Development of novel submerged anaerobic osmosis membrane bioreactor

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**Development of Novel Submerged Anaerobic
Osmosis Membrane Bioreactor**

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2015

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ABSTRACT

Forward Osmosis (FO) process is driven by osmotic energy, which is arisen from the osmotic pressure difference between the draw solution (high concentration) and the feed solution (low concentration) separated by a semi-permeable membrane. Combining anaerobic digestion with FO membrane to retain influent organic waste, this research aims to develop the integrated biological wastewater treatment technology: Anaerobic Osmosis-Membrane Reactor (AnOMBR).

In the preliminary study, mixed organic fouling of the FO membrane in submerged mode was systematically investigated. Fouling behavior of cellulose triacetate (CTA) FO membrane and thin film composite (TFC) polyamide FO membranes were studied and compared. It was interesting to find under mild FO fouling conditions, TFC FO membranes could have greater fouling tendency as compared to CTA FO membranes due to their greater surface roughness. Although FO is believed to have superior fouling resistance in the AL-FS orientation, severe fouling could occur even at moderate flux levels, especially for TFC membranes or for unstable feed solutions. In this case, solution chemistries such as pH and presence of calcium ions posed remarkable effect on the cake layer composition due to the effect of foulant-foulant interaction(s); In contrast, the foulant composition was not strongly affected by the membrane type (CTA versus TFC) nor the testing mode (pressure-driven NF mode versus osmosis-driven FO mode).

With the understanding of FO organic fouling mechanisms, a novel submerged AnOMBR utilizing CTA FO membrane in anaerobic bioreactor was developed and feasibility of using the AnOMBR to treat low-strength synthetic wastewater at mesophilic temperature was evaluated. Flux declined under the effect of both feed conductivity build-up and membrane fouling. Generally fouling on membrane was mild, while both organic fouling and inorganic scaling could still be observed at the

edge of membrane. Bulk pH could be sustained within neutral to slightly alkaline due to the retention of alkalinity by FO membrane. The AnOMBR showed good and stable soluble chemical oxygen demand (sCOD) removal and perfect total phosphorous removal. However the removal of total nitrogen and ammonia still needed improvements. The elevated salt environment had marginal effect on bioactivity of methanogens and methane production of AnOMBR system was stable.

Based on the promising results, the AnOMBR was operated at both mesophilic temperature and room temperature to compare the performance in terms of membrane flux level and mixed liquor conductivity, nutrient removal and methane production. At room temperature, the flux decreased and conductivity increased both at a slower speed than at mesophilic temperature. The membrane durability was also better and tap water cleaning was practical at room temperature with 90% flux recovery. At both temperatures, the AnOMBR showed good rejection to nutrients. However, at higher temperature, the nutrient concentration in supernatants was relatively lower, indicating the faster and efficient nutrient degradation by microbial at higher temperature. Methane production rate at mesophilic temperature was also significant higher than at room temperature.

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CHAPTER 1: INTRODUCTION

1.1. Background

Anaerobic membrane bioreactor (AnMBR) is an integrated biological wastewater treatment technology which combines anaerobic digestion with membrane filtration. It carries over the significant advantages of anaerobic digestion such as small sludge yield, lower operational cost and net energy generator by methane production (Skouteris, Hermosilla et al. 2012). In addition, it also solves the biomass retention dilemma, which is the weakness in most of the anaerobic treatment process which is due to the extremely slow growth rate of anaerobic micro-organisms and the relatively poor settling properties of anaerobic biomass (Lin, Peng et al. 2013; Ozgun, Dereli et al. 2013). The avoidance of biomass loss to the effluent is achieved by coupling with membrane. Under the stress of urbanization and energy crisis, AnMBR is considered as a promising alternative for wastewater treatment thanks to the significant advantages over conventional anaerobic treatment and aerobic membrane bioreactor (MBR) technology (Ozgun, Dereli et al. 2013).

Continuous efforts are required to further enhance the performance of AnMBR performance. One direction is to increase the treatment efficiency of small molecular weight substances such as natural organic matters and trace organics which could not be effectively removed by porous membrane (i.e. micro-filtration/ultra-filtration membranes used in conventional AnMBR). The high energy consumption to drive the pressure-driven membrane filtration process is also a concern to the overall energy efficiency of conventional AnMBR.

