerobic, CSTR/CSTR+M	External, L (0.007 m ³)	Ceramic, pore size = 0.2 µm	37±2	1/4	-- /29.7 -78.6	--/3- 19.78	~8.5	68.6 ± 3.3	18%/79%
Olive mill wastewater (Stamatelatou et al. 2009)	Anaerobic baffled reactor	External, L (0.015 m ³)	Ceramic tubular UF/RO	35	3.75- 17.5	--	0.94- 6.0	12.84	19.49- 25.23	58-82%

Table 2.2 AnMBR performance for treatment of food processing and non-food processing industry wastewater (modified from Lin et al. 2011) (*continued*)

Wastewater	Type of reactor	Configuration, scale and volume	Characteristics of membrane	Temp (°C)	HRT (d)	SRT (d)	OLR (kg COD/m ³ d)	MLSS (g/L)	Feed COD (mg/L)	COD removal efficiency
<i>Non-food processing wastewater</i>										
Kraft bleach plant effluent (Hall et al. 1995)	Anaerobic, CSTR	External, L (0.015 m ³)	Tubular UF membrane, MWCO =10k Da MF	35	1.0	--	0.04	7.6-15.7	40 ^e	61% ^e
Evaporator condensate (Minami et al. 1991, Minami et al. 1994)	Anaerobic UFAF	External, P (5 m ³)	Membrane, pore size = 0.2 µm	53	0.5	--	35.5	7.6	17800 ^f	93 ^f
Thermo-mechanical pulping whitewater (Gao et al. 2010)	Anaerobic, CSTR	Submerged, L (0.01 m ³)	Membrane, MWCO = 70k Da PVDF UF	37	~2.5	280	2.4±0.4	5.7-10.0	2600, 5500, 10000	>95%
Kraft evaporator condensate (Lin et al. 2009)	Anaerobic, CSTR	Submerged, L (0.01 m ³)	Membrane, MWCO = 70k Da	37,55	--	~230	--	10.0	10000	97-99%
Fresh landfill leachate (Zayen et al. 2010)	Anaerobic, CSTR	External, L (0.05 m ³)	UF, MWCO = 100k Da	37	7	--	1-6.27	0.44-3	15-41	90%
Petrochemical effluent (Van Zyl et al. 2008)	Anaerobic, CSTR	Submerged, L (0.023 m ³)	Kubota, flat sheet, pore size = 0.45 µm	37	1.31	175	>25	>30	19	97%

^a CSTR = completely stirred tank reactor, UFAF = upflow anaerobic filter, UASB = upflow anaerobic sludge blanket, M designates the location of the membrane. ^d indicates value not reported.

^b L = laboratory/bench scale, P = pilot scale, F = full scale. ^c PSf = polysulfone, UF = ultrafiltration, MWCO = molecular weight cutoff, PE = polyethylene, MF = microfiltration, RO = reverse osmosis.

^e Units are AOX (absorbable organic halogen). ^f Units are BOD instead of COD

Chapter 3

Experimental Materials and Methods

3.1 SAnMBR Setup

A laboratory-scale hollow fiber submerged AnMBRs was used for this study. The schematic diagram of the experimental setup is shown in Figure 3.1. The SAnMBR has an effective working volume of 6.0L (diameter: 16 cm; height: 48 cm). A vertically oriented hollow fiber ultrafiltration membrane module with a membrane pore size of 0.04 μm and a membrane surface area of 0.03 m^2 , was located in the center of the SAnMBR. The hollow fiber membranes used in this study were made of polyvinylidene fluoride. Through the membrane module, headspace biogas was continuously recirculated by a biogas recycle pump (Masterflex Console Drive, Model 7520-40, Thermo Fisher Scientific, USA). The purpose of the biogas recirculation is to provide sludge mixing and biogas scouring to control solids deposition over the membrane surface. A magnetic stirrer (Thermolyne Cimarec, Model S47030) was located at the bottom of the bioreactor to provide necessary mixing of the sludge liquor. The temperature of the bioreactor was maintained constant at a mesophilic temperature of 35 ± 1 °C throughout the course of the experiment. This was done by circulating warm water heated by a temperature-controlled water bath to the water jacket of the reactor. The pH was monitored by a pH electrode (Thermo Scientific, Beverly, MA), and automatically adjusted to 7.0 ± 0.2 by a pH regulation pump using 0.5M NaOH solution.

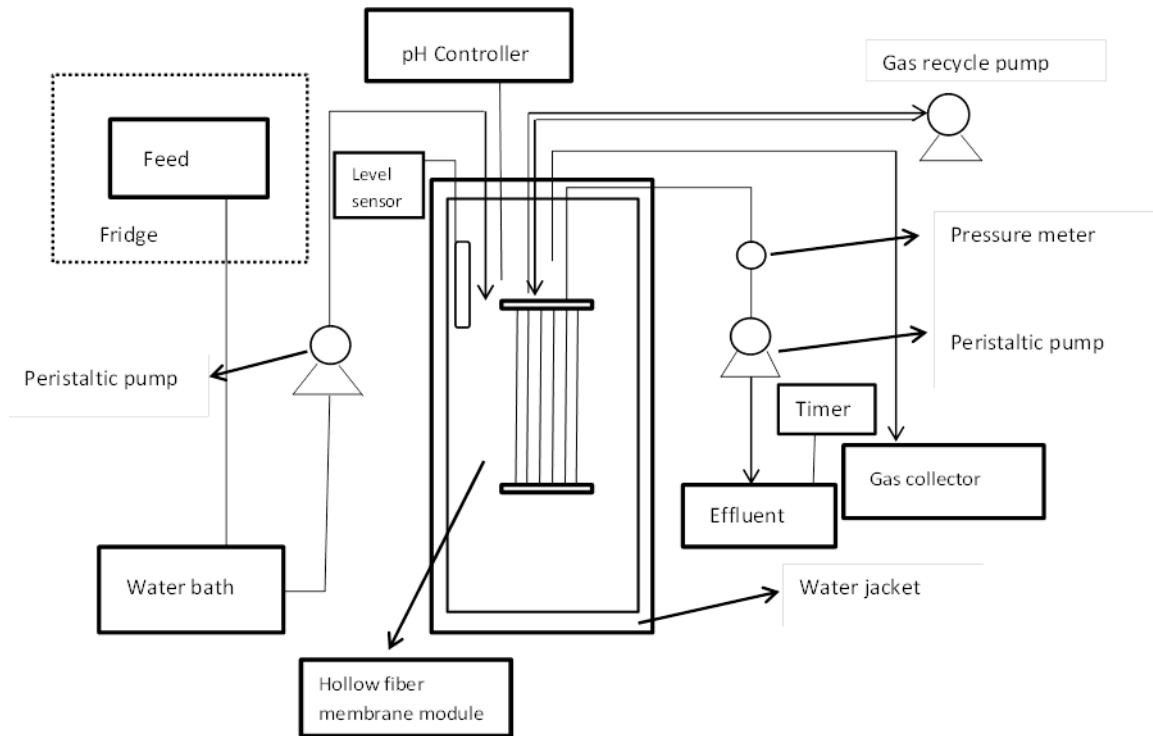


Fig. 3.1 Schematic of the submerged anaerobic membrane bioreactor and experimental setup

The anaerobic seed sludge added into the SANMBRs was from a full-scale upflow anaerobic sludge blanket (UASB) at Tembec Industries Inc. (Temiscaming, Quebec). During the operation of the reactors, no sludge was discharged except for sludge sampling. The feed wastewater was pumped into the bottom of the bioreactor by a feeding pump (Masterflex Model 7520-50, Barnant Co., USA), which was controlled by a level sensor model (Madison Co., USA), so that the liquor level in the reactor can be maintained. The permeate was acquired intermittently by a vacuum driven peristaltic pump (Masterflex, C/L, Model 77120-70, Barnant Co., USA). The pump was controlled by a timer. To slow down the membrane fouling process, the mode of 4 minutes on and 1

minute off was applied on the timer. Membrane flux was controlled by adjusting the pump speed and two calibrations were made each day.

When the trans-membrane pressure (TMP) reached 40k Pa, the reactor was shut down and a physical cleaning procedure was carried out on the membrane module. Physical cleaning was conducted by scraping off cake layer from the membrane surface carefully using a plastic sheet followed by wiping and rinsing the membrane surfaces with a soft sponge and tap water, respectively. After the washing of the fouled membrane, the operation was resumed. This procedure happened because it was difficult to maintain flux at a constant level under TMP above 40k Pa. If the flux cannot be recovered to the initial level, further chemical cleaning of the membrane module was conducted by immersing the module into 200 ppm sodium hypochloride (NaClO) solution for 2 hours and then into 300 ppm citric acid solution for 3 hours. The purpose of the operation was to remove the biofouling and inorganic fouling that cannot be removed by the physical cleaning.

3.2 Experimental Operations

3.2.1 Types of Wastewater

In the first part of this thesis, a synthetic biorefining effluent comprising of glucose, acetic acid and guaiacol was used. The composition determined and used for the simulated aqueous products (AP) from the wastewater sludge hydrothermal liquefaction process was at a mass ratio of 84%, 15% and 1% for glucose, acetic acid and guaiacol, respectively (Zhang et al. 2011). The tested COD concentration of the synthetic biorefining effluent was 3000, 5000 and 7000 mg/L, respectively. The characteristics of the synthetic wastewater are listed in Table 3.1.

Table 3.1 The characteristics of biorefining synthetic wastewater

COD concentration of composition	COD 3000 mg/L	COD 5000 mg/L	COD 7000 mg/L
Glucose	2520 mg/L	4200 mg/L	5880 mg/L
Acetic Acid	450 mg/L	750 mg/L	1050 mg/L
Guaiacol	30 mg/L	50 mg/L	70 mg/L

In the second part of this thesis, thermo-mechanical pulping pressate (TMP) wastewater from a local pulp and paper mill was used as substrate. The chemical composition and concentration of the real TMP wastewater were determined in terms of the chemical oxygen demand (COD) and metal ion concentrations (ICP). The analytical results of TMP are listed in Table 3.2. TMP wastewater was diluted using distilled water to certain influent COD (3000 mg/L and 5000 mg/L) prior to feeding and pH adjustment. Since the TMP wastewater did not contain sufficient nutrients, the feed wastewater was enriched with macro-nutrients, nitrogen (NH_4Cl) and phosphorus (KH_2PO_4), in a ratio of COD: N: P of 100: 2.6: 0.4 to sustain the nutrient concentrations required for biomass growth in an anaerobic environment. Trace elements were added to the feed water to prevent trace metal limitations of methanogens. Some mineral salts and trace elements added to the TMP wastewater can be seen in Table 3.3. Additionally, Na^+ and Mg^{2+} ions were added to the wastewater to provide sufficient hardness for biomass growth and granulation. Na^+ concentration was maintained at 1.8 mM, and Mg^{2+} concentration at 0.5 mM. The feed had a COD of about 5000 mg/L. Distilled water was added to the feed to

decrease the COD level to approximately 3000 mg/L to decrease the organic loading rate (OLR).

In the third part of this thesis, four types of industrial wastewaters collected from different process locations of a local thermomechanical pulping mill were studied: thermomechanical pulping pressate (named TMP pressate 1) and thermomechanical pulping whitewater (named TMP whitewater) were treated by the SAnMBR system (Gao et al. 2010; Gao et al. 2011), while thermomechanical pulping pressate (named TMP pressate 2) and a mixture of different thermomechanical pulping wastewaters (named TMP wastewater) were treated by a TSAMBR system (Qu et al. 2012)

Table 3.2 Main characteristics of thermo-mechanical pulping pressate

pH	4.0-4.2
COD (mg/L)	4900-5100
Total Nitrogen (mg/L)	0.1-0.5
Total Phosphorus (mg/L)	1.078-1.406
Total Sulfur (mg/L)	42.44-47.5
Aluminum (mg/L)	0.2-0.238
Barium (mg/L)	0.386-0.429
Calcium (mg/L)	33.424-37.609
Copper (mg/L)	0.008-0.019
Iron (mg/L)	0.147-0.183
Potassium (mg/L)	39.41-44.28
Magnesium (mg/L)	6.49-7.26
Manganese (mg/L)	2.7456-3.0819
Sodium (mg/L)	43.05-48.75
Strontium (mg/L)	0.101-0.114
Zinc (mg/L)	0.241-0.164

Note: other metals (arsenic, beryllium, cadmium, cobalt, chromium, molybdenum, nickel, lead, titanium, vanadium) are under determining limitation.

Table 3.3 List of mineral salts and trace element nutrients (for both biorefining synthetic wastewater and TMP wastewater)

Chemicals	Concentration in the feed (M = mol/L)
MgCl ₂	0.1 mM
FeCl ₂	5 μM
CaCl ₂	5 μM
MnCl ₂	0.1 μ M
CoCl ₂	0.1 μ M
NiCl ₂	0.1 μ M
CuCl ₂	0.01 μM
ZnCl ₂	0.01 μM
NaSeO ₃	0.01 μM

3.2.2 Analytical Methods

3.2.2.1 Water Quality Measurements

Samples of influent were collected every time after the preparation of the feed water. The mixed liquor and effluent samples were taken from the system routinely 2-3 times each week during the steady state of the operation. The supernatant samples were obtained by centrifuging the mixed liquor for 20 minutes at 18,700×g. They were then filtered through 0.45µm membranes (Millipore) and stored at 4°C prior to analysis. The filtrates were subjected to COD measurements to determine the soluble COD in supernatants. The effluent COD were analyzed without further treatment. Mixed liquor suspended solids (MLSS), influent COD, soluble COD and effluent COD were routinely measured 2–3 times each week as defined in Standard Methods (APHA, 2005).

3.2.2.2 Biogas Determination and Quantification

Biogas samples were taken from the headspace of the membrane bioreactor by a syringe. The composition of biogas (methane, carbon dioxide, and nitrogen) was determined and quantified by gas chromatography (Shimazu, GC-2014) equipped with a thermal conductivity detector (TCD) and silica gel packed columns (5,486 × 3.18 mm). The flow rate of the carrier gas (Helium) was 30 mL/min. Nitrogen (N₂) was used as a sparging gas to purge air out of the bioreactor.

The biogas quantity (volume) and yield were determined by using a water displacement method developed in previous studies (Xie et al. 2010; Gao et al. 2010).

3.2.2.3 Particle Size Distribution

The particle size distribution (PSD) measurements were conducted 2-3 times each week. The PSD was determined by a Malvern Mastersizer 2000 instrument (Worcestershire, UK) with a detection range of 0.02–2000 μm . The scattered light is detected by means of a detector that converts the signal to a size distribution based on volume or number. Each sample was measured three times with a standard deviation of 0.1–4.5%. Cake layer was gently scratched from the membrane surface and mixed with distilled water. The same mixing intensity (2,500rpm) was maintained for each sample by the particle size analyzer during PSD analysis.

3.2.2.4 Extracellular polymeric substances (EPS) Extraction and Measurement

Sludge samples were regularly collected at each phase for EPS extraction. The extraction of EPS from sludge suspensions samples were based on a cation exchange resin (CER) (Dowex Marathon C, Na^+ form, Sigma–Aldrich, Bellefonte, PA) method (Frolund et al, 1996). 100mL sample of the sludge suspension was taken and centrifuged (IEC MultiRF, Thermo IEC, Needham Heights, MA, USA) at $18,700\times g$ for 20 min at 4°C . The sludge pellets were resuspended to their original volume using a buffer consisting of 2mM Na_3PO_4 , 4mM NaH_2PO_4 , 9mM NaCl and 1mM KCl at pH 7. Then, the sludge was transferred to an extraction beaker with buffer and the CER (80 g/g-MLSS) was added. The suspension was stirred for extraction of EPS for 2 hours at 4°C . The selected EPS was recovered by centrifugation of a sample of the CER/sludge suspension for 20 min at $18,700\times g$ at 4°C in order to remove the CER and MLSS. The EPS was normalized as the sum of proteins and polysaccharides, which were measured colorimetrically by the

methods of Lowry et al. (1951) and Dubois et al. (1956), respectively. Bovine serum albumin (BSA) and glucose were used as protein and polysaccharides standards, respectively.

3.2.2.5 SMP Measurement

Soluble microbial products (SMP) (proteins and polysaccharides) were measured using the methods of Lowery et al. (1951) and DuBois et al (1956), respectively. Bovine serum albumin (BSA) was used as protein standards and glucose was used as polysaccharides standards.

3.2.2.6 Membrane Fouling Characterization

Part of the cake layers were carefully scraped off from membrane surfaces using a plastic sheet. The collected cake layer was rinsed with distilled water and then gently resuspended for PSD measurement. The purpose was to maintain the real structure of flocs by using minimum external forces. Control was made by stirring the samples under the same mixing intensity (2,500 revolutions per minute) and time. Several pieces (5-8 pieces) of membrane with cake layer were cut from the membrane module to characterize the cake layer. The samples were dehydrated in the oven (105°C) for 24 h to obtain dry foulants. A Bruker Ten 37 Fourier Transform Infrared Spectroscopy (FTIR) (Bruker Co. Ltd.) was used to characterize the major functional groups of biopolymers in the membrane foulants. The SEM coupled with an energy-dispersive X-ray analyzer (Hitachi SU-70) was used to observe the surface morphology and to determine the inorganic components of the cake layer.

The thickness of sludge cake layers formed on membrane surfaces was observed by conventional optical microscopy (Olympus, Japan), combined with the use of a micro-slicing technique. A series of membrane pieces (4-8 pieces) with cake layers was cut from the hollow fiber membranes. In order to prevent the structure and thickness of cake layer from changing, the layer was saturated with 0.85% NaCl aqueous solution (Zhang et al. 1994) and then frozen at $-22\text{ }^{\circ}\text{C}$. These samples pieces were then fixed on to a sample stage using optimal cutting temperature (O.T.C) compound (Sakura Finetechnical Co. Ltd. Tokyo, 103, Japan). After mounting the stage on a cryostate microtome (Histostate Microtome, Model: 855, Reichert Scientific Instruments Division of Warner Lambert Technologies Inc., NY, USA), the samples were the cut into a series of $100\text{ }\mu\text{m}$ -thick cross-sections.

3.2.2.7 Wastewater and Mixed Liquor Characterization

The study was conducted using a lab-scale SAnMBR and a lab-scale thermophilic SAMBR (TSAMBR) system. The details of the experimental systems are described in our previous publications (Gao et al. 2011; Qu et al. 2012). Each system (SAnMBR or TSAMBR) treated two types of industrial wastewaters (described in 3.2.1) with significant difference in characteristics. Both systems were equipped with a flat sheet microfiltration membrane module (0.03 m^2 , $10\text{ cm width} \times 15\text{ cm length} \times 2$, Shanghai SINAP Membrane Science & Technology Co. Ltd., China). The material of the membrane and the molecular weight cut off (MWCO) were polyvinylidene fluoride (PVDF) and 70,000 Daltons, respectively. The pore size of the membrane is $0.3\text{ }\mu\text{m}$. Biogas or air was used for sparging to control membrane fouling in the SAnMBR and

TSAMBR system, respectively. The details of the operating conditions are provided in Table 3.4.

Table 3.4 Operating conditions of SAnMBR and TSAMBR.

Parameters	SAnMBR		TSAMBR	
	TMP pressate 1	TMP whitewater	TMP pressate 2	TMP wastewater
Types of wastewater				
Reactor Working Volume (L)	10	10	6	6
Temperature (°C)	37 ± 1	37 ± 1	51 ± 1	51 ± 1
pH	7.0 ± 0.2	7.0 ± 0.2	6.9 ± 0.1	6.9 ± 0.1
HRT (d)	2.5 ± 0.2	3.8 ± 0.2	1.1 ± 0.1	1.1 ± 0.1
SRT (d)	350	220	20	20
MLSS (g/L)	10.9 ± 0.5	8.7 ± 0.4	11.0 ± 0.5	11.0 ± 0.5
Flux (L/m ² /h)	6.9 ± 0.6	4.6 ± 0.3	9.2 ± 0.5	9.2 ± 0.5
Sparging Rate (L/min)	1.5	1.5	3.2	3.2
Organic Loading Rate (kg COD/m ³ /d)	2.6 ± 0.5	1.8 ± 0.1	3.3 ± 0.2	3.4 ± 0.3

Wastewater characteristics were characterized by the total suspended solids (TSS) by filtration of the wastewater through a glass fiber filter circle (Particle Retention: 1.2µm). Colloids were obtained by filtration the feed supernatant after centrifugation (18,700×g for 20 minutes) using a membrane filter with pore size of 0.45µm (Durapore, Millipore). Additionally, a liquid sample containing only the soluble substances was obtained after filtration with 0.45 µm pore size membrane.

The soluble samples were obtained by centrifuging feed wastewater or mixed liquor at 18,700×g for 20 minutes, and then filtering through 0.45 µm pore size membrane filter.

Consequent ultrafiltration (UF) was performed with a 180 mL stirred filtration cell (Amicon, USA) (Fig. 3.2) at the room temperature ($25 \pm 1^\circ\text{C}$). Three regenerated cellulose ultrafiltration membranes (Millipore) with nominal molecular weight limits (NMWL), also known as molecular weight cut-off (MWCO), of 100k, 10k, 1k Da were used in series with the highest MWCO at first and the lowest MWCO at last. After the ultrafiltration, 4 molecular weight distributions (MWD) were obtained: The 100k Da retentate, called as “>100k”; the sample passed through 100 kDa membrane but retained by 10k Da membrane, regarded as “10k<MW<100k”; the retentate of 1k Da, “1k<MW<10k”; and the permeate of 1k Da, “<1k”. Nitrogen was applied as pressure over the liquid in the stirred cell. The operating pressures were 10 psi for the membranes with NMWL of 100k Da, 20 psi for the membranes with NMWL of 10k Da, and 30 psi for the membranes with NMWL of 1k Da (Leiviskä et al. 2008), respectively. All membranes were cleaned according to the operating instruction before the filtration. To minimize the build-up of a dense macromolecular layer (e.g. protein) at the surface of the membrane surface, a magnetic stirrer was used above the membrane surface to create gentle turbulence. Triplicate measurements of each type of wastewater and supernatant were conducted.