In the meantime, there is a growing interest to apply the energy-efficient technology in water treatment process: Forward Osmosis (FO). Rather than driven by an externally applied pressure, forward osmosis process is driven by osmotic energy,

that is arisen from the osmotic pressure difference between a concentrated draw solution and a dilute feed solution across the membrane. Under this osmotic driving force, water flows spontaneously across the membrane from the low-concentration feed solution side to the high-concentration draw solution side. Where a natural source of high osmotic pressure solution is available (e.g. typical seawater has an osmotic pressure of ~ 2.5 MPa), FO can be highly attractive in terms of energy input as only the circulation of streams requires external energy (Cath, Childress et al. 2006). In addition, FO produces high quality permeate which is nearly free of organic matter as a result of the highly retentive nature of the membrane (Cath, Childress et al. 2006; Holloway, Childress et al. 2007).

A lot of work has been done to improve the performance of FO membrane. An ideal FO membrane shall possess high water permeability, high solute rejection and as well as good chemical stability (Wang, Shi et al. 2010). The cellulose triacetate (CTA) FO membranes are commercially available (Wei, Qiu et al. 2011), while recent developments in thin film composite (TFC) polyamide FO membranes show these membranes can have significantly higher water flux and better solute rejection as compared to CTA FO membranes (Wang, Shi et al. 2010; Yip, Tiraferri et al. 2010; Wei, Qiu et al. 2011). In addition, TFC membranes have better pH stability and resistance to hydrolysis and biological degradation (Vos, Burris et al. 1966; Mulder 1996; Geise, Lee et al. 2010).

In recent years, beyond the research interest, FO technology has been considered for various industrial applications, such as seawater desalination, power generation, food processing and wastewater treatment. One of the niche applications is the combined FO and bioprocess, known as Osmosis Membrane Bioreactor (OMBR), an enhanced version of the MBR. (Lay, Zhang et al. 2011). In the aerobic OMBR, the non-porous FO membrane acts as a complete barrier for organic retention and biomass separation. Such a hybrid process enjoys the advantages of both high

permeate water quality and lower operation cost as compared to conventional aerobic bioreactors.

Need for research

Membrane fouling is a major problem for membrane based bioreactor as fouling reduces permeate flux and increases the frequency of membrane cleaning and replacement (Le-Clech, Chen et al. 2006; Li and Wang 2006). Although FO was once considered as a low fouling tendency membrane process compared to other pressure driven processes such as reverse osmosis and ultra-filtration (Cath, Childress et al. 2006; Achilli, Cath et al. 2009), the performance of FO process can still be limited by membrane fouling (Tang, She et al. 2010; Wang, Wicaksana et al. 2010; Xiao, Tang et al. 2011). Especially when the FO membrane is applied to treat wastewater which consists of mixed inorganic and organic contaminants, where the fouling mechanisms of FO membrane could be extremely complex and thus affects the overall treatment efficiency.

Nonetheless, the hybrid of FO and aerobic bioreactor is still facing the obstacles such as the costs of aeration and sludge wasting. Therefore, a new type of MBR combining the FO technology and anaerobic bioprocess is proposed. The FO serves the dual purposes of concentrating wastewater and retaining biomass for enhanced biological treatment in the proposed novel anaerobic osmosis membrane bioreactor (AnOMBR). In addition to the merits of OMBR, It could achieve energy recovery from biogas production and lower sludge wasting.

The research needs would be the compatibility of FO technology with anaerobic bioprocess as anaerobic digestion is known to be a complex process (Skouteris, Hermosilla et al. 2012). The performance could be significantly influenced by a number of factors like the type and variability of wastewater, the type of organic contaminants in the influent, its pH, etc.(Gao, Lin et al. 2010). In addition, membrane

fouling is a big concern in AnOMBR as it reduces membrane life-time and increases capital and operational costs.(Spagni, Casu et al. 2010).

Research objectives and scope

This research aims to incorporate FO-based membrane process and anaerobic digestion of low-strength wastewater. The AnOMBR will be studied to find the optimal condition to achieve high treatment and separation efficiency simultaneously. Specific objectives including:

- 1) Membrane performance and fouling evaluation for mixed foulants solution treatment and wastewater treatment;
- 2) Development of integrated submerged osmosis anaerobic membrane reactor;
- 3) Performance evaluation of the reactor under different operation temperature.