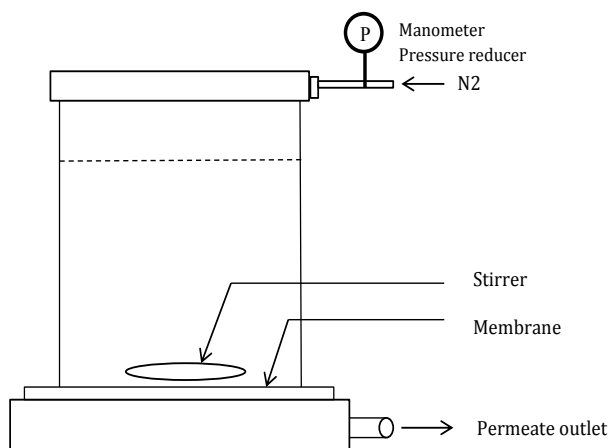


Figure 3.2 Schematic diagram of a stirred filtration cell.

A total COD and soluble COD were determined by the colormetric methods (APHA, 2005). Total COD was analyzed for feed water, supernatant and permeate, and soluble COD was measured for feed water and supernatant after the 0.45 μm filtration. Also, each molecular weight fraction was measured for COD value. The soluble organic materials were normalized as the sum of protein (PN) and polysaccharides (PS), which were measured colorimetrically by the Lowry's method (Lowry et al. 1951) and anthrone method (DuBois et al. 1956), respectively. Bovine serum albumin (BSA) and glucose were used as protein and polysaccharides standards, respectively.

The particle size distribution (PSD) was measured as described in 3.2.2.3, by a Malvern Mastersizer 2000 instrument (Worcestershire, UK) with a detection range of 0.02-2000 μm . The scattered light is detected by means of a detector that converts the signal to a size distribution based on volume or number. Each sample was measured 3 times.

Membrane fouling was evaluated by calculation of membrane filtration resistance. The total fouling resistance (R_t) can be calculated by Darcy's Law with temperature correction to 20 °C to account for the dependence of viscosity on temperature (Rosenberger et al., 2006):

$$Rt = \frac{\Delta P}{J \cdot \eta_T}, \quad (1)$$

$$\eta_T = \eta_{20^\circ\text{C}} \cdot e^{-0.0239(T-20)} \quad (2)$$

Where R_t is the total resistance (1/m), J is the permeate flux ($\text{m}^3/\text{m}^2\text{h}$), ΔP is the trans-membrane pressure difference (Pa), and η_T is the permeate dynamic viscosity (Pa·s). T is the permeate temperature in °C.

The one-way analysis of variance (ANOVA) was performed to identify the statistical significance of the experimental results by using the Statistical Package for the Social Science (SPSS) V18.0 produced by SPSS Incorporation (America). A significance level of 95% ($P < 0.05$) was selected.

Chapter 4

Results and Discussion

4.1 Performance and Membrane Fouling of SAnMBR for Biorefining

Effluent Treatment

4.1.1 COD removal

In this study, a hollow fiber SAnMBR was operated for over 5 months at a constant biogas sparging rate of 2.4 LPM. After 20 days acclimation, the mixed liquor suspended solids (MLSS) concentration was maintained at 10.7 ± 0.7 g/L for the rest days of operation (Fig. 4.1.1). The membrane flux was maintained at 8.4 ± 0.3 L/m² h throughout the operation. The organic loading rate (OLR) was controlled by changing the chemical oxygen demand (COD) concentration in the influent, starting from 3178 ± 55 mg COD/L followed by 5212 ± 89 mg COD/L and 7217 ± 255 mg COD/L. The whole operation could be divided into 3 stages according to the differences in OLR: the first 75 days with a lower OLR of 2.11 ± 0.09 kg COD/m³ d; day 76-day 138 with an OLR of 3.35 ± 0.14 kg COD/m³ d; in the third stage from day 138 it was expected to increase the OLR by increasing the influent COD concentration to 7000 mg/L, however, the flux decreased unexpectedly to no more than 4 L/m² h due to the severe membrane fouling. The average OLR in the third phase was 2.42 ± 0.24 kg COD/m³ d (Fig. 4.1.1).

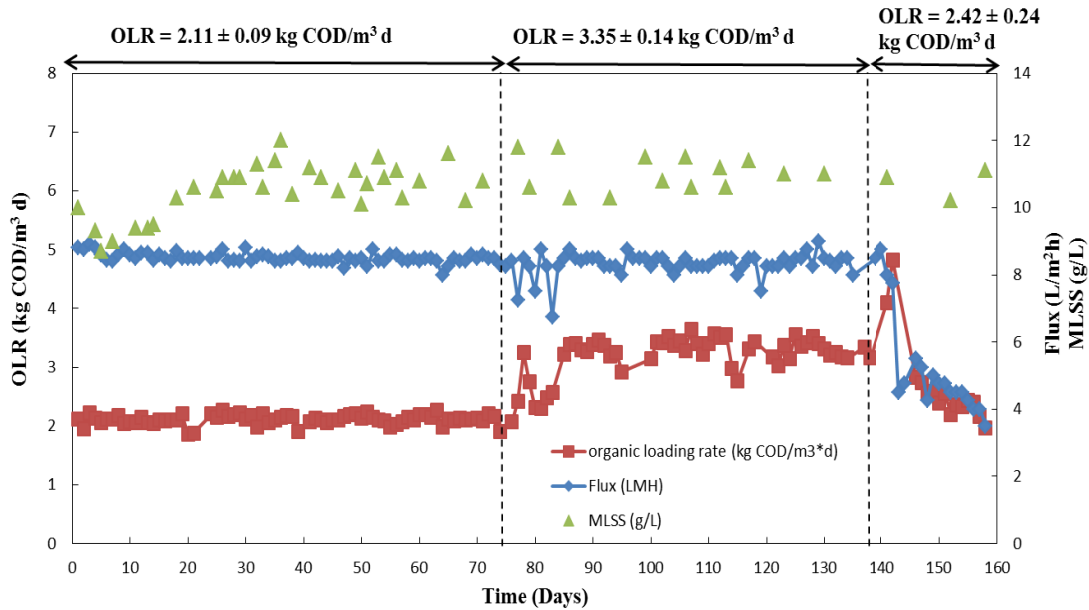
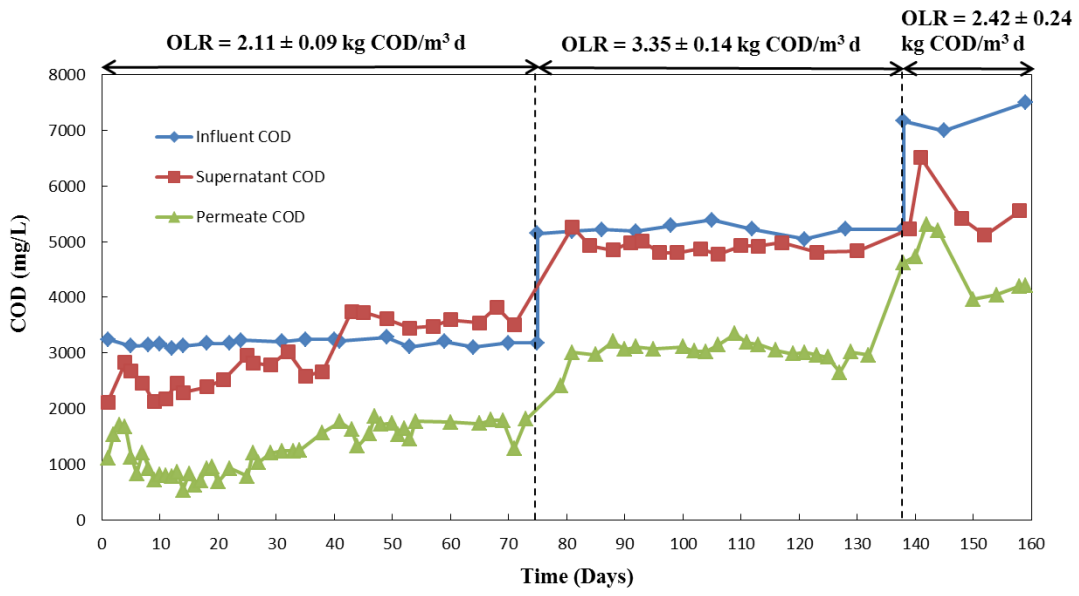


Fig. 4.1.1 Variations of MLSS, organic loading rate, and membrane flux.

At the steady-state with an OLR of $2.11 \pm 0.09 \text{ kg COD/m}^3 \text{ d}$, the residual COD value in permeate was about 1480 mg/L (Fig. 4.1.2). At an OLR of $3.35 \pm 0.14 \text{ kg COD/m}^3 \text{ d}$ from day 76, the steady permeate COD was about 2960-3180 mg/L. In addition, as shown in Fig. 4.1.2, the supernatant COD in the bioreactor was consistently higher than the permeate COD, indicating the retention of organic compounds by the membrane and the formed cake layer. These results are consistent with the findings of previous studies (Hernandez Rojas et al. 2005; Kurian et al. 2006). The significantly high supernatant COD which was even higher than the influent COD may contribute to the rapid membrane fouling as discussed later. The COD removal efficiency was about 45% under the tested OLRs (Fig. 4.1.3). The relatively low COD removal efficiency indicates that the inhibitions of methanogenic activity in the SANMBR.



=8u

Fig. 4.1.2 Variation of the influent, supernatant and permeate COD

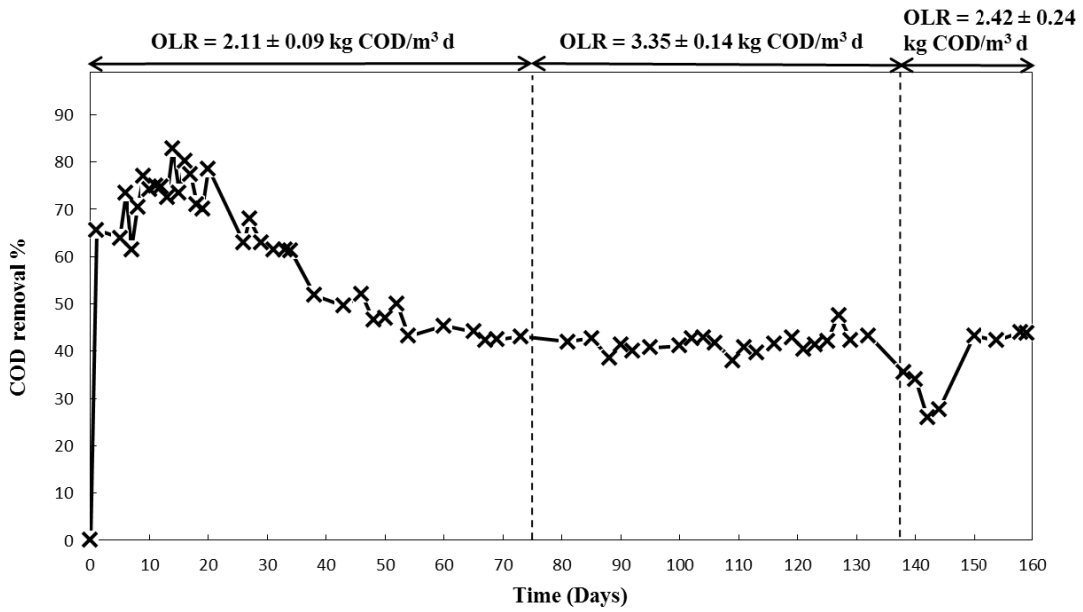


Fig. 4.1.3 COD removal efficiency

4.1.2 Biogas production

Fig. 4.1.4 shows the biogas production rate with experimental time. At an OLR of 2.11 ± 0.09 COD/m³ d, the biogas production rate was 0.29 ± 0.05 L/g COD removed with 50 – 70 % methane content (Fig. 4.1.5). After the OLR was increased to 3.35 ± 0.14 kg COD/m³ d, the biogas production rate reduced to less than 0.1 L/g COD removed and the methane content in the produced biogas was decreased to 40 – 50 %. Furthermore, the biogas production rate was sharply decreased to almost 0 as a response to the further increased influent COD concentration to 7000 mg/L. This suggests the loss of methanogenic activity at a high influent COD concentration, which is consistent with the finding of previous study in that no biogas was produced when glucose wastewater was anaerobically treated (Ren et al. 2006). The variation in influent concentration will affect F/M (food to microorganism ratio), which will affect the microbial metabolism, including the production of biogas. The decreased biogas yield indicated that a new balance was quickly achieved among the microbial groups at the new influent concentration. No biogas composition was tested after day 138 because no biogas was produced after the influent COD concentration increased to 7000 mg/L. The situation of biogas production presents that the SANMBR is feasible for treating synthetic biorefining effluent with low influent concentration. The reduction in biogas production rate and biogas content with the increase of the influent concentration reflects the limitation of the technology for high influent concentration of biorefining wastewater.

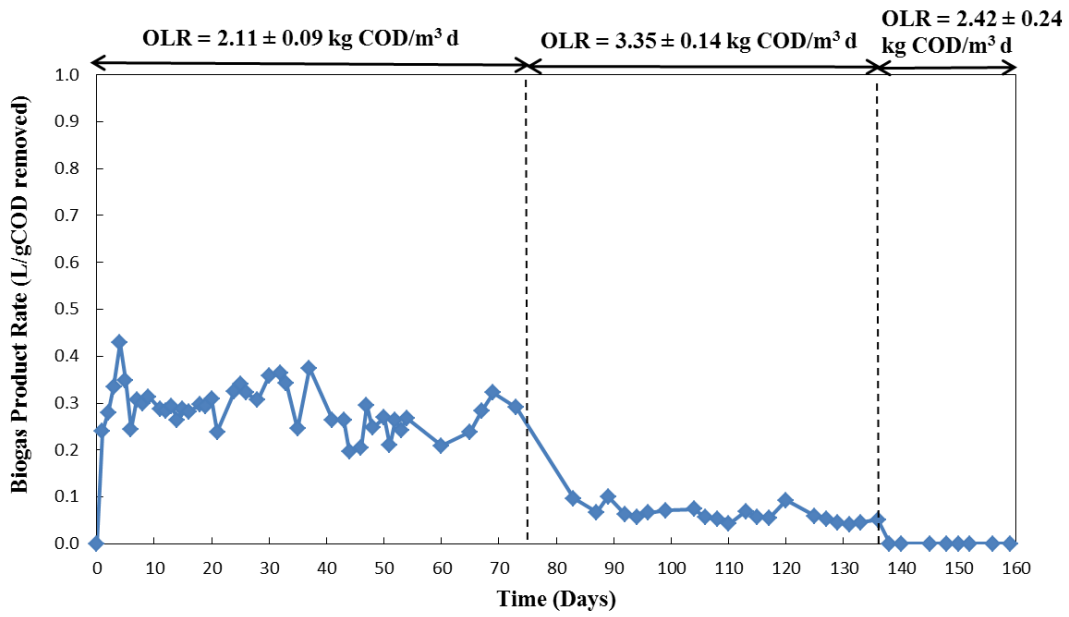


Fig. 4.1.4 Variation of biogas production rate

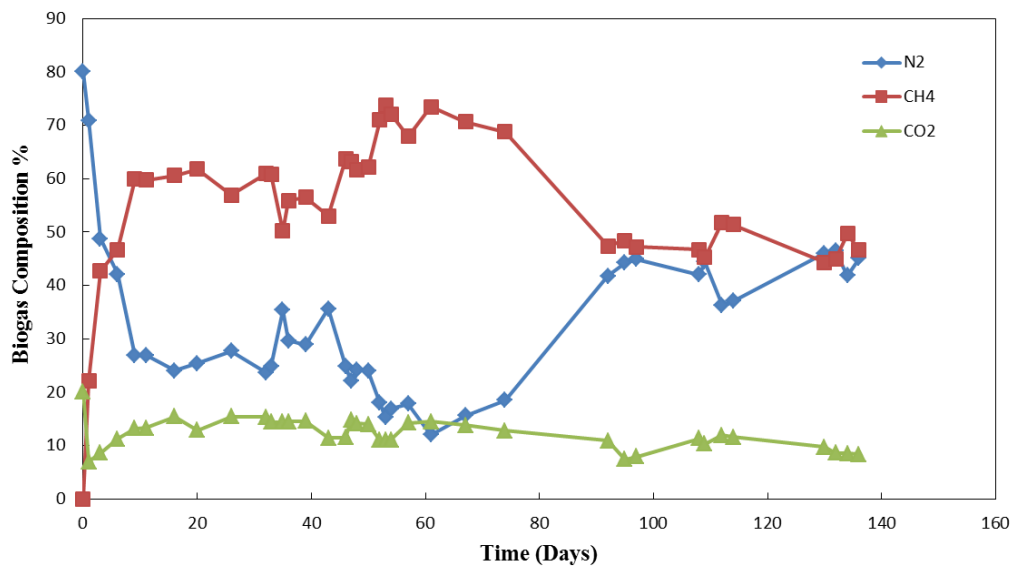


Fig. 4.1.5 Biogas composition

4.1.3 Transmembrane pressure (TMP) profiles

The TMP rise profiles in Fig. 4.1.6 present membrane fouling behavior under different OLRs. The TMP profiles at an OLR of 2.11 ± 0.09 and 3.35 ± 0.14 kg COD/m³ exhibit similar two-stage behaviour: a very low and steady TMP increase with subtle fluctuations at the first stage followed by an abrupt and rapid jump at the second stage. Preferably, membrane filtration should be operated under sustainable condition with a long-term continuous filtration mode. This finding is similar with other investigations in which an abrupt and rapid jump at the second stage was observed (Le-Clech et al. 2006, Qu et al. 2012, Zhang et al. 2006). As expected, a higher OLR corresponding to a higher influent concentration resulted in a faster membrane fouling and a steeper jump of TMP. This is consistent with the findings of Trussell et al. (2006) in that a high OLR increased membrane fouling rates. Also, a reactor with a higher OLR showed sudden increase of TMP, while a reactor with a lower OLR showed delayed increase of the pressure in Nagaoka's research (Nagaoka et al. 1996).

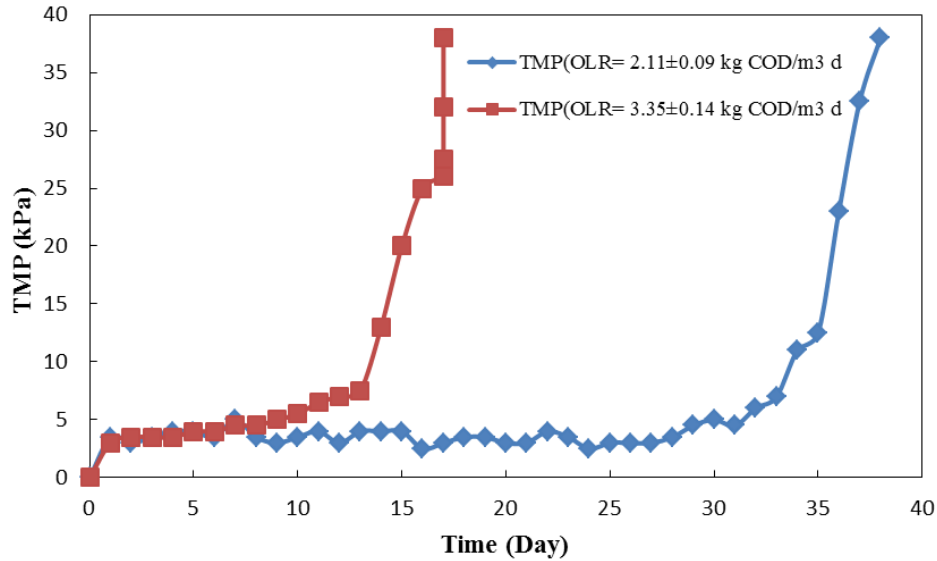


Fig. 4.1.6 Comparison of TMP profiles under different operating conditions

4.1.4 Particle size distributions (PSDs)

The particle size distributions of mixed liquor in SANMBR at different OLRs are shown in Fig. 4.1.7. With the increase in OLR, the mean particle size shifted from 65 to 53 μm . It is also interesting to note that there were more small particles ($2 \mu\text{m} < \text{diameter} < 10 \mu\text{m}$) in the bulk sludge at the higher OLR. The PSDs of cake layer (Fig. 4.1.8) demonstrate the similar trend as the PSDs of mixed liquor do: an increase in OLR leads to a decrease in particle size. A significant difference in the particle size distribution of cake sludge at the two OLRs was observed. When compared to the bulk sludge particle size distributions as shown in Fig. 4.1.7, the cake sludge particles contained much smaller particles. The small particles can be accumulated in the cake layer because smaller flocs have lower back transport and more preferably deposit on the membrane surface than the large particles do (Bae and Tak 2005, Gao et al. 2010). Meng et al (2007) and Wang and Tarabara (2008) reported that mean size of the washed liquid of cake layer was much

lower than that of bulk sludge. Additionally, due to the fact that the size of small particles is actually much larger than the pore size of the membrane ($0.04\ \mu\text{m}$), the small particles cannot block the pore entrances instead of forming the cake layer on the membrane surface.