1.2. Organisation of Thesis

This thesis comprises in total 6 chapters and scope and highlights of each chapter are listed below:

Chapter 1:

This chapter briefly introduces the background knowledge of AnMBR, FO and identifies the need for combining these two energy efficient technology together into one integrated system: Anaerobic osmosis membrane bioreactor (AnOMBR). The objective and significance of the study are also highlighted.

Chapter 2:

In this chapter, the principles and advantages of both FO and AnMBR are detailed elaborated. It also introduces the current development of FO and FO membrane as well as the challenges facing. The operation configurations, conditions and efficiency of different AnMBRs are also reviewed.

Chapter 3:

Mixed organic fouling of FO membrane in submerged mode was systematically investigated as a preliminary research. Fouling behavior of cellulose triacetate (CTA) FO membrane and thin film composite (TFC) polyamide FO membranes FO membrane were studied. The major finding was under mild FO fouling conditions, TFC FO membranes could have greater fouling tendency compared to CTA FO membranes due to their greater surface roughness.

Chapter 4:

A novel AnOMBR which utilizes CTA FO membrane in anaerobic bioreactor is developed and feasibility of using the AnOMBR to treat low-strength synthetic wastewater at mesophilic temperature is evaluated. The AnOMBR was stable with promising treatment efficiency for a period of 120 days at SRT of 90 days.

Chapter 5:

Performance of AnOMBR to treat low-strength wastewater under mesophilic (35 °C) and room temperature (25 °C) are compared. In both conditions, the AnOMBR was stable with promising treatment efficiency for a period of 120 days at SRT of 90 days. However, the methane production rate at mesophilic condition is 50% higher than at room temperature.

Chapter 6:

The last chapter summarizes the important findings of the research.

CHAPTER 2: LITERATURE REVIEW

2.1. Forward osmosis

2.1.1 Basic principles

Forward osmosis (FO) is a membrane separation process in which water flows from a low-osmotic-pressure feed solution to a high-osmotic-pressure draw solution across a semi-permeable membrane (Cath, Childress et al. 2006; Zhao, Zou et al. 2012). The driving force for transport of water across the FO membrane is the osmotic pressure difference ($\Delta\Pi$) across the membrane. The general equation for water flux across the membrane is given by:

$$J_w = A (\Delta\Pi - \Delta P) \quad (1)$$

J_w : water flux ($\text{L}/\text{m}^2 \text{ h}$);

A : water permeability coefficient ($\text{m}/\text{s Pa}$);

ΔP : applied pressure (bar);

$\Delta\Pi$: osmotic pressure difference across the membrane (bar)

According to van't Hoff Formula, osmotic pressure Π of relatively low concentration solution is proportional to concentration and it can be determined by:

$$\Pi = \beta CRT \quad (2)$$

β : Dimensionless Van't Hoff coefficient (Cath, Childress et al. 2006);

C : Concentration in molarity (mol/L);

R : Gas constant ($0.08206 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1} \cdot \text{K}^{-1}$);

T : Thermodynamic (absolute) temperature (K)

For FO process, the applied pressure ΔP , equals zero and water flux is proportional to the osmotic pressure difference $\Delta \Pi$ across the membrane.

Under same concentration, osmotic pressures of different salt solutions are also different. Therefore, to ensure a large flux, among different types of salt solutions, higher osmotic pressure is the main criterion when selecting a draw solution. The osmotic pressure of different types of solutions at different concentration is plotted in Figure 2-1 based on calculation of OLI Stream Analyzer2.0 (Cath, Childress et al. 2006). The curves show a non-linear dependency between concentration and osmotic pressure especially at high concentration region. It verifies that Van't Hoff Formula does not apply to high concentration solutions.

Figure 2-1. Osmotic pressure of different solutions at different concentration (Cath, Childress et al. 2006)

At the same time, salt will also pass through the membrane from high salt concentration side to low salt concentration end due to the concentration difference and the imperfect salt rejection efficiency of the membrane. The salt flux is calculated as:

$$J_s = B \Delta C \quad (3)$$

J_s : salt flux (g/s);

B : salt permeability coefficient of membrane (m/s);

ΔC : concentration difference across the membrane

2.1.2 Advantages of forward osmosis

Forward osmosis attracts growing interest over the past decade due to its wide range of potential benefits. It enjoys the advantage that lower energy input thus lower cost input is required to drive the process when concentrated draw solution is available or can be easily regenerated (McGinnis and Elimelech 2008; Elimelech and Phillip 2011). In addition, the osmotic power could even be harvested from the salinity-gradient resources by pressure retarded osmosis process (Achilli, Cath et al. 2009; She, Jin et al. 2012). This advantage becomes even more attractive under the pressure of sharp population growth and energy shortage globally. Furthermore, FO applies high retention FO membrane so that various contaminants, even with small size, could be rejected at the membrane surface. Additionally, Recent studies have showed that as compared to the pressure-driven processes, membrane fouling, either organic or inorganic, appears to be more reversible in FO process. This could be attributed to a thicker but less compact foulant cake layer structure formed during FO (Mi and Elimelech 2010; Mi and Elimelech 2010; Kim, Elimelech et al. 2014). By optimizing the hydrodynamics, the extend of FO fouling could be mild (Achilli, Cath et al. 2009; Lee, Boo et al. 2010).

2.1.3 Major challenges in forward osmosis

In osmotic-driven membrane processes, the osmotic pressure difference across the active layer is much lower than the bulk osmotic pressure difference, which results in much lower water flux than expected (Cath, Childress et al. 2006). The lower-than-expected water flux is often attributed to several membrane-associated transport phenomena. Specifically, two most dominant factors could be the concentration polarization and membrane fouling.

- **Concentration Polarization (CP)**

External Concentration Polarization (ECP)

When active layer is facing the feed solution, solutes build up at the active layer, leading to an increase of osmotic pressure at the surface. This is called concentrative external concentration polarization (ECP). In the other orientation, draw solution at the interface of active layer is diluted by permeated water, lowers the osmotic pressure near the membrane surface. This is called dilutive ECP (Cath, Childress et al. 2006). Both concentrative and dilutive ECP weaken the driving force across the membrane and reduce the flux. The adverse effect of ECP can be minimized by increasing cross flow velocity or by manipulating the water flux (M. Mulder, 1997). However, because the current water flux level of FO is still relatively low, the flux deterioration effect due to ECP is less dominant comparing to pressure-driving osmosis such as RO. Internal Concentration Polarization (ICP) in the other hand, plays a more important role (McCutcheon, McGinnis et al. 2006). With the development of new generation of FO membrane which provides higher flux, ECP could become important.

Internal Concentration Polarization (ICP)

ICP is the other type of the concentration polarization, which is due to the asymmetric property of the membrane and exists within the porous support layer.

Figure 2-2. mechanism of concentrative and dilutive concentration polarization (T.Y.Cath et.al, 2006)

ICP can be subdivided into concentrative ICP and dilutive ICP (T.Y.Cath et.al,2005).

Figure 2-2 above compares the differences between these two mechanisms. When active layer is facing the draw solution side, water passes through membrane from the low-concentration feed to the concentrated draw solution side and the solutes against the interior surface of the active layer becomes more concentrated. At the same time, salt particles travels from the draw solution to the feed water side, accumulating inside the porous supporting layer. These two concentrating effects are counteracted by solute back-diffusion away from the active layer, but the steady state concentration is much higher than in the bulk feed solution, building up the salt concentration C_3 on the membrane walls, leading to a higher concentration compared to bulk feed water concentration C_f . Consequently, the effective osmotic pressure difference as the driving force is smaller than apparent pressure difference, causing a reduced flux. This is called concentrated ICP and showed in figure 2-2a.

More severe ICP occurs when active layer facing the feed water as shown in figure 2-2b. The solute in the draw solution must penetrate the porous support layer to the interior surface of the active layer before flux can occur. As pure water travel from the feed water side to the draw solution side, it dilutes the draw solution within the porous support layer by convection. At the same time, the solute diffuses back to the active layer and a steady-state is quickly reached. However, due to the severe diluting effect on the high concentration of draw solution, the interface concentration at draw solution side C_3 is much lower than the bulk draw solution concentration, leading to a much lower driving force as the concentration difference across the membrane is much lower than apparent concentration difference.

Since ICP takes place at porous supporting layer rather than active layer and the effect is established immediately, it cannot be mitigated by altering hydrodynamic conditions such as increasing the flow rate or turbulence.

- **Membrane fouling in forward osmosis process**

Membrane fouling is an important and inevitable obstacle to conquer in all membrane processes (Hoek and Elimelech 2003; Lee, Boo et al. 2010). Severe membrane fouling may limit permeate production and reduce membrane life, thereby increase operational and capital costs (Zhao, Zoua et al. 2012). As little or no external pressure is applied to FO process, it was first been recognized as a low fouling process based on the early study of Cath et.al. as no sign of flux reduction due to fouling was observed in their studies (Cath, Childress et al. 2006). With the rapid development of FO technologies, it reveals that membrane fouling does exist in FO.