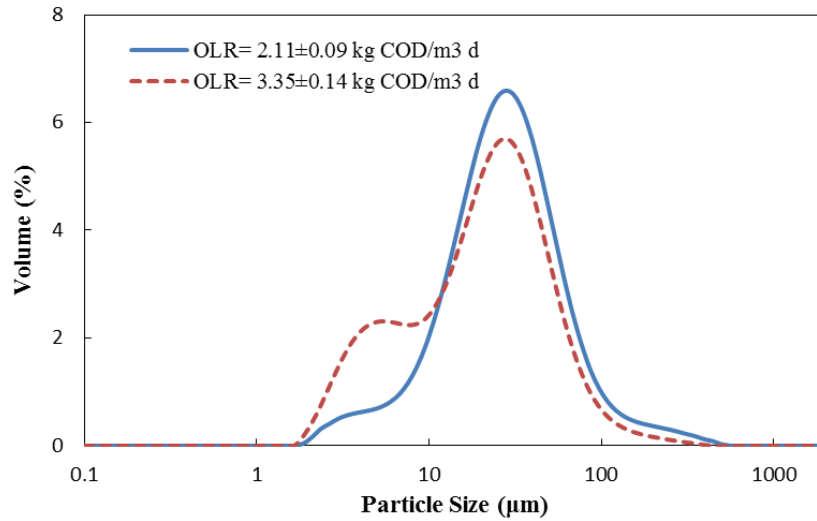


Fig. 4.1.7 Particle size distributions of bulk sludge under different OLRs

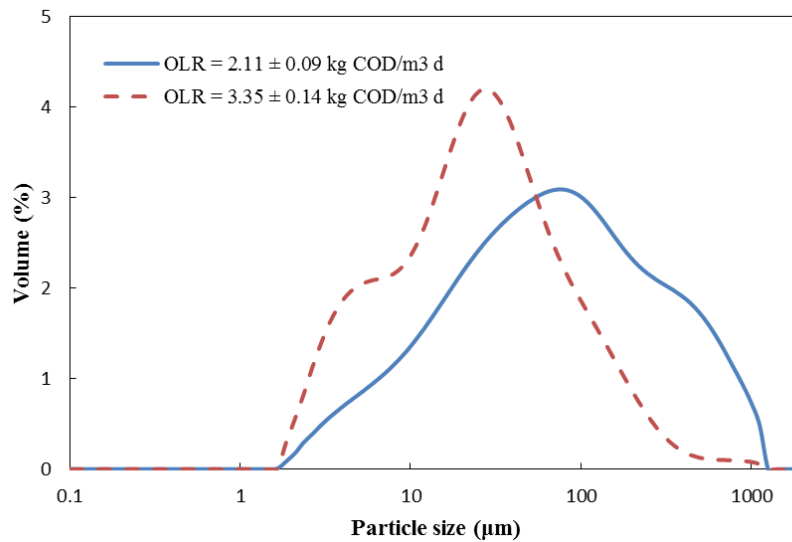


Fig. 4.1.8 Particle size distributions of cake layer under different OLRs

4.1.4 Extracellular Polymeric Substances (EPS)

EPS has been identified as a key membrane fouling parameter in MBR system (Meng et al. 2009). Fig. 4.1.9 (a) shows the comparison of bound EPS of the bulk sludge in the SAnMBR under different OLRs. Proteins were found to be the dominant component in the EPS at the low OLR of 2.11 ± 0.09 kg COD/m³ d. However, the polysaccharides were the major component in the EPS at the high OLR of 3.35 ± 0.14 kg COD/m³ d. With an increase in OLR, the total EPS increased (Fig. 4.1.9 (a)) while the protein to polysaccharide (PN/PS) ratio decreased (Fig. 4.1.9 (b)). The influent COD concentration controlled the food to microorganisms (F/M) ratio: the F/M increased with an increase in the influent COD concentration. The EPS in the bulk sludge is growth-related and produced in direct proportion to substrate utilization, thus there are more EPS generation as F/M ratio increases (Meng et al. 2009). It was similarly reported that the increased F/M induced high EPS concentration and high sludge viscosity (Meng et al. 2007). The decrease in the PN/PS ratio could correlate to the increase of non-flocculating flocs with the increase of OLR. It has been indicated in early research (Liao et al. 2001) that a decrease in the PN/PS ratio in EPS led to poorer bioflocculation, which caused sludge particles shifting to smaller sizes (Fig. 4.1.7) and resulted in higher potential of membrane fouling.

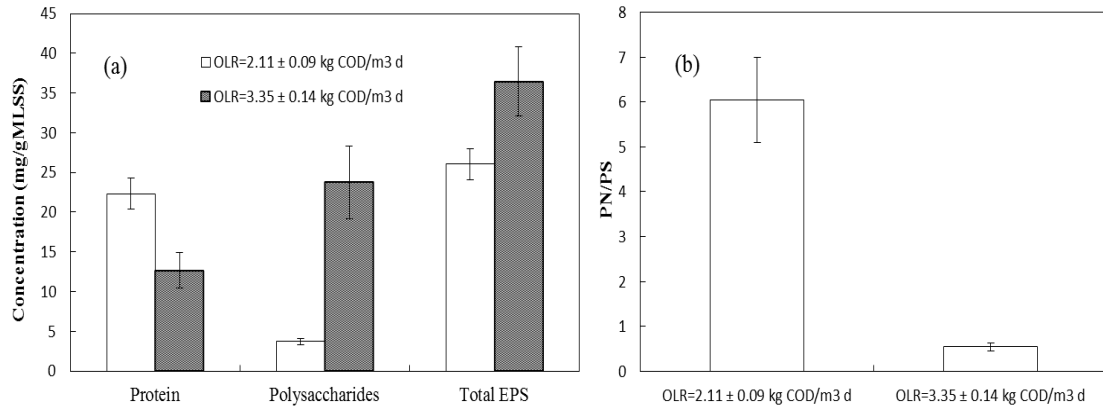


Fig. 4.1.9 EPS contents (a) and PN/PS (b) of bulk sludge under different OLRs

Fig. 4.1.10 presents the EPS of cake sludge at an OLR of 2.11 ± 0.09 kg COD/m³ d and 3.35 ± 0.14 kg COD/m³ d. Similar to the findings in the bulk sludge, proteins were the dominant component in the EPS at the low OLR of 2.11 ± 0.09 kg COD/m³ d, while the polysaccharides were the major component in the EPS at the high OLR of 3.35 ± 0.14 kg COD/m³ d. The total EPS increased (Fig. 4.1.10 (a)) but the PN/PS ratio decreased (Fig. 4.1.10 (b)) as the OLR increased. The similar trend between the cake sludge EPS and the bulk sludge EPS can be explained by the fact that the bulk sludge in the SAnMBR was the source of the cake sludge on the membrane in the reactor (Wang et al. 2007).

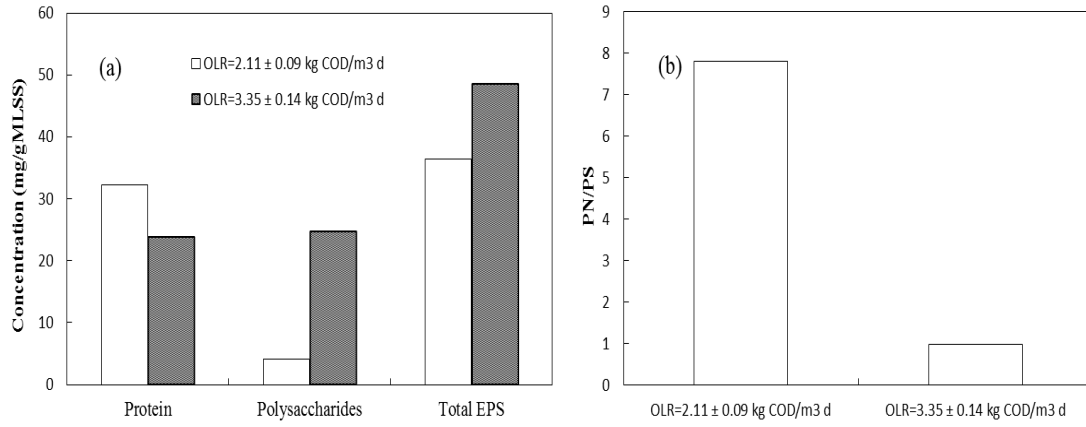


Fig. 4.1.10 EPS contents (a) and PN/PS (b) of cake sludge under different OLRs

4.2 Performance and Membrane Fouling of SAnMBR for TMP Wastewater Treatment

4.2.1 COD removal

The hollow fiber SAnMBR was operated at three biogas sparging rates (2.4, 4.3 and 6.1L/min (LPM)). The whole operation period was divided into 4 phases according to the differences in biogas sparging rates and influent COD concentrations as illustrated in Table 4.2.1.

Table 4.2.1 Operating conditions at each stage

	Start-up	Phase 1	Phase 2	Phase 3	Phase 4
Days	0-20 th	21 st -60 th	61 st - 89 th	90 th -131 st	132 nd -160 th
Influent COD (mg/L)	3022 ± 100	3022 ± 100	3022 ± 100	4599 ± 259	4599 ± 259
Biogas Sparging Rate (LPM)	2.4	2.4	4.3	4.3	6.1

Throughout the 160 days of operation, the mixed liquor suspended solids (MLSS) concentration was maintained at 12.0 ± 0.7 g/L (Fig. 4.2.1). The slight increase in MLSS was observed at a higher influent COD concentration because sufficient substrates promoted the biomass growth. The first 20 days were considered as the initial start-up period to allow the acclimation of the biomass. During this period, the COD removal efficiency gradually increased to over 80% (Fig. 4.2.3), and then remained at a relatively constant level during the steady-state operation. The decline in reactor performance observed during day 110 and 128 was due to a feed toxic shock caused by using a new drum of thermo-mechanical pulping wastewater. The COD removal efficiency recovered

to above 80% on day 139 after the feed toxic shock. Phases 1, 2, 3, 4 corresponded to an organic loading rate (OLR) of 2.13 ± 0.60 , 2.03 ± 0.35 , 2.23 ± 0.14 , 2.64 ± 0.80 and 3.35 ± 0.17 kg COD/m³ d, respectively. Although the highest OLR tested in this study was 3.5 kg/ m³ d, due to the limitation of the influent COD concentration of the real industrial thermomechanical pulping wastewater, the highest OLR the system could handle was not achieved. Considering the low MLSS concentration (12.0 ± 0.7 g/L) used in this study, the OLR, expressed as kg COD/kg MLSS d, is 0.27, which is close to the results of some high rate AnMBRs (Grant et al., 2007).

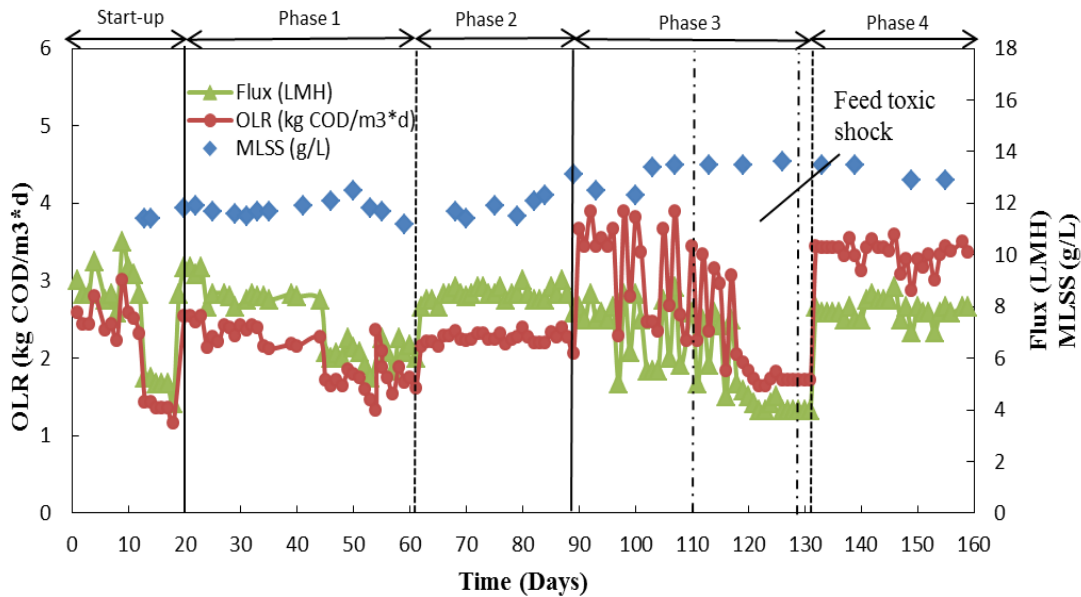


Fig. 4.2.1 Variations of MLSS, organic loading rate, and membrane flux.

At the beginning, the SAnMBR was operated at a biogas sparging rate of 2.4 LPM with an influent COD of 3022 ± 100 mg/L (Fig. 4.2.1). The membrane flux first maintained at 8.6 ± 0.5 L/m² h followed by a drop to 6.2 ± 0.4 L/m² h at this operating condition. When the biogas sparging rate was adjusted to 4.3 LPM on day 61, the

membrane flux was brought back to around $8.5 \text{ L/m}^2 \text{ h}$ again. In practical operation, both membrane flux and biogas sparging rate are very important for effective permeate production rate, energy consumption, and membrane fouling control. The higher biogas sparging rate increased the turbulence in the mixed liquor and hollow fiber membrane movement, which effectively prevented the loss of filtration area by scouring the particles and deposited materials away from the membrane surface. After the influent COD concentration was increased to $4599 \pm 259 \text{ mg/L}$, the membrane flux fluctuated between $4.5\text{-}8.2 \text{ L/m}^2 \text{ h}$. The low sustainable flux may be the result of the increased mixed liquor viscosity caused by the high influent COD concentration and slightly increased MLSS concentration. After the feed toxic shock, the biogas sparging rate was increased to 6.1 LPM for the purpose of maintaining a relatively high flux around $8 \text{ L/m}^2 \text{ h}$.

At the steady-state operation with an influent COD of $3022 \pm 100 \text{ mg/L}$, COD and BOD_5 values of permeate were about 430 mg/L and 85 mg/L , respectively (Fig. 4.2.2). The change in biogas sparging rate did not affect treatment performances in the hollow fiber SAnMBR. At an influent COD of $4599 \pm 259 \text{ mg/L}$ since day 89, steady-state permeate COD was about $610\text{-}810 \text{ mg/L}$, and permeate BOD_5 was 266 mg/L . In addition, as shown in Fig. 4.2.2, the soluble COD showed a similar trend with permeate COD. The stable and high COD removal efficiency in Fig. 4.2.3 shows that the SAnMBR presents operational flexibility under the variations in feed strength and biogas sparging rate. In industrial applications, this is considered as advantage, as the influent tends to vary from time to time. It is always appealing to improve the treatment efficiency and stability for industrial processes.

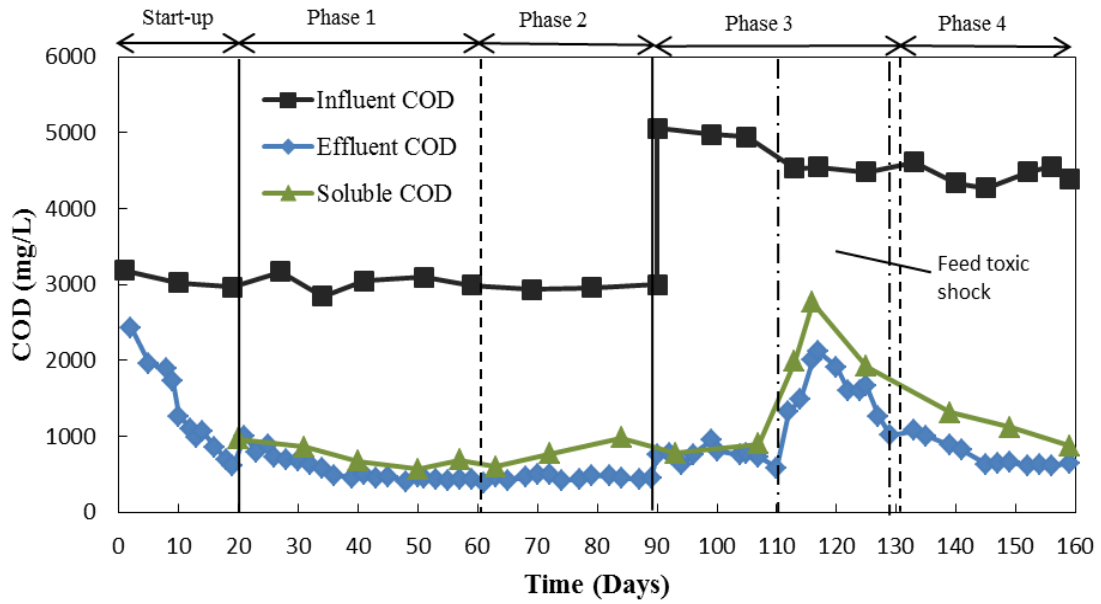


Fig. 4.2.2 Variation of the influent, supernatant and permeate COD

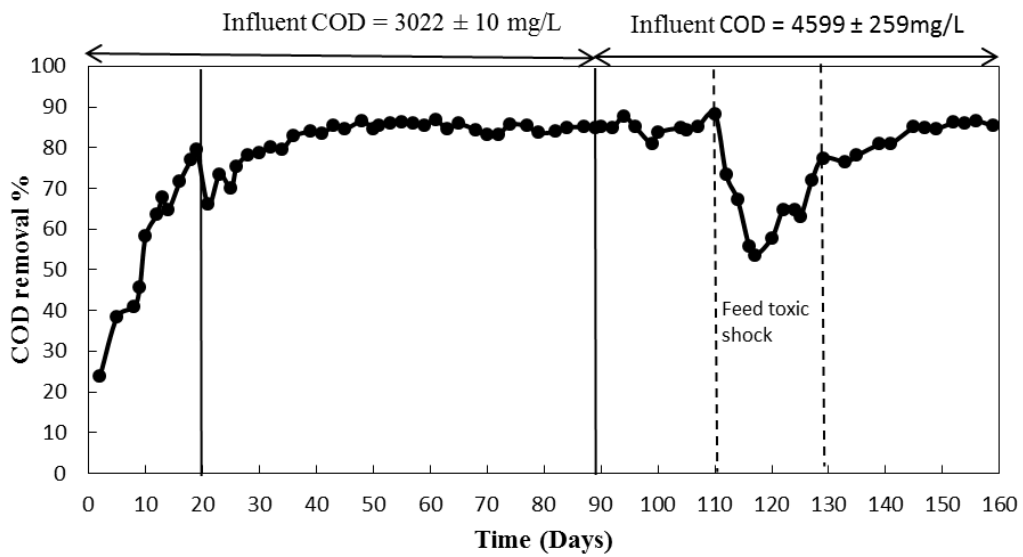


Fig. 4.2.3 COD removal efficiency

4.2.2 Biogas production

Fig. 4.2.4 presents the biogas composition throughout the operation, showing that the methane content was 70 - 80 % in produced biogas with a biogas yield of 0.20 - 0.27 L/g COD removed. After the influent COD increased from 3000 to 5000 mg/L, the biogas yield slightly reduced from 0.26 ± 0.03 to 0.22 ± 0.01 L/g COD removed (Fig. 4.2.5). The increase in biogas sparging rate did not affect the biogas production no matter in phase 2 or phase 4. The variation in influent concentration will affect F/M (food to microorganism ratio), which will affect the microbial metabolism, including the production of biogas. The decreased biogas yield indicated a new balance was quickly achieved among the microbial groups at the new influent concentration. No biogas composition was tested from day 110-120 because no biogas was produced after the feed toxic shock. Although the SAnMBR successfully pulled through the crisis, it still reflected the presence of inhibitors in the feed. Most of the organic inhibitors are only biodegradable to a certain extent, thus the inhibitors to the anaerobic digestion process present in high strength thermo-mechanical pulping wastewater might be responsible for the lower biogas yield (Ali and Sreekrishnan, 2001; Chen et al. 2008).

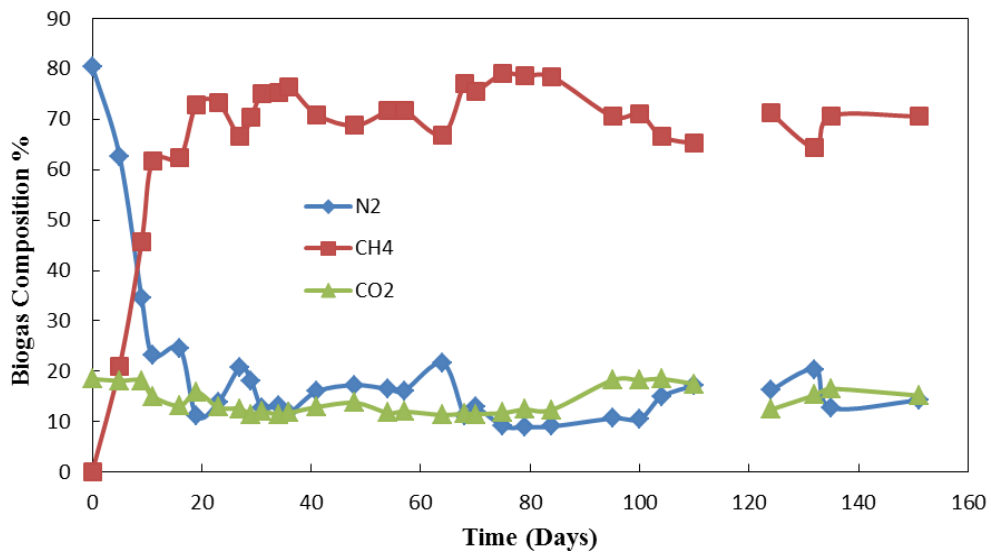


Fig. 4.2.4 Biogas composition

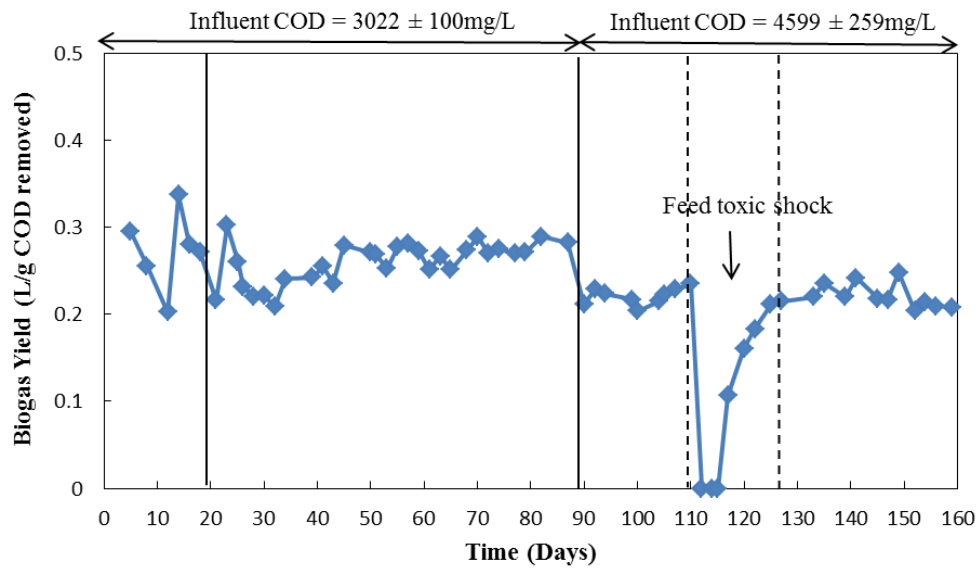


Fig. 4.2.5 Variation of biogas production rate

4.2.3 Particle size distributions (PSDs)

Figure 4.2.6 shows the effect of biogas sparging rate on the particle size distributions of sludge flocs at different influent COD concentrations. At a influent COD of 3022 ± 100 mg/L, an increase in biogas sparging rate from 2.4 to 4.3 LPM (phase 1 vs. phase 2) resulted in a reduction of the number of large size particles but no significant impact on the lower size range (small flocs) of sludge flocs. The reduction in large floc size could also be at least partially the results of nature reaction of floc size from granular sludge (large size) (the sludge seed) to conventional sludge in a CSTR, due to the change in bioreactor configuration (UASB to CSTR). No further reduction in floc size was observed at the high influent COD concentration (4599 ± 259 mg/L), although the biogas sparging rate was further increased to 6.1LPM (phase 3 vs. phase 4). The results suggest that sludge floc size would change to adapt to new environmental and operating conditions. After that, the sludge floc size was relatively stable and not further affected by the biogas sparging rate under tested conditions.

The PSDs of cake layer demonstrate the similar trends with the bulk sludge at four phases (Fig. 4.2.7), although they are all bimodal instead of single peaked distribution of bulk sludge. More small particles were accumulated in the cake layer because smaller flocs have lower back transport and more preferably deposit on the membrane surface than the large particles. The results of bimodal PSD of cake layer are consistent with that of previous publications (Gao et al. 2011a, Meng et al. 2007).

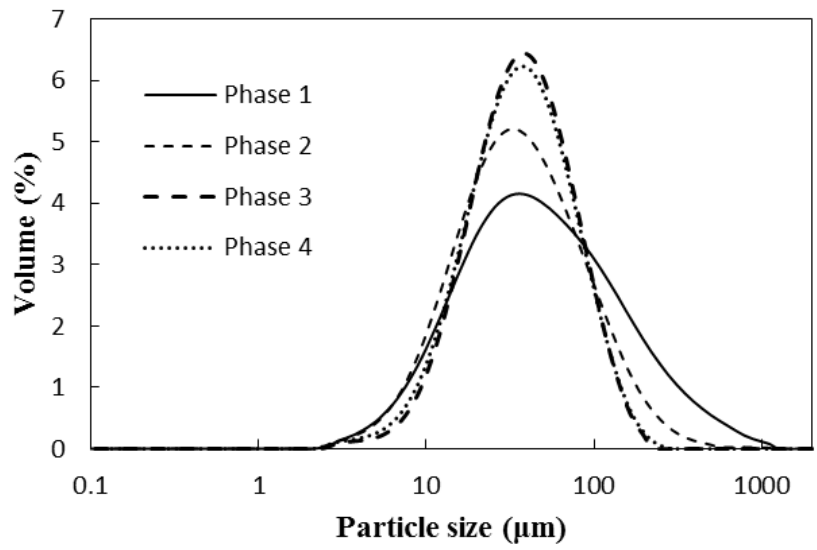


Fig. 4.2.6 Particle size distributions of sludge flocs under different conditions

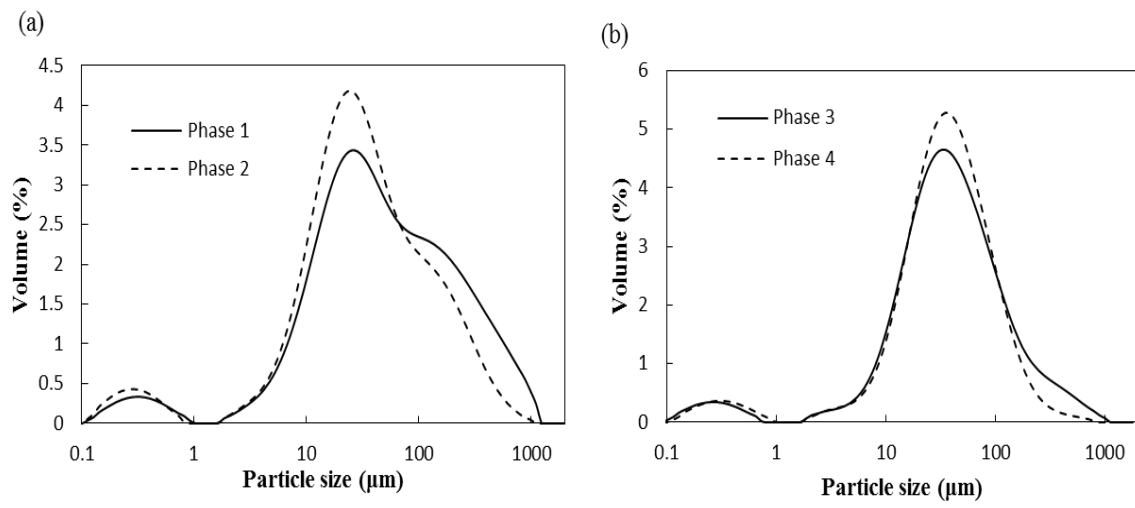


Fig. 4.2.7 Particle size distributions of cake layer under different conditions

4.2.4 Extracellular Polymeric Substances (EPS)

Fig. 4.2.8 shows the protein and carbohydrate concentrations normalized to biomass (as MLSS). Phase 3 and 4 had higher EPS concentrations (both protein and polysaccharides) than phase 1 and 2, suggesting that more EPS was produced at a higher feed concentration because EPS production is in direct proportion to substrate utilization. The results are consistent with the findings of Zhou et al. (2007). There is no significant difference between phase 1 and phase 2. This indicated that the increase in biogas sparging rate from 2.4 to 4.3 LPM (with the same feed concentration of 3022 ± 100 mg/L) did not affect the EPS contents. On the other hand, the further increase in EPS production in phase 4, as compared to phase 3, could be attributed to both the effect of OLR and biogas sparging rate. A large fluctuation in OLR was observed in phase 3, due to the challenge in maintaining the membrane flux at $8 \text{ L/m}^2 \text{ h}$. The increased biogas sparging rate (6.1 LPM) might result in a reduction of bound EPS, due to the stripping of EPS from sludge flocs under higher shear stress (Mennitia et al. 2009). The increased OLR in phase 4 could enhance EPS production, as compared to phase 3. The net increase in EPS production in phase 4 suggests that OLR was the dominant factor in affecting EPS production. Bound EPS plays an important role in maintaining architecture of sludge flocs. The increased EPS production in phase 3, as compared to phase 2, led to an increased membrane fouling and thus needs the use of a high biogas sparging rate (6.1LPM) to maintain the membrane flux at $8.0 \text{ L/m}^2 \cdot \text{h}$ for long term operation in phase 4.

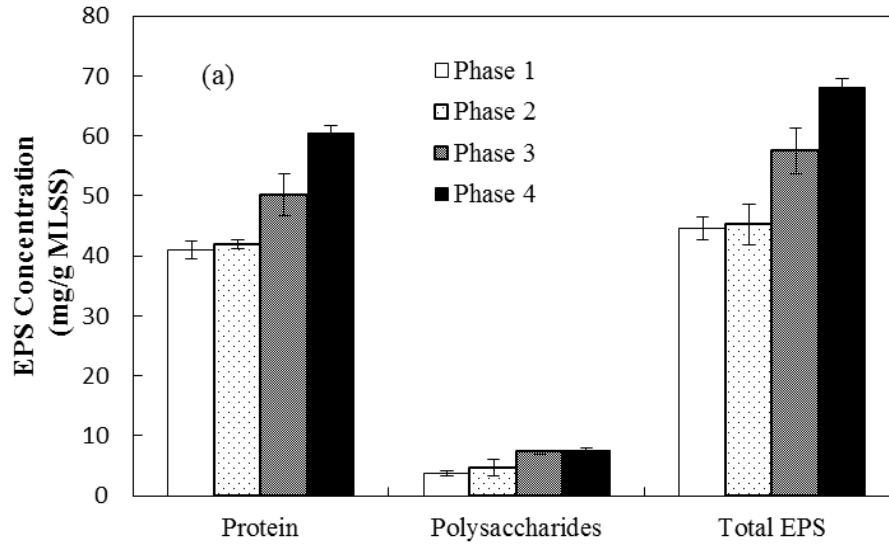


Fig. 4.2.8 EPS contents at different operating conditions

4.2.5 TMP profiles

The four TMP rise profiles in Fig. 4.2.9 reflect membrane fouling behavior at different biogas sparging rates and influent CODs. Phase 3 shows a rapid rise in TMP, while Phase 1, 2, and 4 shows a slow increase followed by an abrupt increase, namely TMP jump. Preferably, membrane filtration should be operated under sustainable flux condition with a long-term continuous filtration mode.

At the same biogas sparging rate (4.3 LPM), an increase in COD concentration reduced the time of stable operation (phase 2 vs. phase 3). At an influent COD concentration of 3022 ± 100 mg/L, the TMP increased much more slower than that at the influent COD concentration of 4599 ± 259 mg/L (phase 2 vs. phase 3). The sustainable flux was reduced from 8-8.5 L/m² h to 4.5 L/m² h after the influent COD was increased from 3022 ± 100 mg/L to 4599 ± 259 mg/L. Particle size distribution of sludge flocs is an

important factor to affect membrane fouling in MBRs. Due to a significant amount of colloidal particles (0.1-10 μm) existing in the influent (Fig. 4.2.10), the increased influent COD could lead to great accumulation of colloidal particles in the mixed liquor. These small particles have been reported to be more prone to form reversible/irreversible fouling on/within membrane than large flocs (Lin et al. 2009). In other words, the membrane can be more easily fouled. Also, high amounts of bound EPS have a negative impact on the filterability of sludge, leading to loss of membrane permeability (Al-Halbouni et al. 2008). Therefore, the higher F/M ratio at higher influent concentration was found to promote the production of EPS (Fig. 4.2.8), which is believed to be the reason of greater fouling tendency.

On the other hand, when the SAnMBR was fed with the same influent COD concentration, an increase in biogas sparging rate corresponded to a longer stable operation time. At the influent COD concentration of $3022 \pm 100 \text{ mg/L}$, the TMP increased gradually for up to 24 days followed by a TMP jump at the biogas sparging rate of 4.3 LPM. Nevertheless, at the biogas sparging rate of 2.4 LPM, the TMP jump occurred after 10 days of operation. Similar phenomenon was observed in Fig. 4.2.8 for the influent COD concentration of $4599 \pm 259 \text{ mg/L}$. TMP increased right after the reactor started to run at 4.3 LPM (phase 3). When the biogas sparging rate increased to 6.1 LPM, a stable membrane flux of $8 \text{ L/m}^2\text{h}$ could be lasted 6 days before the TMP jump. No biogas sparging rate higher than 6.1 LPM was tested, due to the maximum pump capacity of biogas sparging pump. It is anticipated that a longer operation time at a stable membrane flux can be achieved if a higher biogas sparging rate (like in pilot-scale and

full-scale operation) is available. The results suggest that membrane fouling can be effectively mitigated by enhanced biogas sparging intensity.

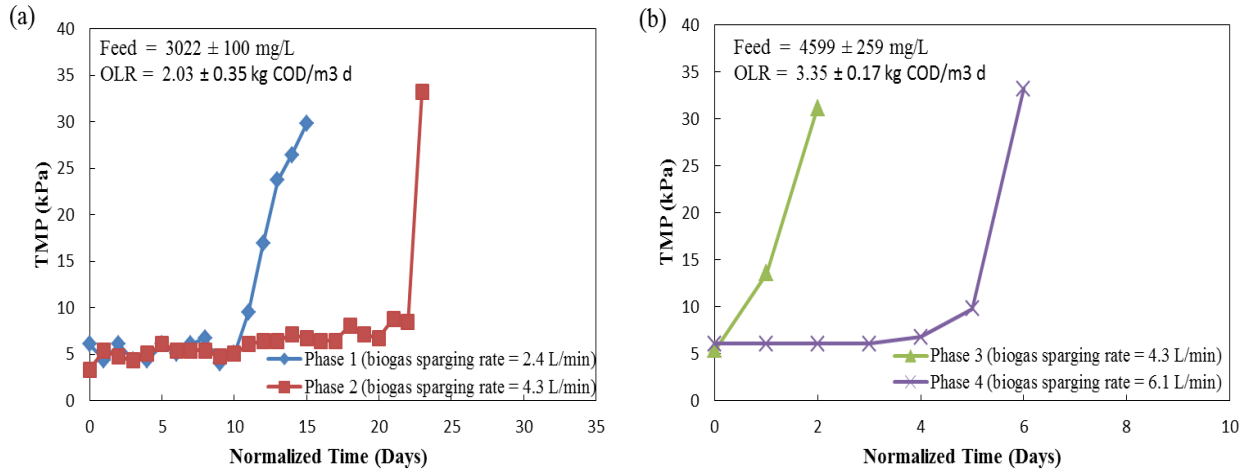


Fig. 4.2.9 Comparison of TMP profiles at different operating conditions

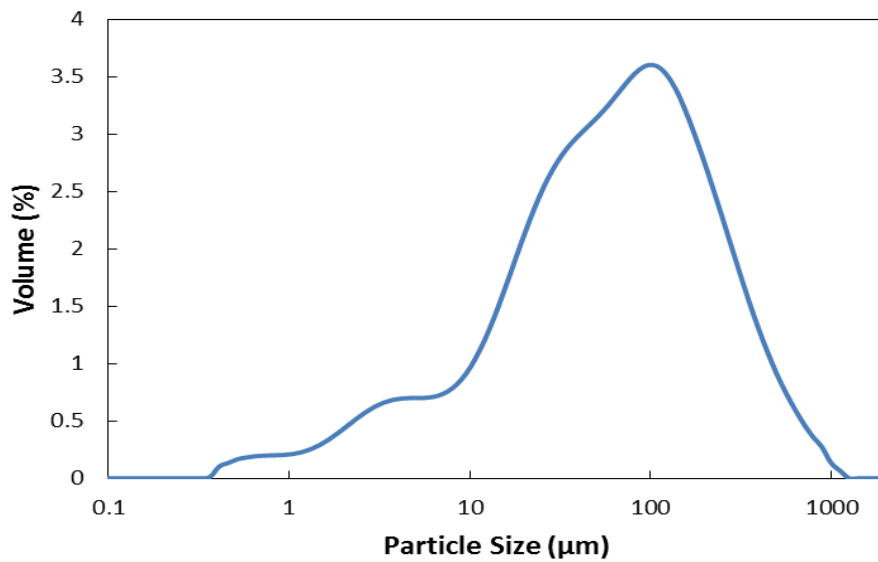


Fig. 4.2.10 Feed particle size distribution

4.2.6 Fouling characteristics

Sludge cake layer formation was identified as the dominant mechanism of membrane fouling in SAnMBRs. The fouling layer samples were characterized by COM, SEM-EDX, and FTIR after 25 and 4 days operation at phase 2 and 4, respectively.

Element analysis was further performed in order to identify the chemical components of the foulants by EDX analysis (Fig. 4.2.11). Inorganic fouling was detected for the samples without clear presence of cake layer on membrane. The elements of C, N, O, Na, Mg, Al, P, and S were detected, as shown in Fig. 4.2.11. Al and Mg are the two dominant inorganic foulants. The concentrations of Al and Mg are higher for fouled membrane with clear presence of cake layer, as compared to that without clear presence of cake layer on membrane. The origin of the inorganic foulants in the SAnMBR can be the metal clusters or metal ions present in the influent and the accumulation of trace metal element solution added. The deposition of inorganic foulants may play a key role in the formation of the strongly attached cake layer through concentration polarization, charge neutralization and bridging, thereby limiting membrane permeability in anaerobic bioreactor.

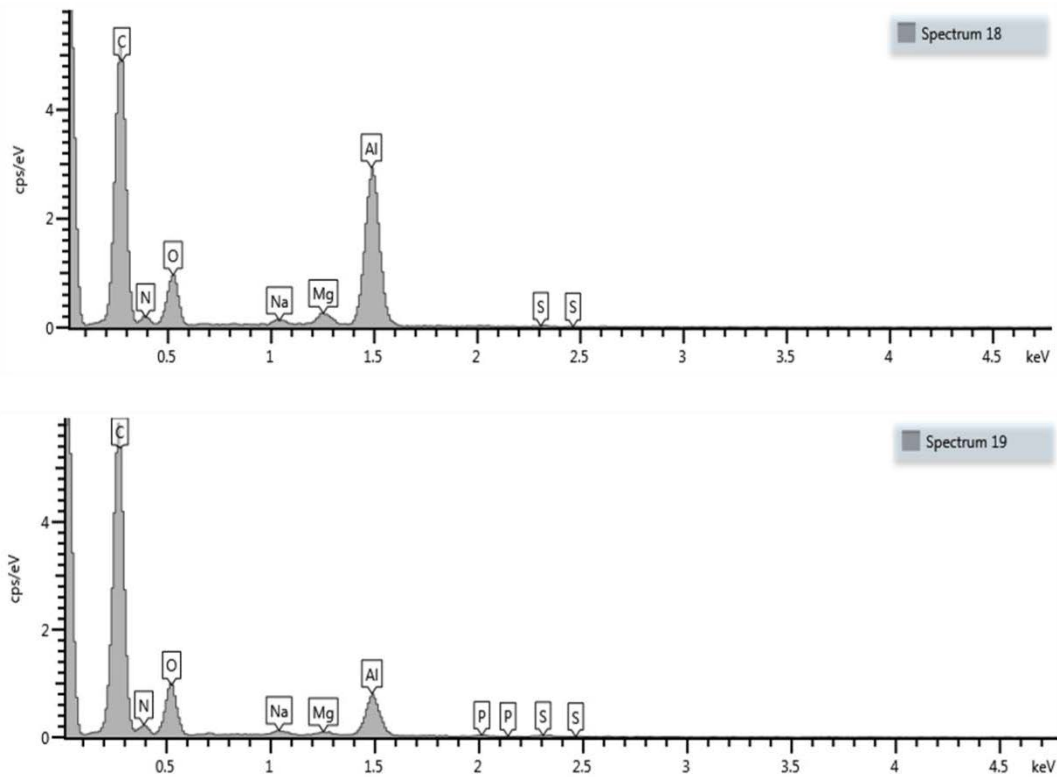


Fig. 4.2.11 EDX analysis for cake layer on fouled membrane surface(Spectrum 18) and membrane with no visible cake layer (Spectrum 19).

The FTIR spectra of membrane foulants are presented in Fig. 4.2.12. The cake layer contained proteins as indicated by the peaks at 1659 cm^{-1} (stretching vibration of C=O and C–N amide I) and 1545 cm^{-1} (N–H deformation and C=N stretching amide II), and polysaccharides as indicated by peaks at 3341 cm^{-1} (stretching of the O–H bonds) and 1049 cm^{-1} (C–O stretching, polysaccharides, aromatics, characteristics for polysaccharides). The asymmetrical stretching peak was noticed at 1726 cm^{-1} , suggesting the presence of carboxyl groups and representing typical characteristics of humic acids. Peaks in the vicinity of 2947 , 2899 and 1427 cm^{-1} are indicative of the C–H bonds in the alkanes class. By the FTIR spectra, the major components of the foulants were identified as proteins, polysaccharides and humic acids materials, indicating a significant organic

fouling. With the assistance of these biopolymers, sludge flocs would catch metal clusters and metal ions present in the mixed liquor during the development of cake layer along the hollow fiber membranes. As a result, the combined effects of organic fouling and inorganic precipitation can enhance the membrane fouling problem in this SAnMBR system.

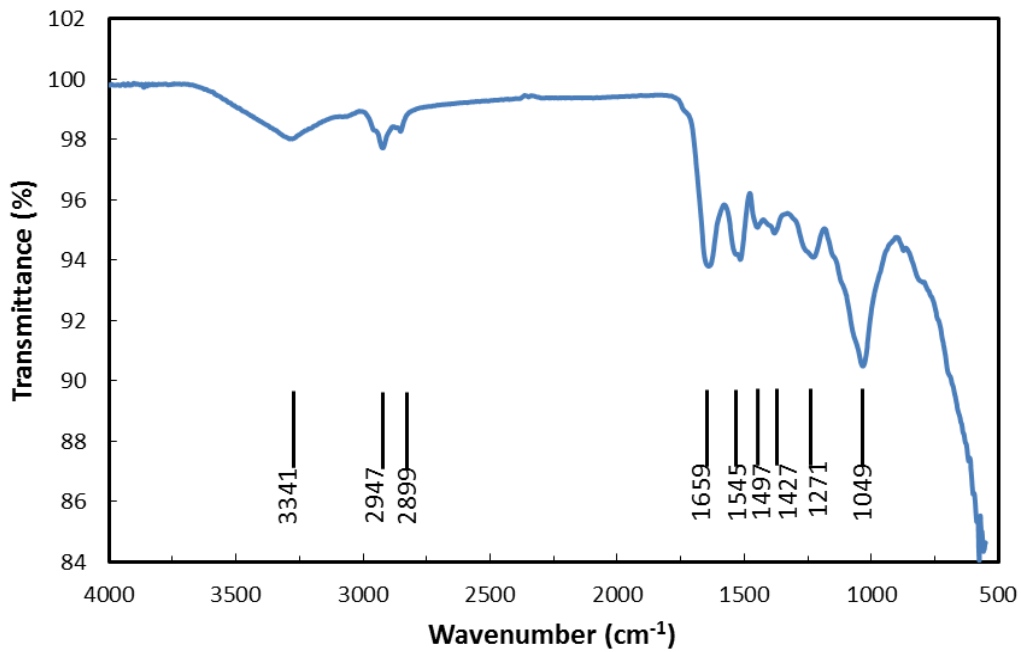


Fig. 4.2.12 FTIR spectra of fouled membrane surface

Non-uniform sludge deposition was observed along the hollow fiber and within the fiber bundle in this study. Measurement of membrane filtration resistance indicates that sludge cake layer accounts for more than 90% of the total filtration resistance. Citric acid cleaning can effectively reinstall the membrane flux. Cake layer thickness from the central part of the hollow fibers is observed by COM (Fig. 4.2.13). The cake layer was around 40 μ m after 25 days operation at phase 2 and 30 μ m after 4 days operation at phase 4. SEM images specifically reveal the fouled hollow fiber membrane surface with

and without cake layer in details (Fig. 4.2.14). The accumulation of the organic and inorganic foulants slowly reduced the effective filtration area, following a gradually increased TMP required to maintain the same flux observed in Fig. 4.2.9. For the abrupt TMP rise, several possible mechanisms have been proposed (Zhang et al. 2006), such as local flux effect, pore narrowing, pore loss and percolation theory. In the present study, the reduction in effective membrane surface area, due to sludge cake formation, could be the dominant mechanism of TMP jump.