Depending on the different species of foulants, FO fouling could be generally categorized into organic fouling, inorganic fouling (scaling) and biofouling. For organic fouling, natural organic matter (NOM) has been found to be a serious fouling

agent in FO (Lee et al., 2010; Valladares Linares et al., 2012). Model foulants including sodium alginate, bovine serum albumin (BSA)/ lysozyme as well as Aldrich Humic Acid (AHA) have been used to test the fouling behaviors of different NOM (polysachloride, protein and humic compounds) on FO membranes (Liu and Mi, 2012, Mi and Elimelech, 2008, Qi et al., 2012 and Tang et al., 2010).

Zhao et al. (2011) found organic fouling to be more severe and irreversible than inorganic fouling in FO, but inorganic scaling may be a greater issue for FO application in wastewater. Precipitation such as calcium carbonate or calcium sulphate (gypsum) could occur on membrane surface and gypsum scaling cannot be controlled by simple pH adjustments, and is also affected by the membrane material, i.e. heterogeneous/surface crystallization on PA membranes causes severe flux decline (Mi and Elimelech, 2010). In addition, precipitations such as BaSO_4 , $\text{Mg}(\text{OH})_2$ and silica also contribute to membrane scaling.

Biofouling can also be an important limiting factor to FO process, due to microorganisms' strong adhesion onto the membrane surface and their secretion of extracellular polymeric substances (EPS) to establish biofilm integrity (Flemming et al., 2000 and Staudt et al., 2004). Different from organic and inorganic fouling, which could be alleviated by physical cleaning (Mi and Elimelech 2008; Mi and Elimelech 2010; Mi and Elimelech 2010), flux decline caused by biofouling could not be easily recovered by physical cleaning and chemicals like chlorine must be added to enhance the fouling control (Yoon, Baek et al. 2013).

Generally for FO application in practice, fouling occurs as a result of combined interactions among foulants and various factors. It was investigated by Mi and Elimelech that similar to RO process, FO fouling is also governed by the coupled effect of chemicals and hydrodynamic conditions. The occurrence of ICP makes FO fouling even more complicated (Tang et al., 2010).

Operational parameters such as cross-flow velocity and use of spacers can affect the rate and extent of membrane fouling (T.Y. Cath, 2009; Choi et al., 2005). Increasing the cross-flow velocity, prior to cake-forming compaction, can reduce NOM accumulation and hamper growth of the fouling layer in FO membranes. However once the cake layer forms, changes in hydrodynamic conditions barely affect the fouling behaviour (Mi and Elimelech, 2008). Spacers placed alongside the membrane induce mixing and have been shown to prevent the attachment of foulants (Boo, Elimelech et al. 2013) (Valladares Linares, Bucs et al. 2014) . In addition, use of flow pulsation (Boo, Elimelech et al. 2013), and introducing air bubbles (Mi and Elimelech 2010) could also mitigate fouling but will increase the energy consumption of the system.

Fouling propensity in FO is also dictated by the affinity between foulants and the membrane surface. Therefore, membrane surface property could also influence the development of a fouling layer on the membrane surface. Specific properties include charge (Boo et al., 2012 and Xu et al., 2006), roughness (Li et al., 2007), hydrophilicity and electrostatic attraction.

Effect of membrane orientation on fouling was studied by Tang et.al. (Tang, She et al. 2010). Results showed that active layer-facing-feed solution (AL-FS) configuration had inherently stable water flux and in contrast, the active layer-facing-draw solution (AL-DS) configuration was highly prone to flux reduction under fouling conditions due to the pore clogging of the FO supporting layer, which greatly enhances the ICP effect in addition to the reduced membrane permeability.

There are both on-line and off-line methods to detect and characterize FO membrane fouling. Non-invasive and visual on-line methods can detect early signs of fouling in real-time such as flux decline and solute rejection. Off-line methods could help to determine morphological, chemical and physical properties of the foulant type

influencing FO membrane fouling. Specific techniques include scanning electron microscopy (SEM), energy dispersed X-ray (EDX), fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) etc. To further investigate FO fouling, direct microscopic observation, an important fouling characterization method used to study membrane fouling in pressure-driven membrane processes (Kang, Subramani et al. 2004), was firstly applied to FO fouling studies by Tang's group (Wang, Wicaksana et al. 2010). This application makes the detection of large foulants deposition (e.g. microbes or particles) in bio-fouling or colloidal fouling visible and straightforward.