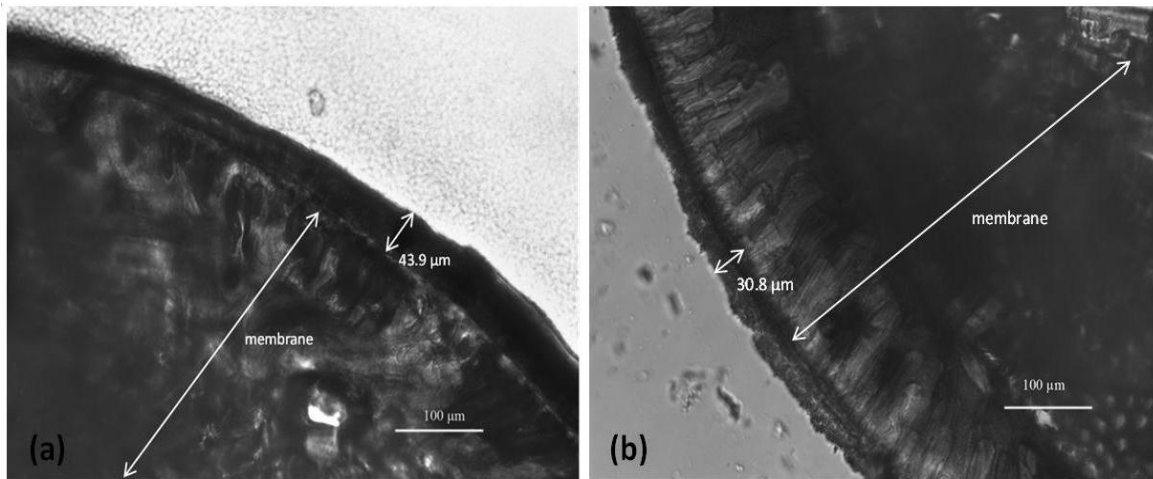


Fig. 4.2.13 Cake layer thickness observed by COM (a) Phase 2 (cake age: 25 days) (b) Phase 4 (cake age: 4 days)

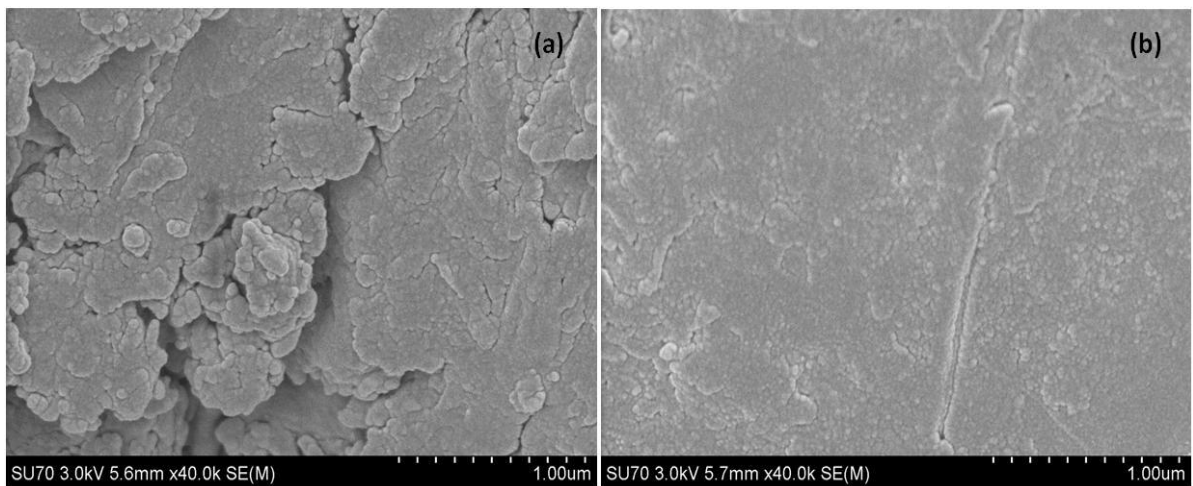


Fig. 4.2.14 SEM images of the (a) cake layer on fouled membrane surface (b) fouled membrane with no visible cake layer

4.3 Wastewater and Mixed Liquor Characteristics and Their Role in Membrane Fouling

4.3.1 Particle size distribution of wastewaters and mixed liquor

The particle size distributions (PSDs) of feed wastewaters and mixed liquor in SAnMBR and TSAMBR systems are shown in Fig. 4.3.1. As shown in Fig. 4.3.1(a) and (b), the two types of wastewaters used in either the SAnMBR system or the TSAMBR systems showed significant difference in PSDs. It is noted that the TMP whitewater contained a larger amount of colloidal particles in the size range of 1-10 μm than that of the TMP pressate 1 treated by the SAnMBR system. Similarly, the TMP wastewater contained a significantly larger amount of colloidal particles in the size range of 0.1-10 μm than that of the TMP pressate 2 treated by the TSAMBR system.

The PSDs of mixed liquor in the SAnMBR system for TMP pressate 1 and TMP whitewater treatment were significantly different, as shown in Fig. 4.3.1 (c). A bimodal curve was observed in TMP pressate 1 treatment whereas sludge particles from TMP whitewater treatment showed a unimodal distribution with one peak. The results of PSDs in mixed liquors are consistent with the results of PSDs in feed wastewaters in that particles in the TMP pressate 1 treatment were larger than that in TMP whitewater treatment. Part of the large particles in the second peak might be from the feed particles in TMP pressate 1, as both the feed and mixed liquor contained this size fraction of particles as shown in Fig. 4.3.1(a) and 4.3.1(c). The results suggested that the PSD of the feed wastewater can partially influence the PSD of the mixed liquor in SAnMBR. On the other hand, the PSD of mixed liquor for TMP pressate 2 treatment was similar to that

from TMP wastewater treatment in the TSAMBR system, as shown in Fig. 4.3.1 (d), despite the difference of fine particles distribution in TMP pressate 2 and TMP wastewater showed in Fig. 4.3.1(b). This result suggests that the sludge particles from anaerobic treatment were generally smaller than that from thermophilic aerobic treatment.

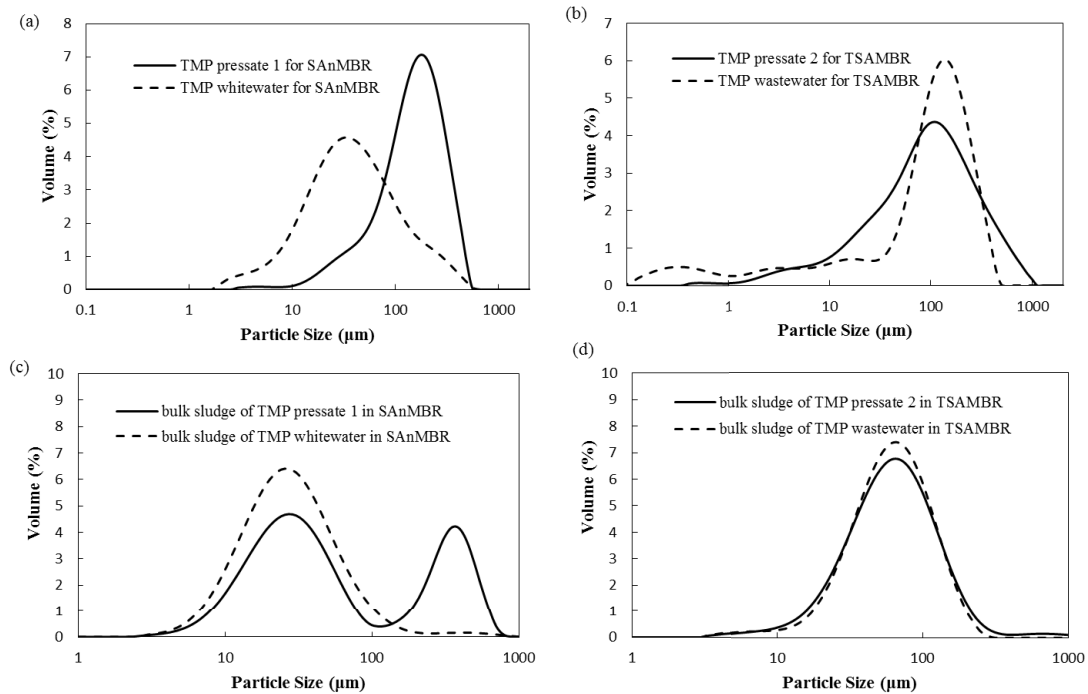


Fig. 4.3.1 Particle size distribution of (a) feed wastewater (TMP pressate 1 and TMP whitewater) for SANMBR, (b) feed wastewater (TMP pressate 2 and TMP wastewater) for TSAMBR, (c) mixed liquor in SANMBR, and (d) mixed liquor in TSAMBR.

4.3.2 Total suspended solids and colloids content of wastewaters and mixed liquor

The total suspended solids (TSS) in TMP pressate 1 and TMP pressate 2 was found much higher than that in the TMP whitewater and TMP wastewater, respectively (Fig. 4.3.2). In spite of that, it is well-known that small particles (particularly colloids) in mixed liquor are much more important in governing membrane filtration performance in

MBRs (Lin et al. 2011). Thus, specific attention was paid to the quantity and size of colloids in both feed wastewater and mixed liquor. In this study, the colloids were defined as the particles that cannot be settled by the centrifugation at $18,700\times g$ centrifugation force for 20 minutes but can be retained by the membrane filter with pore size of $0.45\ \mu\text{m}$. Fig. 4.3.3(a) shows the concentration of the colloids in the feed wastewaters. It was evident that the TMP whitewater contained a higher level of colloids than that of the TMP pressate in the SAnMBR system. Similarly, the TMP wastewater contained a larger amount of colloids than that of the TMP pressate 2 in the TSAMBR system. The difference in the colloids content in the feed wastewaters is consistent with the difference observed by PSD measurement.

Mixed liquor for TMP whitewater treatment contained more colloids than the sludge for TMP pressate 1 treatment in the SAnMBR system (ANOVA, $P=0.019$), as shown in Fig. 4.3.3 (b). Similarly, mixed liquor for TMP wastewater treatment had a larger amount of colloids than that for TMP pressate 2 treatment in the TSAMBR system (ANOVA, $P=0.001$). The higher level of colloids in the mixed liquor is consistent with the higher level of colloids in the feed wastewaters in both the SAnMBR and TSAMBR system. It is interesting to note that the colloid contents of mixed liquor in the SAnMBR system was higher than that of TSAMBR system treating TMP pressate 2, although the colloids content in the feed wastewaters (TMP pressate 1 and TMP whitewater) for SAnMBR system was lower than or compatible to that of TMP pressate 2 in the TSAMBR system. This result suggests that the anaerobic sludge might contain higher level of colloids than that of aerobic system even though the feed wastewater contained lower level of colloids.

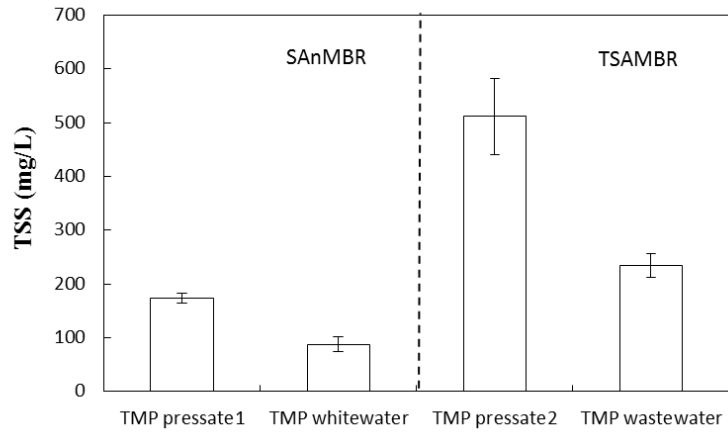


Fig. 4.3.2 TSS in the feed wastewaters

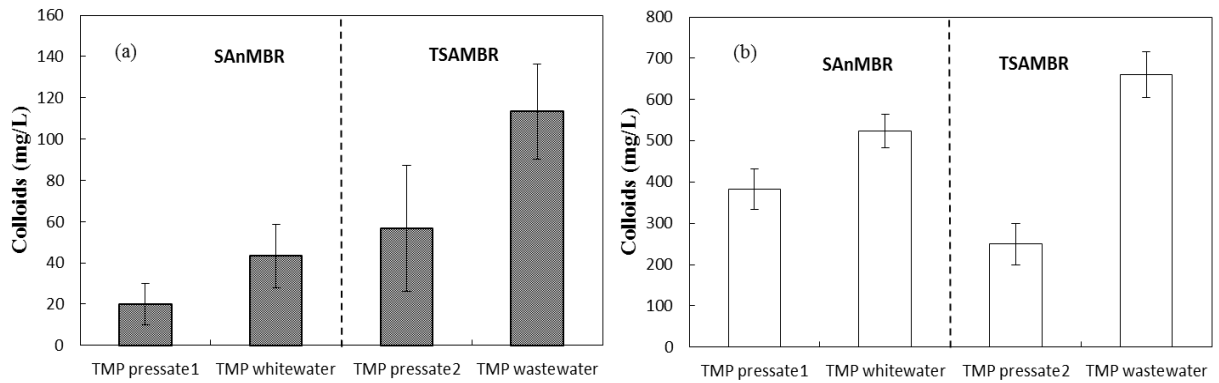


Fig. 4.3.3 The concentration of colloids in (a) feed wastewaters and (b) mixed liquors for treating different wastewater.

4.3.3 Soluble organic substances and the ratio of proteins to polysaccharides in wastewater and mixed liquor

The total COD values of the feed wastewaters and supernatants from mixed liquors are shown in Fig. 4.3.4. There were significant difference in total COD either between the two feed wastewaters or between the supernatants in the SAnMBR system (ANOVA, $P=0.001$ and $P=0.000$, respectively), while no significant difference in total COD were observed either between the two feed wastewaters or between the supernatants in the TSAMBR system (ANOVA, $P=0.054$ and $P=0.058$, respectively).

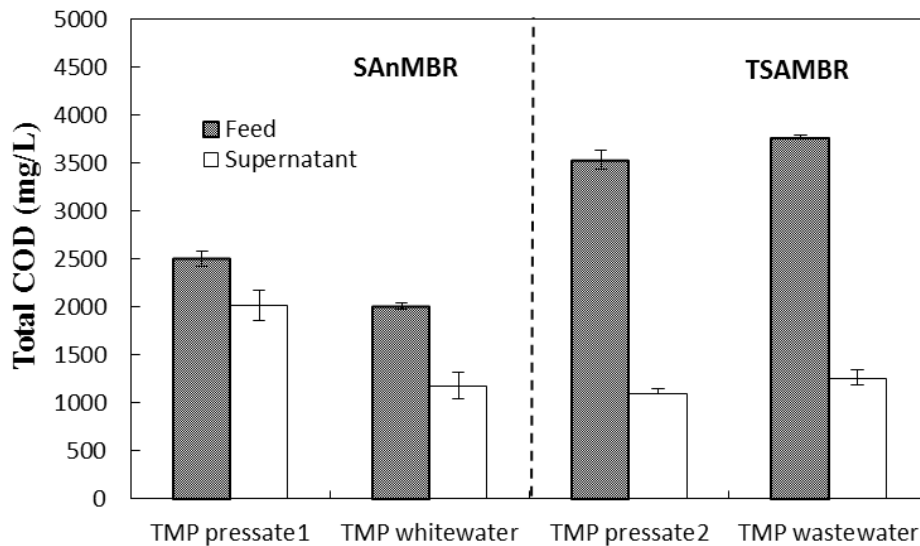


Fig. 4.3.4 Concentrations of total COD in different feed wastewaters and supernatants

The soluble COD values of the feed wastewaters, supernatants from mixed liquors, and the permeate are shown in Fig. 4.3.5. The results show that there was no significant difference in soluble COD between the two feed wastewaters treated by the SAnMBR system (ANOVA, $P=0.874$) while significant difference was observed between the two

feed wastewaters treated by the TSAMBR system (ANOVA, $P=0.001$). On the other hand, significant difference in soluble COD was observed between the two supernatants or the permeates either treated by the SAnMBR or the TSAMBR system (ANOVA, $p<0.05$). Comparing the soluble COD values of the feed and their corresponding permeates, the SAnMBR system achieved higher COD removal efficiency for treating TMP whitewater than that TMP pressate 1, and the TSAMBR showed a higher COD removal efficiency for the treatment of TMP wastewater than the TMP pressate 2. For the same system, different constituents in each feed wastewater might lead to the differences in their biodegradability.

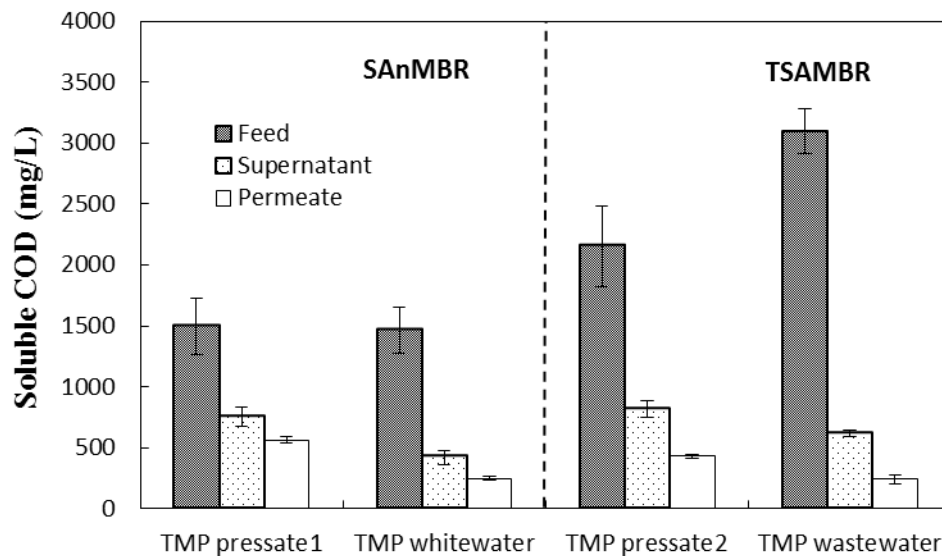


Fig. 4.3.5 Concentrations of soluble COD in different feed wastewaters and supernatant

The protein and polysaccharide concentrations as well as the sum of protein and polysaccharide concentrations (total organic substances) in the feed wastewaters and supernatants of mixed liquors are shown in Fig. 4.3.6 and 4.3.7. The results show that no

matter for the TMP pressate 1 and TMP whitewater treated by the SAnMBR system or for the corresponding supernatants, there was no significant difference in both protein and polysaccharide concentrations (ANOVA, $P > 0.05$), while significant difference existed in the PN/PS ratio (ANOVA, $P = 0.022$ for feed wastewaters and $P = 0.002$ for supernatants). For the feed wastewaters (TMP pressate 2 and TMP wastewater) and supernatants in the TSAMBR system, significant differences were observed in protein and polysaccharide concentrations as well as the PN/PS ratio (ANOVA, $P < 0.05$). The PN/PS ratios in the supernatants were inconsistent with the feeds, because they were not only introduced by the feed but also largely influenced by the biological activity inside the bioreactors.

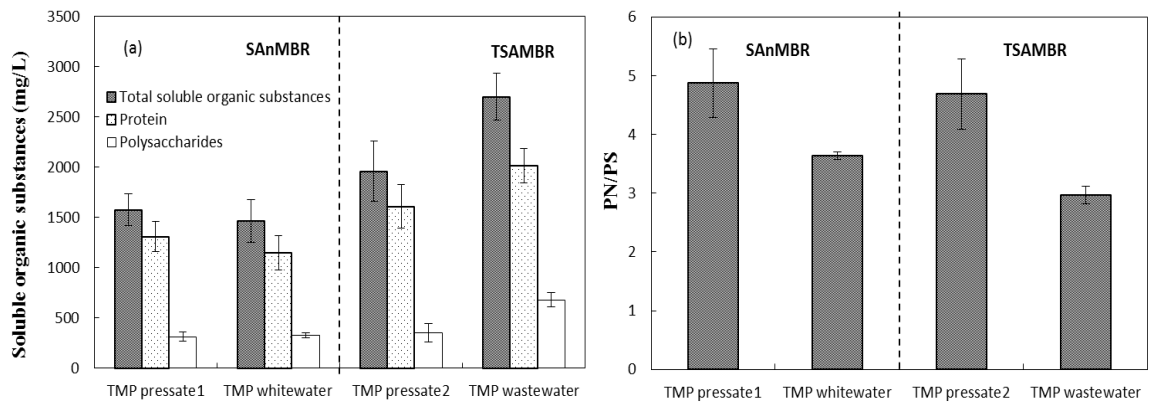


Fig. 4.3.6 Comparison of (a) the concentration of total soluble organic substances, protein and polysaccharides in different feed wastewaters and (b) PN/PS in different feed wastewaters.

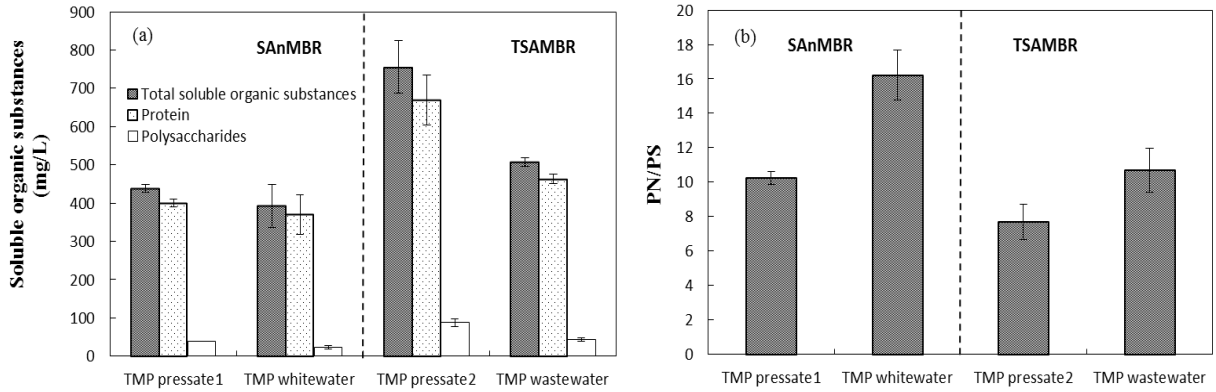


Fig. 4.3.7 Comparison of (a) the concentration of total soluble organic substances, protein and polysaccharides in supernatant and (b) PN/PS in supernatant.

4.3.4 Molecular weight distribution of soluble organic substances in wastewater and mixed liquor

The molecular weight distribution (MWD) of the feed wastewaters, after filtering with 0.45 μm pore size membrane, is shown in Fig. 4.3.8. The results suggest that the MWD of all four types of feed wastewaters covers a broad range of size from less than 1k Da to more than 100k Da. The two feed wastewaters for SANMBR treatment peaked at a size of $10\text{k} < \text{MWD} < 100\text{k}$, while the TMP wastewater for TSAMBR treatment peaked at a molecular weight larger than 100k and the TMP pressate 2 contained similar fractions of MW between $10\text{k} < \text{MWD} < 100\text{k}$ and $\text{MWD} > 100\text{k}$. There were no significant differences in MWD between the two streams treated by the SANMBR system, while a larger fraction of molecules at $\text{MWD} > 100\text{k}$ was observed in the TMP wastewater, as compared to that of the TMP pressate 2, treated by the TSAMBR system.

Fig. 4.3.9 shows the MWD of soluble organic substances (in terms of protein and polysaccharides) in the supernatants. For both SANMBR and TSAMBR, the dominant

molecular weight of the supernatant was >100k Da. High molecular weight compounds in the reactors could be retained by membrane while the lower molecular weight compounds passed through the membrane freely. Over 50% COD, protein and polysaccharides had a MW >100k Da in the supernatants of both the SAnMBR and the TSAMBR system. There were no significant differences in MWD between the two supernatants from the SAnMBR system, while a larger fraction of soluble COD and proteins at a MW >100k Da was observed in the TMP wastewater, as compared to that of the TMP pressate 2, treated by the TSAMBR system.

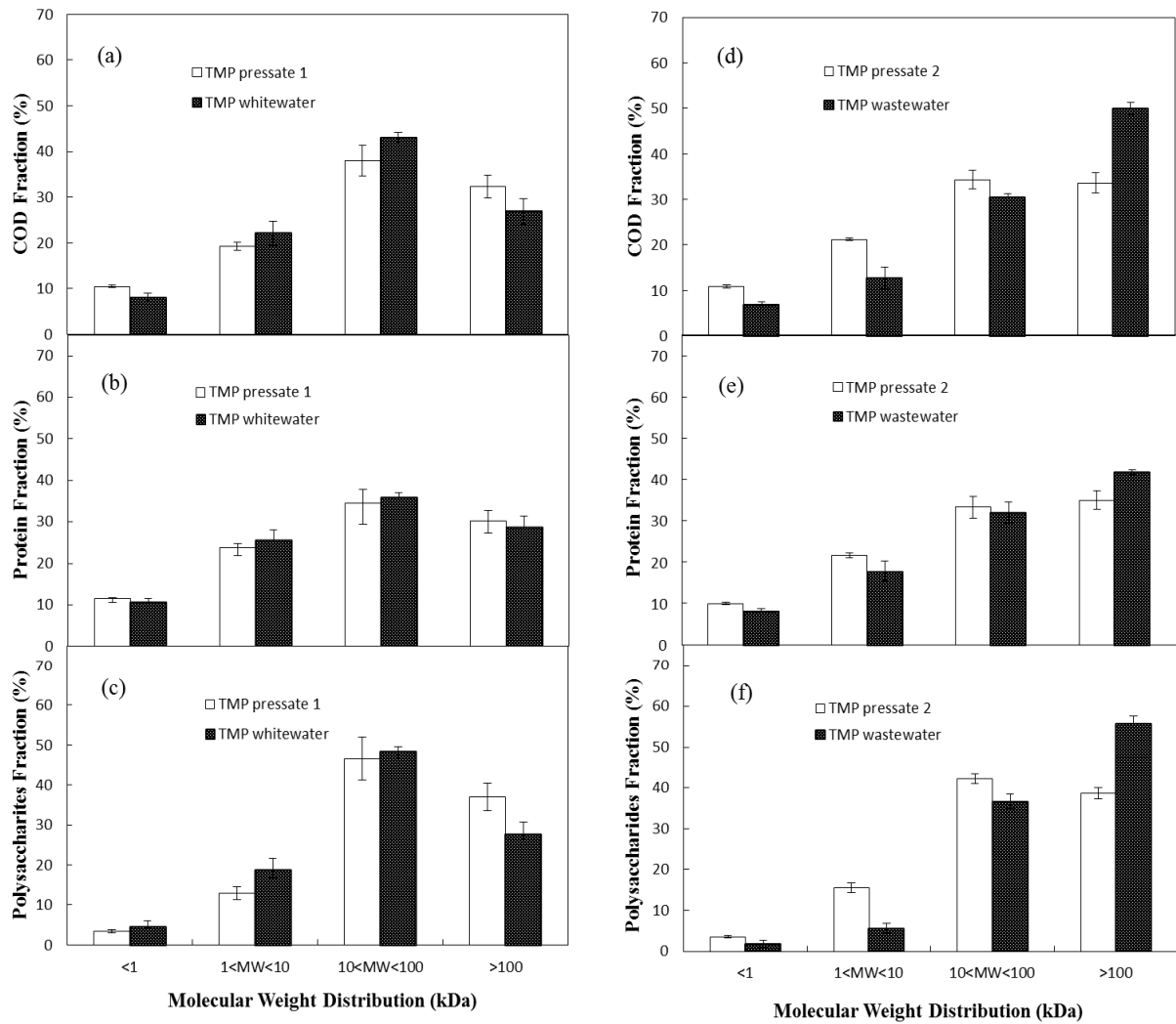


Fig. 4.3.8 Molecular weight distribution of COD, protein and polysaccharide in different feed wastewaters: TMP pressate 1 and whitewater (a,b,c); TMP pressate 2 and TMP wastewater (d,e,f).

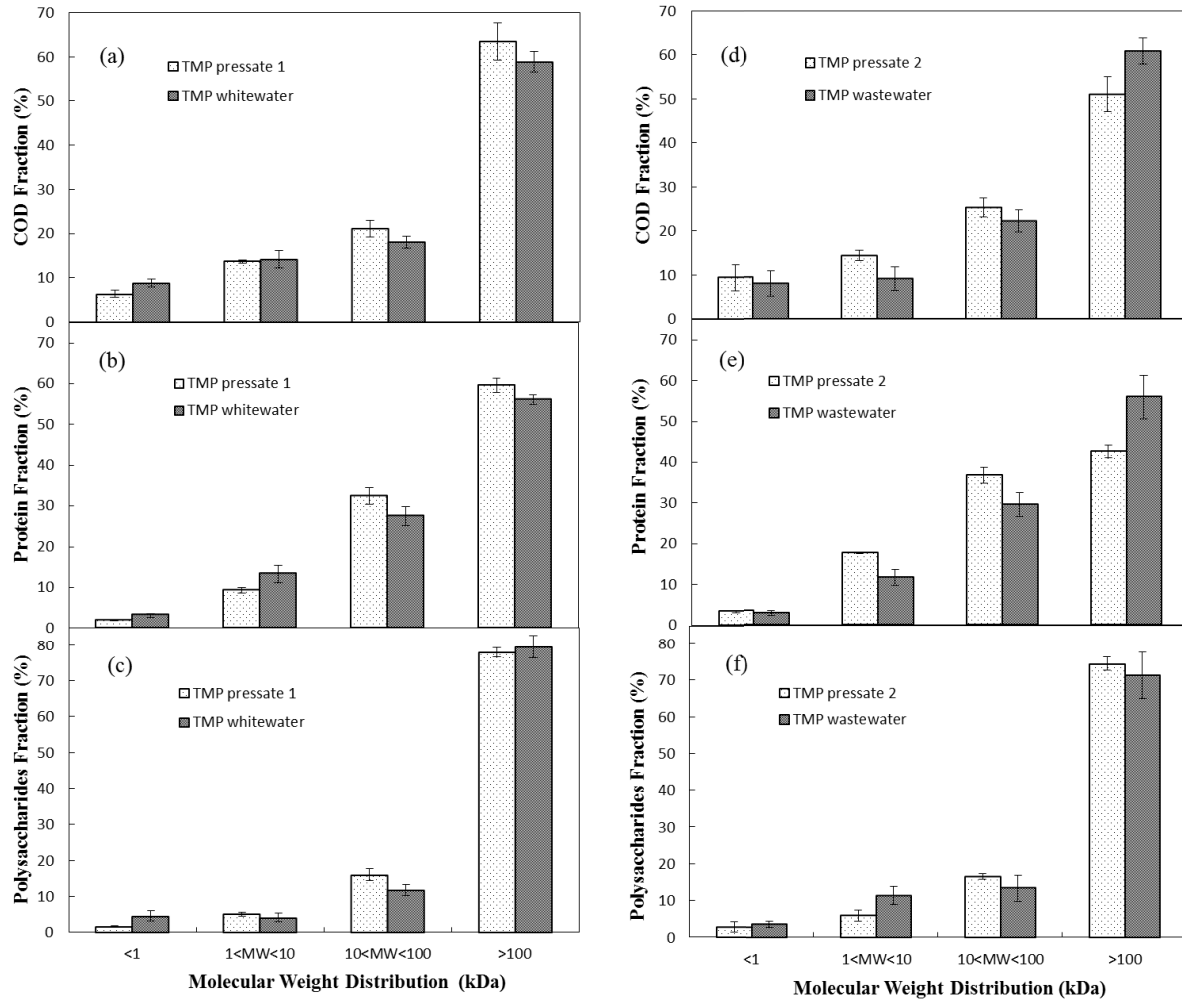


Fig. 4.3.9 Molecular weight distribution of soluble organic substances in mixed liquor supernatants: TMP pressate 1 and whitewater (a,b,c) for SAnMBR; TMP pressate 2 and TMP wastewater (d,e,f) for TSAMBR.

4.3.5 Membrane performance

A long-term study over 3 months was conducted for TMP pressate 1 and TMP whitewater treatment, respectively, using the SAnMBR system (Gao et al. 2011a, Gao et al. 2011b). The typical membrane filtration resistance profiles are shown in Fig. 4.3.10. The sustainable membrane flux ($4.6 \text{ L/m}^2 \text{ h}$) of the SAnMBR for TMP whitewater treatment was much lower than that ($6.9 \text{ L/m}^2 \text{ h}$) of the SAnMBR system for TMP pressate 1 treatment. Significantly high membrane filtration resistance was observed even at a lower operating flux (Fig. 4.3.10(a)). Similarly, significant difference in the membrane filtration resistance was observed between the TMP pressate 2 and TMP wastewater treatment using the TSAMBR system, as shown in Fig. 4.3.10 (b). At the membrane flux ($9.2 \pm 0.5 \text{ L/m}^2 \text{ h}$), the membrane fouling rate of the TMP wastewater treatment was much higher than that of the TMP pressate 2 treatment, as indicated by the much shorter operation cycle, implying significant difference in membrane performance of the TSAMBR system.

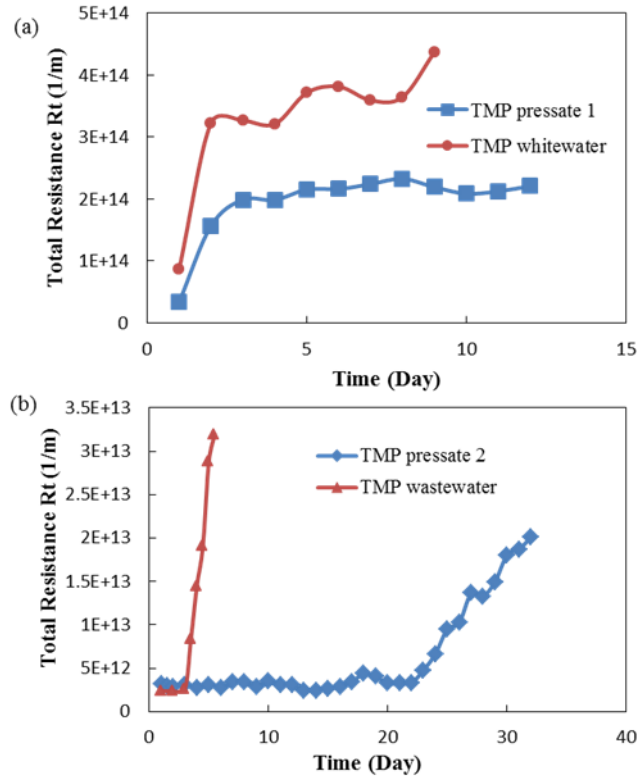


Fig. 4.3.10 Typical total filtration resistance (R_t) profiles of (a) SANMBR (stable flux: $4.6 \text{ L/m}^2 \text{ h}$ for whitewater; $6.9 \text{ L/m}^2 \text{ h}$ for TMP pressate 1) and (b) TSAMBR for different types of wastewater (stable flux: $9.2 \pm 0.5 \text{ L/m}^2 \text{ h}$ for both TMP pressate 2 and TMP wastewater).

4.3.6 Discussion

Among a number of factors affecting membrane fouling (e.g. feed wastewater characteristics, sludge properties, operating and environmental conditions, hydrodynamic conditions, and membrane properties) (Drews, 2010; Meng et al. 2009), this study focused on the effects of feed wastewater and sludge characteristics on membrane fouling in both an SANMBR and a TSAMBR system. The relative importance of different size fractions of particles and molecules in the feed wastewater and sludge was assessed and correlated to membrane performance.

In the operation of the SAnMBR, the membrane filtration resistance and fouling rate in TMP whitewater treatment were much higher than that in TMP pressate 1 treatment even under lower membrane flux. For the TSAMBR, no operating parameters (e.g. flux, MLSS, OLR) could be accounted for the different fouling behaviour as the operating conditions were kept constant during the operation period (Table 3.3). Thus, it is the feed wastewater characteristics and sludge properties that were responsible for the different fouling behaviour.

The presence of a larger fraction of small particles in the size range of 0.1-10 μ m, as shown in Fig. 4.3.1, in the feed wastewaters correlated well with the higher membrane filtration resistance and fouling rate in both the SAnMBR and TSAMBR system. This correlation was further verified by the colloidal contents in both the feed wastewater and supernatants. It is clear that the higher colloidal contents in the feed wastewaters and supernatants corresponded to a higher membrane filtration resistance and fouling rate in both the SAnMBR and TSAMBR system. However, the TSS level in the feed wastewaters and MLSS level in the MBRs could not explain the observed differences in membrane fouling behavior in both the SAnMBR and the TSAMBR system. The results suggest that it is the quantity of colloidal particles rather than the total suspended solids that determines the membrane fouling behavior. This is because smaller particles have a higher tendency to accumulate on membrane surfaces (Lin et al. 2011). The presence of a fraction of colloidal particles (0.1-10 μ m) in cake layers formed on membrane surface (Gao et al. 2011a, Qu et al. 2012) also indicated the importance of colloidal particles in the feed wastewaters and mixed liquor in controlling membrane fouling. This study suggests that attentions should be paid to the fractions of colloidal particles and strategies

to minimize the quantity of colloidal particles should be developed. This can be achieved by optimizing the hydrodynamic conditions (Stricot et al. 2010), controlling operating and environmental conditions (Delrue et al. 2011), addition of flocculants (Ji et al. 2010), and even selectively wasting the colloidal particles at the beginning of operation (Liao et al. 2010). The results also suggest that a characterization of colloidal contents in both the feed wastewater and mixed liquor may be used as a tool to predict the membrane performance in MBRs.

It is well known that the membrane performance in MBRs is affected not only by particles in the supernatant but also by the solutes in it (Defrance et al. 2000, Bouhabila et al. 2001, Lee et al. 2003). The soluble organic substances consisting of proteins (PN), polysaccharides (PS), lipids, nucleic acids and other polymeric compounds could cause the deterioration of filterability. Among these compounds, PN and PS played important role in membrane fouling (Jarusutthirak and Amy, 2007; Meng et al. 2007). However, our results suggest that neither the total COD nor the soluble COD, and the quantity of PN and PS in the feed wastewaters and supernatants were correlated to the membrane filtration resistance and fouling rate in the SAnMBR and the TSAMBR system. On the other hand, the PN/PS ratios in the supernatants corresponded well with the filtration resistance. A higher PN/PS (Fig. 4.3.7b) ratio correlated to higher filtration resistance (Fig. 4.3.10), which is consistent with the findings of Arabi and Nakhla (2008). The results suggest that the nature of the chemical compositions in the feed and supernatants is more important than the quantity of soluble organic substances in controlling membrane fouling. The PN/PS ratio in the feed wastewater in MBRs has been found to

have impact on the chemical characterization of main foulants, as well as the membrane fouling (Arabi and Nakhla, 2008).

Although MWD of the feed and SMPs are considered as an important factor in determining membrane fouling (Arabi and Nakhla, 2010), no universe conclusion about the role of MWD of the SMPs in membrane fouling was reached in this study in both the SAnMBR and the TSAMBR system. The larger amount of molecules with a MWD > 100k (and < 0.45 μm) corresponded a higher membrane filtration resistance and fouling rate in the TSAMBR system, while no significant difference in MWD was observed in the SAnMBR system treating two different wastewaters. Shen et al. (2010) also found large molecules (>100 kDa) in hydrophilic fraction were responsible for membrane due to pores clogging. However, the higher MW is not always related with higher fouling potential (Jiang et al. 2010). This result may suggest that the nature (chemical composition and structure) of the soluble organic substances is more important than the MWD of these molecules in controlling membrane fouling.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions for the Performance and Membrane Fouling of SAnMBR for Biorefining Effluent Treatment

The first part of the thesis studied the feasibility of using a hollow fiber SAnMBR for the treatment of synthetic biorefining effluent and the effect of organic loading rate on the membrane performance, sludge properties and membrane fouling of the SAnMBR. The results show that the SAnMBR is not ideally feasible for the treatment of the synthetic biorefining effluent due to the relatively low removal efficiency, the reduction in biogas production rate and the intolerability of the high organic loading rate. Membrane fouling is still a problem associated with the SAnMBR system. The TMP profiles exhibit two-stage behaviour: a very low and steady TMP with subtle fluctuations at the first stage followed by an abrupt and rapid jump at the second stage. A higher organic loading rate corresponding to a higher influent concentration resulted in a steeper jump of TMP. The properties of bulk sludge varied with the organic loading rate. The high organic loading rate resulted in high EPS concentration and small sludge particles which have negative effects on membrane fouling. Organic loading rate also has influences on cake sludge properties. With the increase of organic loading rate, the EPS concentration of the cake sludge increased and more small sludge particles attached on the membrane. Therefore, too high organic loading rate should be avoided for the operation of SAnMBR.

5.2 Conclusions for the Performance and Membrane Fouling of SAnMBR for TMP Wastewater Treatment

Based on the second part of experimental results, a hollow fiber SAnMBR is a promising alternative to treat thermo-mechanical pulping wastewater. The SAnMBR easily reached a new steady state after the change in feed concentration, suggesting a successful anaerobic treatment in reactor stability. A high influent concentration introduced accumulation of colloidal particles and resulted in a higher permeate COD value and accelerated TMP rise. More EPS was produced at a high feed concentration and a high biogas sparging rate. High gas sparging rate led to no significant impact on the mixed liquor and it effectively enhanced membrane flux and extended the continuous operation period to some extent. Non-uniform cake layer formation with combined effects of organic and inorganic fouling is the dominant mechanism of membrane fouling.

5.3 Conclusions for the Wastewater and Mixed Liquor Characteristics and Their Role in Membrane Fouling

The third part of the experimental results investigated the effects of wastewater characteristics and mixed liquor properties on membrane fouling in a SAnMBR and a TSAMBR system treating different types of industrial wastewaters. Based on the results presented in this study, the following conclusions can be drawn:

- The presence of a fraction of colloids (0.1-10 μ m), as determined by floc size distribution measurement, strongly corresponded to a higher membrane filtration resistance and fouling rate in both the SAnMBR and the TSAMBR system.

- The amount of the colloids in feed waters and mixed liquors were more important than the total suspended solids in controlling membrane fouling in both the SAnMBR and TSAMBR system.
- The PN/PS ratio in the supernatants was a more important factor than the quantity of soluble organic substances in governing the performance of membrane in membrane bioreactors.
- A full characterization of the feed and mixed liquor, particularly the particle size distribution and colloidal particle contents, may be used as a tool to predict the membrane performance of membrane bioreactors.

5.4 Recommendations for Future Work

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

In hollow fibre membranes in particular the hollow fiber length is a critical parameter. Therefore, since membrane performance cannot be scaled up directly from laboratory to plant dimensions, especially in the case of HF-based technology, further studies of HF-

SAnMBR technology on an industrial scale are needed in order to facilitate its design and implementation in full-scale wastewater treatment plants (WWTP).

References

- Ahmad, A.L., Ismail, S. and Bhatia, S. (2005) Membrane treatment for palm oil mill effluent: Effect of transmembrane pressure and crossflow velocity. *Desalination* 179(1–3), 245-255.
- Akram, A., Stuckey, D.C. (2008). Flux and performance improvement in a submerged anaerobic membrane bioreactor (SAMBR) using powdered activated carbon (PAC). *Process Biochemistry* 43, 93-102.
- Al-Amoudi, A. and Lovitt, R.W. (2007) Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. *Journal of Membrane Science* 303(1-2), 6-28.
- Al-Halbouni, D., Traber, J., Lyko, S., Wintgens, T., Melin, T., Tacke, D., Janot, A., Dott, W. and Hollender, J. (2008) Correlation of EPS content in activated sludge at different sludge retention times with membrane fouling phenomena. *Water Research* 42(6–7), 1475-1488.
- Ali, M. and Sreekrishnan, T.R. (2001) Aquatic toxicity from pulp and paper mill effluents: a review. *Advances in Environmental Research* 5(2), 175-196.
- APHA, Standard methods for the examination of water and wastewater. 21th ed ed. 2005, Washington, DC: American Public Health Association (APHA)/American Water Works Association (AWWA)/Water Environment Federation (WEF).
- Arabi, S. and Nakhla, G. (2008) Impact of protein/carbohydrate ratio in the feed wastewater on the membrane fouling in membrane bioreactors. *Journal of Membrane Science* 324(1–2), 142-150.
- Arabi, S. and Nakhla, G. (2010) Impact of molecular weight distribution of soluble microbial products on fouling in membrane bioreactors. *Separation and Purification Technology* 73(3), 391-396.
- Bae, T.-H. and Tak, T.-M. (2005) Interpretation of fouling characteristics of ultrafiltration membranes during the filtration of membrane bioreactor mixed liquor. *Journal of Membrane Science* 264(1–2), 151-160.
- Baek, S. H.; Pagilla, K. (2003) Comparison of Aerobic and Anaerobic Membrane Bioreactors for Municipal Wastewater Treatment, Proceedings of the 76th Annual Water Environment Federation Technical Exposition and Conference [CD-ROM]; Los Angeles, California, Oct. 11–15; Water Environment Federation: Alexandria, Virginia.
- Bai, R. and Leow, H.F. (2002) Microfiltration of activated sludge wastewater—the effect of system operation parameters. *Separation and Purification Technology* 29(2), 189-198.