Another interesting topic is the critical flux concept applied to pressure-driven membrane processes, which generally defined as the flux level above which membrane fouling becomes noticeable (Field, Wu et al. 1995; Wu, Howell et al. 1999; Chan and Chen 2001; Bacchin, Aimar et al. 2006), were also first raised to be applied in FO processes. Studies regarding fouling caused by other organic macromolecules such as algae done by Zou et.al (Zou, Gu et al. 2011) verified the effect of membrane orientation and the existence of critical flux, below which fouling was rather mild to be observed. The phenomenon of multivalent-ion diffusion across membrane and severe fouling caused by coagulation between ions and macromolecules were also investigated.

2.1.4 FO membranes

Technology of FO membrane development is rapidly growing in last decade. An ideal FO membrane shall possess high water permeability, high solute rejection and as well as good chemical stability (Wang, Shi et al. 2010). The majority of membranes currently employed in industry are asymmetric membranes (Wang, Dlamini et al. 2014) and cellulose triacetate (CTA) FO membrane is one of the dominant types in the market. CTA has many advantages over other polymers such

as relatively high hydrophilicity and mechanical strength, wide availability and good resistance to chlorine degradation (Baker 2004; Geise, Lee et al. 2010; Meng, Liao et al. 2010). Based on these unique characteristics, cellulose acetate has been widely used to prepare RO and FO membranes. On the other hand, drawbacks of cellulose acetate such as poor resistance to hydrolysis and biological attack (Vos, Burris et al. 1966; Mulder 1996; Baker 2004; Geise, Lee et al. 2010) also limit its usage for developing FO membrane. The best pH and temperature range to slow down the hydrolysis of CTA is pH 4–6, and ambient solution temperature below 35 °C (Vos, Burris et al. 1966; Mulder 1996; Baker 2004).

In the meantime, recent developments in thin film composite (TFC) polyamide FO membranes show these membranes can have significantly higher water flux and better solute rejection compared to CTA FO membranes (Wang, Shi et al. 2010; Yip, Tiraferri et al. 2010; Wei, Qiu et al. 2011). As compared to typical TFC-RO membranes which experienced low water fluxes due to their dense support layers and thick fabric backing, dramatic decreases in the structural parameter have been observed in TFC-FO membranes thanks to the major advance of phase inversion-formed supports that were specifically tailored to minimize the structural parameter (Shaffer, Werber et al. 2015). Those FO membrane researches have rapidly contributed to the development of commercially-available, high-flux, TFC-FO membrane modules recently (Oasys Water Inc., Boston, MA; HTI). In addition, TFC membranes are also superior to CTA membranes in terms of their better pH stability and resistance to hydrolysis and biological degradation (Vos, Burris et al. 1966; Mulder 1996; Geise, Lee et al. 2010). However, TFC membrane has two major drawbacks. One is the proneness to fouling from all kinds of matters in the influent. The other is its vulnerability to chlorine, which is the most widely used disinfectant in water treatment for biofouling control. This may be due to the presence of

chlorine-sensitive sites in the polyamide film such as amide nitrogen and aromatic rings (Glaser, Hong et al. 1994; Kwon and Leckie 2006).

2.1.5 Recent applications of FO process

In recent years, FO has been considered for various potential applications, such as seawater desalination, power generation, food processing industry and wastewater treatment.

- **Desalination**

Based on the different choices of draw solution, FO desalination process could be generally divided into two types.

One is using draw solution which could be decomposed into volatile gas such as CO_2 and SO_2 when heating-up after osmotic dilution. Pure water also could be recovered and volatile gas could be recycled back as draw solution. Example is the combination of KNO_3 and SO_2 as draw solution for seawater desalination described by McGinnis in patent (McGinnis 2002). As the solubility of KNO_3 is temperature dependent, saturated KNO_3 precipitates out of the diluted draw solution after cooling. The diluted KNO_3 solution is then used as feed solution in another FO unit in which dissolved SO_2 is used as draw solute. After osmotic dilution, the dissolved SO_2 can be removed by heating and pure water is recovered. McCutcheon et al. (McCutcheon, McGinnis et al. 2006) also proposed a novel method using a mixture of CO_2 and NH_3 as the draw solutes for desalination. The highly soluble and thermolytic ammonium bicarbonate (NH_4HCO_3) functions as draw solution and high water fluxes and high feed water recoveries is achieved. However, the cost of artificial draw solution and the energy input for heating up the draw need to be taken into consideration when evaluating the overall cost and energy effectiveness of system.