- Barker, D.J. and Stuckey, D.C. (1999) A review of soluble microbial products (SMP) in wastewater treatment systems. *Water Research* 33(14), 3063-3082.
- Beaubien, A., Bâty, M., Jeannot, F., Francoeur, E. and Manem, J. (1996) Design and operation of anaerobic membrane bioreactors: development of a filtration testing strategy. *Journal of Membrane Science* 109(2), 173-184.
- Beerlange, M.A.M., Mulder, M.H.V., Smoulders, C.A. and Strathmann, H. (2001) Ultrafiltration membranes for non-aqueous systems.
- 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.
- Buhr, H.O. and Andrews, J.F. (1977). *The Thermophilic Anaerobic Digestion Process*. *Wat. Res.*, 11, 129-143.
- Bodik, I., Blst'akova, A., Dancova, L. and Sedlacek, S. (2009) Comparison of Flat-Sheet and Hollow-Fiber Membrane Modules in Municipal Wastewater Treatment. *Polish Journal of Environmental Studies* 18(3), 331-340.
- Bouhabila, E.H., Ben Aim, R. and Buisson, H. (1998) Microfiltration of activated sludge using submerged membrane with air bubbling (application to wastewater treatment). *Desalination* 118(1-3), 315-322.
- Bouhabila, . . , Ben A m, R. and Buisson, . (2001) ouling characterisation in membrane bioreactors. *Separation and Purification Technology* 22–23(0), 123-132.
- Chai, X., Kobayashi, T. and Fujii, N. (1999) Ultrasound-associated cleaning of polymeric membranes for water treatment. *Separation and Purification Technology* 15(2), 139-146.
- Chang, I.-S. and Kim, S.-N. (2005) Wastewater treatment using membrane filtration—effect of biosolids concentration on cake resistance. *Process Biochemistry* 40(3–4), 1307-1314.
- Chen, Y., Cheng, J.J. and Creamer, K.S. (2008) Inhibition of anaerobic digestion process: A review. *Bioresource Technology* 99(10), 4044-4064.
- Chiemchaisri, C. and Yamamoto, K. (1994) Performance of membrane separation bioreactor at various temperatures for domestic wastewater treatment. *Journal of Membrane Science* 87(1–2), 119-129.
- Cho, J., Song, K.-G. and Ahn, K.-H. (2005) The activated sludge and microbial substances influences on membrane fouling in submerged membrane bioreactor: unstirred batch cell test. *Desalination* 183(1–3), 425-429.

Choi, H., Zhang, K., Dionysiou, D.D., Oerther, D.B., Sorial, G.A. (2006) Effect of activated sludge properties and membrane operation conditions on fouling characteristics in membrane bioreactors. *Chemosphere* 63, 1699-1708.

Cui, Z.F., Chang, S. and Fane, A.G. (2003) The use of gas bubbling to enhance membrane processes. *Journal of Membrane Science* 221(1-2), 1-35.

Defrance, L., Jaffrin, M.Y., Gupta, B., Paullier, P. and Geaugey, V. (2000) Contribution of various constituents of activated sludge to membrane bioreactor fouling. *Bioresource Technology* 73(2), 105-112.

Delrue, F., Stricker, A.E., Mietton-Peuchot, M. and Racault, Y. (2011) Relationships between mixed liquor properties, operating conditions and fouling on two full-scale MBR plants. *Desalination* 272(1-3), 9-19.

Drews, A. (2010) Membrane fouling in membrane bioreactors—Characterisation, contradictions, cause and cures. *Journal of Membrane Science* 363(1-2), 1-28.

DuBois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F. (1956) Colorimetric Method for Determination of Sugars and Related Substances. *Analytical Chemistry* 28, 350-356.

Dufresne, R., Lavallee, H.C., Lebrun, R.E., Lo, S.N. and Tappi (1996) 1996 International Environmental Conference Books 1 and 2: Partners in Global Stewardship, pp. 323-330, Tappi Press, Atlanta.

Dvorak, L., Gomez, M., Dvorakova, M., Ruzickova, I. and Wanner, J. (2011) The impact of different operating conditions on membrane fouling and EPS production. *Bioresource Technology* 102(13), 6870-6875.

Fakhru'l-Razi, A. and Noor, M. (1999) Treatment of palm oil mill effluent (POME) with the Membrane Anaerobic System (MAS). *Water Science and Technology* 39(10-11), 159-163.

Field, R.W., Wu, D., Howell, J.A. and Gupta, B.B. (1995) Critical flux concept for microfiltration fouling. *Journal of Membrane Science* 100(3), 259-272.

Frolund, B., Palmgren, R., Keiding, K., Nielsen, P.H. (1996) Extraction of extracellular polymers from activated sludge using a cation exchange resin. *Water Research* 30, 1749-1758.

Fuchs, W., Binder, H., Mavrias, G. and Braun, R. (2003) Anaerobic treatment of wastewater with high organic content using a stirred tank reactor coupled with a membrane filtration unit. *Water Research* 37(4), 902-908.

G.J. B. (1989) Experiences with anaerobic digestion of wheat starch processing waste. *International Biodeterioration* 25(1-3), 71-77.

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

Gao, W.J., Lin, H.J., Leung, K.T., Schraft, H. and Liao, B.Q. (2011a) Structure of cake layer in a submerged anaerobic membrane bioreactor. *Journal of Membrane Science* 374(1-2), 110-120.

Gao, W.J., Leung, K.T., Qin, W.S. and Liao, B.Q. (2011b) Effects of temperature and temperature shock on the performance and microbial community structure of a submerged anaerobic membrane bioreactor. *Bioresource Technology* 102(19), 8733-8740.

Grant, S.R., Christian, S.J., Singh, K.S., Landine, R.C. (2007) Impacts of System Operation and Organic Loading Rate on Membrane Fouling and Sludge Production in Pilot-Scale Flat-Plate MBR Treatment of Potato Processing Wastewater. *Water Environment Federation* 90, 6542-6551.

Grethlein, H.E. (1978) Anaerobic digestion and membrane separation of domestic wastewater. *J. Water Pollut. Control* 50, 754.

Hai, F.I., Yamamoto, K. and Fukushi, K. (2005) Different fouling modes of submerged hollow-fiber and flat-sheet membranes induced by high strength wastewater with concurrent biofouling. *Desalination* 180(1-3), 89-97.

Hall, E.R., Onysko, K.A. and Parker, W.J. (1995) Enhancement of bleached kraft organochlorine removal by coupling membrane filtration and anaerobic treatment. *Environmental Technology* 16(2), 115-126.

He, Y., Xu, P., Li, C. and Zhang, B. (2005) High-concentration food wastewater treatment by an anaerobic membrane bioreactor. *Water Research* 39(17), 4110-4118.

Heran, M., Durante, F., Lebegue, J. and Grasmick, A. (2006) Air lift relevance in a side-stream MBR system. *Desalination* 199(1-3), 485-486.

Hernandez Rojas, M.E., Van Kaam, R., Schetrite, S. and Albasi, C. (2005) Role and variations of supernatant compounds in submerged membrane bioreactor fouling. *Desalination* 179(1-3), 95-107.

Ho, J.H. and Sung, S.W. (2010) Methanogenic activities in anaerobic membrane bioreactors (AnMBR) treating synthetic municipal wastewater. *Bioresource Technology* 101(7), 2191-2196.

Hogetsu T (1992) The cytoskeleton in the Desmidiaceae cell morphogenesis. In: Menzel D (ed) The cytoskeleton of the algae. CRC Press, Boca Raton, Fla, pp 114–13.

Hong, S.P., Bae, T.H., Tak, T.M., Hong, S. and Randall, A. (2002) Fouling control in activated sludge submerged hollow fiber membrane bioreactors. *Desalination* 143(3), 219-228.

Hu, A.Y. and Stuckey, D.C. (2007) Activated carbon addition to a submerged anaerobic membrane bioreactor: Effect on performance, transmembrane pressure, and flux. *Journal of Environmental Engineering-Asce* 133(1), 73-80.

Huang, X. and Wu, J. (2008) Improvement of membrane filterability of the mixed liquor in a membrane bioreactor by ozonation. *Journal of Membrane Science* 318(1–2), 210-216.

Huang Z., Ong S. L. and 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, 705-713.

Iversen, V., Mohaupt, J., Drews, A., Lesjean, B. and Kraume, M. (2008) Side effects of flux enhancing chemicals in membrane bioreactors (MBRS): study on their biological toxicity and their residual fouling propensity. *Water Science and Technology* 57(1), 117-123.

Jarusutthirak, C. and Amy, G. (2007) Understanding soluble microbial products (SMP) as a component of effluent organic matter (EfOM). *Water Research* 41(12), 2787-2793.

Jeison, D. (2007). Anaerobic membrane bioreactors for wastewater treatment Wageningen, The Netherlands, Wageningen University. Ph.D.

Jeison, D. and van Lier, J.B. (2006) Cake layer formation in anaerobic submerged membrane bioreactors (AnSMBR) for wastewater treatment. *Journal of Membrane Science* 284, 227-236.

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, 71-78.

Ji, J., Qiu, J., Wong, F.-s. and Li, Y. (2008) Enhancement of filterability in MBR achieved by improvement of supernatant and floc characteristics via filter aids addition. *Water Research* 42(14), 3611-3622.

Ji, J., Qiu, J., Wai, N., Wong, F.-S. and Li, Y. (2010) Influence of organic and inorganic flocculants on physical–chemical properties of biomass and membrane-fouling rate. *Water Research* 44(5), 1627-1635.

- Ji, L. and Zhou, J. (2006) Influence of aeration on microbial polymers and membrane fouling in submerged membrane bioreactors. *Journal of Membrane Science* 276(1–2), 168-177.
- Jiang, T., Kennedy, M.D., Schepper, V.D., Nam, S.-N., Nopens, I., Vanrolleghem, P.A. and Amy, G. (2010) Characterization of Soluble Microbial Products and Their Fouling Impacts in Membrane Bioreactors. *Environmental Science & Technology* 44(17), 6642-6648.
- Judd, S. (2004) A review of fouling of membrane bioreactors in sewage treatment. *Water science and technology*. 49(2): 229-35.
- Kataoka, N., Tokiwa, Y., Tanaka, Y., Fujiki, K., Taroda, H. and Takeda, K. (1992) Examination of bacterial characteristics of anaerobic membrane bioreactors in 3 pilot-scale plants for treating low-strength waste-water by application of the colony-forming-curve analysis method. *Applied and Environmental Microbiology* 58(9), 2751-2757.
- Khan, S.J. and Visvanathan, C. (2008) Influence of mechanical mixing intensity on a biofilm structure and permeability in a membrane bioreactor. *Desalination* 231(1–3), 253-267.
- Kimura, K., Yamato, N., Yamamura, H. and Watanabe, Y. (2005) Membrane Fouling in Pilot-Scale Membrane Bioreactors (MBRs) Treating Municipal Wastewater. *Environmental Science & Technology* 39(16), 6293-6299.
- Kromkamp, J., Faber, F., Schroen, K. and Boom, R. (2006) Effects of particle size segregation on crossflow microfiltration performance: Control mechanism for concentration polarisation and particle fractionation. *Journal of Membrane Science* 268(2), 189-197.
- Kurian, R., Nakhla, G. and Bassi, A. (2006) Biodegradation kinetics of high strength oily pet food wastewater in a membrane-coupled bioreactor (MBR). *Chemosphere* 65(7), 1204-1211.
- Latt, K.K. and Kobayashi, T. (2006) Ultrasound-membrane hybrid processes for enhancement of filtration properties. *Ultrasonics Sonochemistry* 13(4), 321-328.
- Le-Clech P. (2010) Membrane bioreactors and their uses in wastewater treatments. *Applied Microbiology and Biotechnology* 88 (6), 1253-1260.
- Le-Clech, P., Chen, V. and Fane, T.A.G. (2006) Fouling in membrane bioreactors used in wastewater treatment. *Journal of Membrane Science* 284(1–2), 17-53.

- Lee, S.M., Jung, J.Y. and Chung, Y.C. (2001) Novel method for enhancing permeate flux of submerged membrane system in two-phase anaerobic reactor. *Water Research* 35(2), 471-477.
- Lee, W., Kang, S. and Shin, H. (2003) Sludge characteristics and their contribution to microfiltration in submerged membrane bioreactors. *Journal of Membrane Science* 216(1-2), 217-227.
- Leiviskä, T., Nurmesniemi, H., Pöykiö, R., Rämö, J., Kuokkanen, T., Pellinen, J. (2008) Effect of biological wastewater treatment on the molecular weight distribution of soluble organic compounds and on the reduction of BOD, COD and P in pulp and paper mill effluent. *Water Research* 42, 3952-3960.
- Li, X.Y. and Yang, S.F. (2007) Influence of loosely bound extracellular polymeric substances (EPS) on the flocculation, sedimentation and dewaterability of activated sludge. *Water Research* 41(5), 1022-1030.
- Liao, B.Q., Allen, D.G., Droppo, I.G., Leppard, G.G. and Liss, S.N. (2001) Surface properties of sludge and their role in bioflocculation and settleability. *Water Research* 35(2), 339-350.
- Liao, B.Q., Bagley, D.M., Kraemer, H.E., Leppard, G.G. and Liss, S.N. (2004) A review of biofouling and its control in membrane separation bioreactors. *Water Environment Research* 76(5), 425-436.
- Liao, B.Q., Xie, K., Lin, H.J. and Bertoldo, D. (2010) Treatment of kraft evaporator condensate using a thermophilic submerged anaerobic membrane bioreactor. *Water Science and Technology* 61(9), 2177-2183.
- 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., Gao, W., Meng, F., Liao, B.-Q., Leung, K.-T., Zhao, L., Chen, J. and Hong, H. (2011) Membrane Bioreactors for Industrial Wastewater Treatment: A Critical Review. *Critical Reviews in Environmental Science and Technology* 42(7), 677-740.
- Lin, H. J., Gao, W. J., Leung, K. T. and Liao, B. Q. (2011). Characteristics of different fractions of microbial flocs and their role in membrane fouling. *Water Science and Technology*, 63 (2), 262-269.
- Lin, H.J., Xie, K., Mahendran, B., Bagley, D.M., Leung, K.T., Liss, S.N. and 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, H.J., Xie, K., Mahendran, B., Bagley, D.M., Leung, K.T., Liss, S.N. and Liao, B.Q. (2010) Factors affecting sludge cake formation in a submerged anaerobic membrane bioreactor. *Journal of Membrane Science* 361(1–2), 126-134.
- McAdam, E.J., Eusebi, A.L., Judd, S.J. (2010) Evaluation of intermittent air sparging in an anoxic denitrification membrane bioreactor. *Water Sci Technol* 61, 2219-25.
- Lowry, O.H., Rosebrough, N.J., Farr, A.L., Randall, R.J. (1951) Protein measurement with the Folin phenol reagent. *The Journal of biological chemistry* 193, 265-275.
- Melamane, X. (2003). Cleaning of fouled membranes using enzymes from a sulphidogenic bioreactor. MSc. Thesis, Rhodes University, Grahamstown, South Africa.
- Meng, F., Chae, S.-R., Drews, A., Kraume, M., Shin, H.-S. and Yang, F. (2009) Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material. *Water Research* 43(6), 1489-1512.
- Meng, F., Shi, B., Yang, F. and Zhang, H. (2007) Effect of hydraulic retention time on membrane fouling and biomass characteristics in submerged membrane bioreactors. *Bioprocess and Biosystems Engineering* 30(5), 359-367.
- Menniti, A., Kang, S., Elimelech, M. and Morgenroth, E. (2009) Influence of shear on the production of extracellular polymeric substances in membrane bioreactors. *Water Research* 43(17), 4305-4315.
- Menniti, A. and Morgenroth, E. (2010) The influence of aeration intensity on predation and EPS production in membrane bioreactors. *Water Research* 44(8), 2541-2553.
- Minami, K. (1994) A trial of high-performance anaerobic treatment on waste-water from a kraft pulp-mill. *Desalination* 98(1-3), 273-283.
- Minami, K., Okamura, K., Ogawa, S. and Naritomi, T. (1991) Continuous anaerobic treatment of waste-water from a kraft pulp-mill. *Journal of Fermentation and Bioengineering* 71(4), 270-274.
- Mishima, I. and Nakajima, J. (2009) Control of membrane fouling in membrane bioreactor process by coagulant addition. *Water Science and Technology* 59(7), 1255-1262.
- Miyoshi T., Tsuyuhara T., Ogyu R., Kimura K. and Watanabe Y. (2009) Seasonal variation in membrane fouling in membrane bioreactors (MBRs) treating municipal wastewater. *Water Research* 43, 5109-5118.

- Muthukumar, S., Yang, K., Seuren, A., Kentish, S., Ashokkumar, M., Stevens, G.W. and Grieser, F. (2004) The use of ultrasonic cleaning for ultrafiltration membranes in the dairy industry. *Separation and Purification Technology* 39(1–2), 99-107.
- Nagaoka, H., Ueda, S. and Miya, A. (1996) Influence of bacterial extracellular polymers on the membrane separation activated sludge process. *Water Science and Technology* 34(9), 165-172.
- Ng, H.Y., Tan, T.W., Ong, S.L., Toh, C.A. and Loo, Z.P. (2006) Effects of solid retention time on the performance of submerged anoxic/oxic membrane bioreactor. *Water Science and Technology* 53(6), 7-13.
- Ng, C.A., Sun, D. and Fane, A.G. (2006) Operation of membrane bioreactor with powdered activated carbon addition. *Separation Science and Technology* 41(7), 1447-1466.
- Pan, J.R., Su, Y. and Huang, C. (2010) Characteristics of soluble microbial products in membrane bioreactor and its effect on membrane fouling. *Desalination* 250(2), 778-780.
- Park C., Kim H., Hong S. and Choi S.-I. (2006) Variation and prediction of membrane fouling index under various feed water characteristics. *Journal of Membrane Science* 284, 248-254.
- Park, H.-D., et al. (2010) Reduction of membrane fouling by simultaneous upward and downward air sparging in a pilot-scale submerged membrane bioreactor treating municipal wastewater. *Desalination* 251, 75-82.
- Patsios, S.I. and Karabelas, A.J. (2011) An investigation of the long-term filtration performance of a membrane bioreactor (MBR): The role of specific organic fractions. *Journal of Membrane Science* 372(1-2), 102-115.
- Pendashteh, A.R., Fakhru'l-Razi, A., Madaeni, S.S., Abdullah, L.C., Abidin, Z.Z. and Biak, D.R.A. (2011) Membrane foulants characterization in a membrane bioreactor (MBR) treating hypersaline oily wastewater. *Chemical Engineering Journal* 168(1), 140-150.
- Peng, W.H. and Escobar, I.C. (2005) Evaluation of factors influencing membrane performance. *Environmental Progress* 24(4), 392-399.
- Phattaranawik, J. and Leiknes, T. (2011) Extractive biofilm membrane bioreactor with energy recovery from excess aeration and new membrane fouling control. *Bioresource Technology* 102(3), 2301-2307.

Pokhrel, D. and Viraraghavan, T. (2004) Treatment of pulp and paper mill wastewater—a review. *Science of The Total Environment* 333(1–3), 37-58.

Qu, X., Gao, W.J., Han, M.N., Chen, A., Liao, B.Q. (2012) Integrated thermophilic submerged aerobic membrane bioreactor and electrochemical oxidation for pulp and paper effluent treatment – towards system closure. *Bioresource Technology* 116, 1-8.

Rajeshwari, K.V., Balakrishnan, M., Kansal, A., Lata, K. and Kishore, V.V.N. (2000) State-of-the-art of anaerobic digestion technology for industrial wastewater treatment. *Renewable and Sustainable Energy Reviews* 4(2), 135-156.

Ren, N.Q., Li, J.Z., Li, B.K., Wang, Y. and Liu, S.R. (2006) Biohydrogen production from molasses by anaerobic fermentation with a pilot-scale bioreactor system. *International Journal of Hydrogen Energy* 31(15), 2147-2157.

Rosenberger, S., Evenblij, H., te Poele, S., Wintgens, T. and Laabs, C. (2005) The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes—six case studies of different European research groups. *Journal of Membrane Science* 263(1–2), 113-126.

Rosenberger S., Laabs C., Lesjean B., Gnirss R., Amy G., Jekel M. and Schrotter J. C. (2006) Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment. *Water Research*, 40 (4), 710-720.

Ross, W.R., Barnard, J.P., Strohwal, N.K.H., Grobler, C.J. and Sanetra, J. (1992) Practical application of the aduf process to the full-scale treatment of a maize-processing effluent. *Water Science and Technology* 25(10), 27-39.

Saddoud, A., Hassairi, I. and Sayadi, S. (2007) Anaerobic membrane reactor with phase separation for the treatment of cheese whey. *Bioresource Technology* 98(11), 2102-2108.

Satyawali Y. and Balakrishnan M. (2009) Effect of PAC addition on sludge properties in an MBR treating high strength wastewater. *Water Research* 43, 1577-1588.

Shariati, F.P., Mehrnia, M.R., Salmasi, B.M., Heran, M., Wisniewski, C. and Sarrafzadeh, M.H. (2010) Membrane bioreactor for treatment of pharmaceutical wastewater containing acetaminophen. *Desalination* 250(2), 798-800.

Shen, Y., Zhao, W., Xiao, K. and Huang, X. (2010) A systematic insight into fouling propensity of soluble microbial products in membrane bioreactors based on hydrophobic interaction and size exclusion. *Journal of Membrane Science* 346(1), 187-193.

Sheng, G.-P. and Yu, H.-Q. (2006) Characterization of extracellular polymeric substances of aerobic and anaerobic sludge using three-dimensional excitation and emission matrix fluorescence spectroscopy. *Water Research* 40(6), 1233-1239.

Sipma, J., Osuna, M.B., Emanuelsson, M.A.E. and Castro, P.M.L. (2010) Biotreatment of Industrial Wastewaters under Transient-State Conditions: Process Stability with Fluctuations of Organic Load, Substrates, Toxicants, and Environmental Parameters. *Critical Reviews in Environmental Science and Technology* 40(2), 147-197.

Song, K.-G., Kim, Y. and Ahn, K.-H. (2008) Effect of coagulant addition on membrane fouling and nutrient removal in a submerged membrane bioreactor. *Desalination* 221(1-3), 467-474.

Stamatelatou, K., Kopsahelis, A., Blika, P.S., Paraskeva, C.A. and Lyberatos, G. (2009) Anaerobic digestion of olive mill wastewater in a periodic anaerobic baffled reactor (PABR) followed by further effluent purification via membrane separation technologies. *Journal of Chemical Technology and Biotechnology* 84(6), 909-917.

Stricot, M., Filali, A., Lesage, N., Spérandio, M. and Cabassud, C. (2010) Side-stream membrane bioreactors: Influence of stress generated by hydrodynamics on floc structure, supernatant quality and fouling propensity. *Water Research* 44(7), 2113-2124.

Stuckey, D. C. (2003) The Submerged Anaerobic Membrane Bioreactor (SAMBR): An Intensification of Anaerobic Wastewater Treatment. Abstract of Presentation to the Department of Civil Engineering at the University of Minnesota, Minneapolis, Minnesota, September 10; University of Minnesota: Minneapolis.

Sutton, P. M.; Mishra, N.; Bratby, J. R.; Eneghess, D. (2002) Membrane Bioreactor for Industrial and Municipal Wastewater Applications: Long-Term Operating Experience. Proceedings of the 75th Annual Water Environment Federation Technical Exposition and Conference [CD-ROM]; Chicago, Illinois, Sept. 28-Oct. 2; Water Environment Federation: Alexandria, Virginia.

Thomassen, J.K., Faraday, D.B.F., Underwood, B.O. and Cleaver, J.A.S. (2005) The effect of varying transmembrane pressure and crossflow velocity on the microfiltration fouling of a model beer. *Separation and Purification Technology* 41(1), 91-100.

Tian, J.Y., Liang, H., Li, X., You, S.J., Tian, S. and Li, G.B. (2008) Membrane coagulation bioreactor (MCBR) for drinking water treatment. *Water Research* 42(14), 3910-3920.

Timur, H. and Öztürk I. (1999) Anaerobic sequencing batch reactor treatment of landfill leachate. *Water Research* 33, 3225-3230.

- Trussell, R.S., Merlo, R.P., Hermanowicz, S.W. and Jenkins, D. (2006) The effect of organic loading on process performance and membrane fouling in a submerged membrane bioreactor treating municipal wastewater. *Water Research* 40(14), 2675-2683.
- Vallero, M.V.G., Lettinga, G. and Lens, P.N.L. (2005) High rate sulfate reduction in a submerged anaerobic membrane bioreactor (SAMBaR) at high salinity. *Journal of Membrane Science* 253(1-2), 217-232.
- Van Zyl, P.J., Wentzel, M.C., Ekama, G.A. and Riedel, K.J. (2008) Design and start-up of a high rate anaerobic membrane bioreactor for the treatment of a low pH, high strength, dissolved organic waste water. *Water Science and Technology* 57(2), 291-295.
- Visvanathan, C., Yang, B.S., Muttamara, S. and Maythanukhraw, R. (1997) Application of air backflushing technique in membrane bioreactor. *Water Science and Technology* 36(12), 259-266.
- Visvanathan C. and Abeynayaka A. (2012) Developments and future potentials of anaerobic membrane bioreactors (AnMBRs). *Membrane Water Treatment* 3, 1-23.
- Vyrides, I. and Stuckey D.C. (2009) Saline sewage treatment using a submerged anaerobic membrane reactor (SAMBR): effects of activated carbon addition and biogas-sparging time. *Water Research* 43, 933-42.
- Wang, F. and Tarabara, V.V. (2008) Pore blocking mechanisms during early stages of membrane fouling by colloids. *Journal of Colloid and Interface Science* 328(2), 464-469.
- Wang, Z., Wu, Z. and Tang, S. (2009) Extracellular polymeric substances (EPS) properties and their effects on membrane fouling in a submerged membrane bioreactor. *Water Research* 43(9), 2504-2512.
- Wang, X.-M., Li, X.-Y. and Huang, X. (2007) Membrane fouling in a submerged membrane bioreactor (SMBR): Characterisation of the sludge cake and its high filtration resistance. *Separation and Purification Technology* 52(3), 439-445.
- Wei, C.H., Huang, X., Ben Aim, R., Yamamoto, K. and Amy, G. (2011) Critical flux and chemical cleaning-in-place during the long-term operation of a pilot-scale submerged membrane bioreactor for municipal wastewater treatment. *Water Research* 45(2), 863-871.
- Wijekoon, K.C., Visvanathan, C. and 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.

- 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, 511-521.
- Xu, M., Wen, X., Yu, Z., Li, Y. and Huang, X. (2011) A hybrid anaerobic membrane bioreactor coupled with online ultrasonic equipment for digestion of waste activated sludge. *Bioresource Technology* 102(10), 5617-5625.
- Yamanoi, I. and Kageyama K. (2010) Evaluation of bubble flow properties between flat sheet membranes in membrane bioreactor. *Journal of Membrane Science* 360, 102-108.
- Yamato, N., Kimura, K., Miyoshi, T. and Watanabe, Y. (2006) Difference in membrane fouling in membrane bioreactors (MBRs) caused by membrane polymer materials. *Journal of Membrane Science* 280(1-2), 911-919.
- Yanagi, C., Sato, M. and Takahara, Y. (1994) Treatment of wheat-starch waste-water by a membrane combined 2-phase methane fermentation system. *Desalination* 98(1-3), 161-170.
- You, S.-J. and Teng, J.-Y. (2009) Anaerobic decolorization bacteria for the treatment of azo dye in a sequential anaerobic and aerobic membrane bioreactor. *Journal of the Taiwan Institute of Chemical Engineers* 40(5), 500-504.
- Yu, S.L., Zhao, F.B., Zhang, X.H., Jing, G.L. and Zhen, X.H. (2006) Effect of components in activated sludge liquor on membrane fouling in a submerged membrane bioreactor. *Journal of Environmental Sciences-China* 18(5), 897-902.
- Zayen, A., Mnif, S., Aloui, F., Fki, F., Loukil, S., Bouaziz, M. and Sayadi, S. (2010) Anaerobic membrane bioreactor for the treatment of leachates from Jebel Chakir discharge in Tunisia. *Journal of Hazardous Materials* 177(1-3), 918-923.
- Zhang, H.-f., Sun, B.-s., Zhao, X.-h. and Gao, Z.-h. (2008) Effect of ferric chloride on fouling in membrane bioreactor. *Separation and Purification Technology* 63(2), 341-347.
- Zhang, J., Zhou, J., Liu, Y. and Fane, A.G. (2010) A comparison of membrane fouling under constant and variable organic loadings in submerge membrane bioreactors. *Water Research* 44(18), 5407-5413.
- Zhang, J., Chua, H.C., Zhou, J. and Fane, A.G. (2006) Factors affecting the membrane performance in submerged membrane bioreactors. *Journal of Membrane Science* 284(1-2), 54-66.

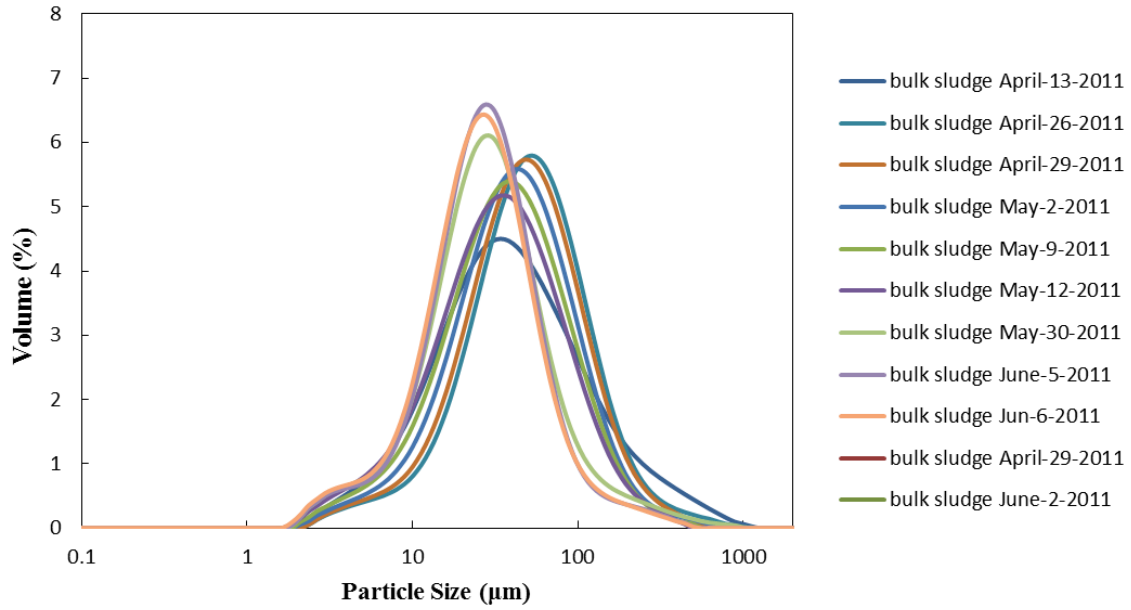
Zhang, T.C. and Bishop P.L. (1994) Density, porosity, and pore structure of biofilms. *Water Research* 28(11), 2267–2277.

Zhang, L., Champagne, P. and Xu, C. (2011) Bio-crude production from secondary pulp/paper-mill sludge and waste newspaper via co-liquefaction in hot-compressed water. *Energy* 36(4), 2142-2150.

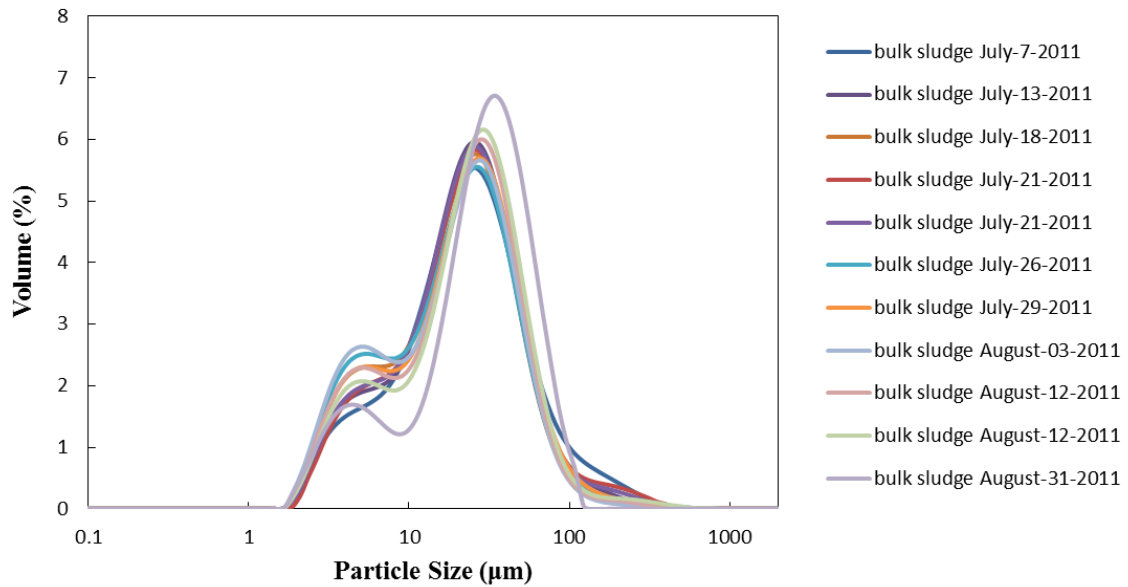
Zhou, J., Yang, F.-l., Meng, F.-g., An, P. and Wang, D. (2007) Comparison of membrane fouling during short-term filtration of aerobic granular sludge and activated sludge. *Journal of Environmental Sciences* 19(11), 1281-1286.

Zhou, W., Imai, T., Ukita, M., Li, F. and Yuasa, A. (2007) Effect of loading rate on the granulation process and granular activity in a bench scale UASB reactor. *Bioresource Technology* 98(7), 1386-1392.

Appendix I Particle Size Distributions of Bulk Sludge under different Organic Loading Rates for Biorefining Effluent

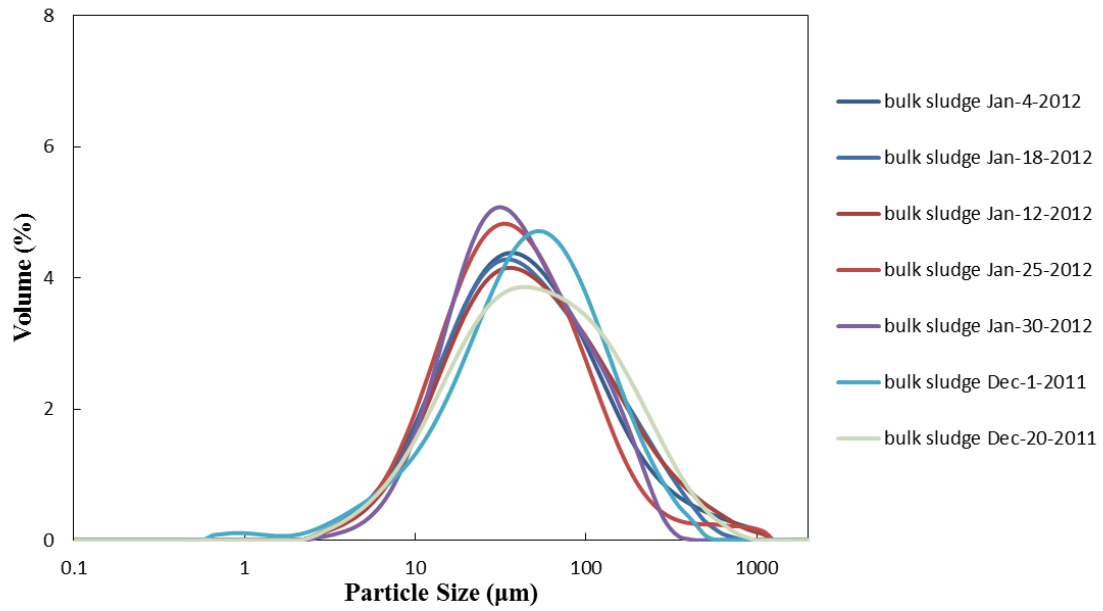


Bulk Sludge Particle size distribution at OLR = 2.11 ± 0.09 kg COD/m³ d.

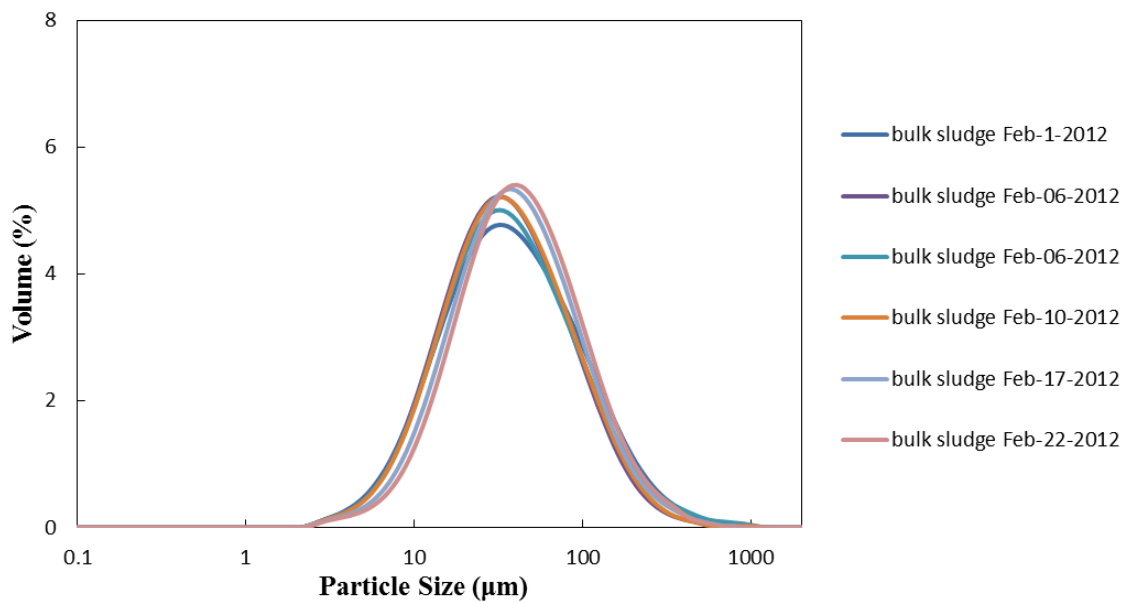


Bulk Sludge Particle size distribution at OLR = 3.35 ± 0.14 kg COD/m³ d.

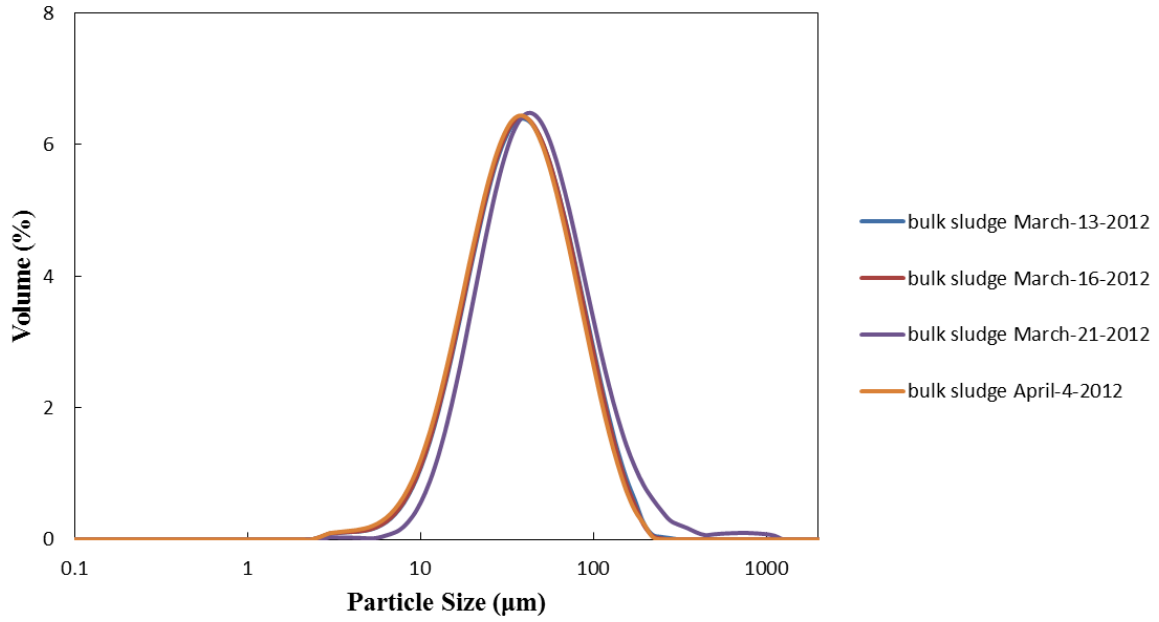
Appendix II Particle Size Distributions of Bulk Sludge under different Organic Loading Rates for Thermo-mechanical Pulping Pressate



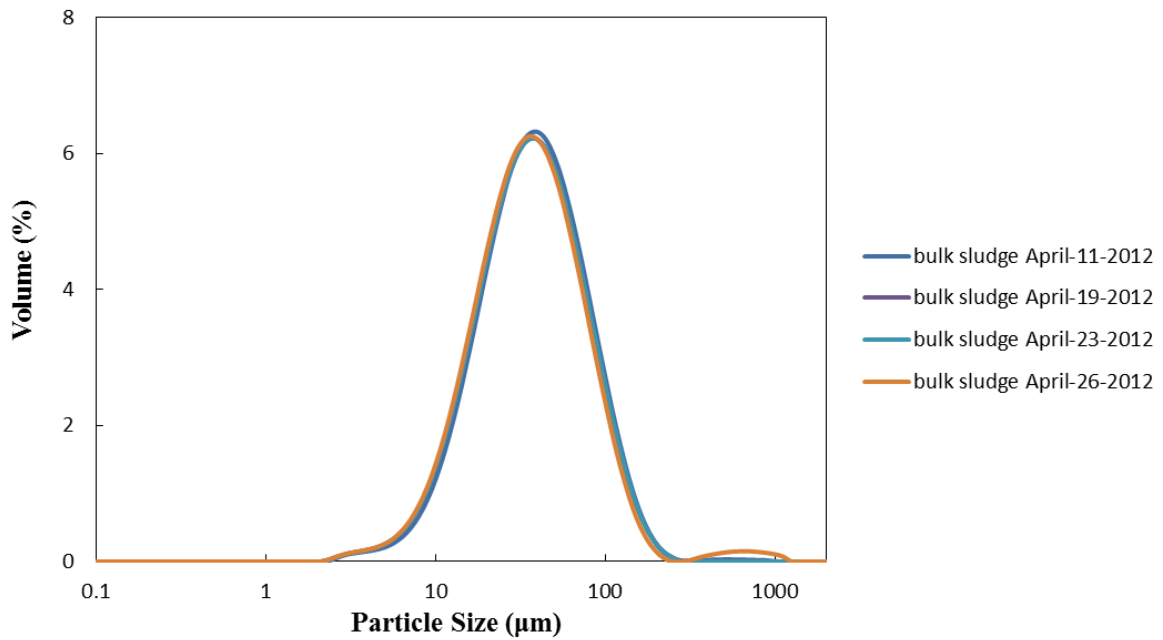
Bulk Sludge Particle size distribution at Phase 1.



Bulk Sludge Particle size distribution at Phase 2.



Bulk Sludge Particle size distribution at Phase 3.



Bulk Sludge Particle size distribution at Phase 4.