The other one is using water-soluble salts as the draw solute. Solutes with monovalent ions such as NaCl, KCl and solutes with bivalent ions such as Na₂SO₄, MgSO₄, MgCl₂, CaCl₂ etc. were tested using a hybrid FO-NF system for desalination by Choi et al. (Choi, Choi et al. 2009). Cath et al. employed FO as an osmotic dilution process to achieve simultaneous seawater desalination and purification of impaired water in a hybrid FO–RO process using seawater as the draw solution (Cath, Hancock et al. 2010). In these hybrid FO-NF or FO-RO system, FO process acts as a pre-treatment process to pre-dilute the draw solution and further pure water recovery process is necessary in order to complete desalinate the draw solution. The energy consumption of the water recovery step needs to be taken into consideration when evaluating the overall system energy efficiency.

- **Power generation**

The osmotic power arising from the salinity gradient between two solutions is sustainable and abundantly available around area where river water mixed with seawater. Theoretically, 1.7 MJ of energy could be generated when 1 m³ of river water is mixed with 1 m³ seawater and the number could rise to 2.5 MJ with a large surplus of seawater (Veerman, Saakes et al. 2009). This salinity gradient energy could be extracted using technique of pressure retarded osmosis (PRO).

Figure 2-3 shows the schematic diagram of a typical PRO power generation plant. In a PRO system, water permeates from a low salinity feed solution through a membrane into a pressurized high salinity draw solution, e.g. seawater. In the meantime, power is obtained by depressurizing part of the diluted seawater through a hydro turbine (Loeb 2002).

Figure 2-3. Schematic diagram of PRO process

- **Food processing**

Dehydration and concentration of food products are usually necessary in order to increase the stability of ingredients and to reduce the storage and transportation cost. Forward osmosis could achieve the goal without pressurizing or heating the ingredients compared to the traditional evaporation process, thus preserving the shape and nutrients (Petrotos and Lazarides 2001). Therefore, FO has already been used as the dehydration unit for the processing of fruit juices such as strawberry, papaya, pineapple (Park, Bin et al. 2002; Singh, Sharma et al. 2008; Blanda, Cerretani et al. 2009; Igual, Contreras et al. 2010; Bchir, Besbes et al. 2012; Sharif, Pirouzifard et al. 2013) and vegetable concentrations such as peppers, tomato sauce and mushrooms (Petrotos and Lazarides 2001; Ozen, Dock et al. 2002; Kurozawa, Azoubel et al. 2012).

- **Wastewater treatment**

Due to the nature of low osmotic pressure of wastewater in general, the idea of coupling the wastewater with high osmotic pressure seawater in forward osmosis

process could be worth-trying. The feasibility of using direct osmosis (previous denotation of FO) for industrial wastewater treatment was investigated back in 1970s and seawater was suggested as the draw solution based on its abundance and low cost (Votta, Barnett et al. 1974; Anderson 1977). Cath et al. also applied impaired water and saline water as the feed and draw solution respectively in FO process for water purification and reuse (Cath, Drewes et al. 2009) . Moreover, there are also studies on applying FO for concentrating the anaerobic digester centrate and activated sludge, reveal the many possibilities of FO in wastewater treatment.

In addition, recent studies had utilized a submerged FO membrane in the bioreactor to construct novel osmotic MBR (OMBR) (Achilli, Cath et al. 2009; Lay, Zhang et al. 2011). Figure 2-4 shows the schematic diagram of a typical OMBR. In an OMBR system, wastewater is fed into a reactor which is continuously aerated to supply oxygen for the biomass and to scour the membrane. Concentrated brine water, either from sea water or wasted brine from desalination plant, flowing as a loop within submerged membrane cell. Clean permeate flows from low concentration feed sludge to high concentration brine loop, the diluted DS is sent for re-concentration (e.g., RO or distillation) to produce high quality water permeate. Thus, in most wastewater treatment applications, FO is not the ultimate process but a pretreatment step.. In the case where pure water is required as a final product, i.e. water reclamation, an extra step of recovery of pure water from draw solution and the associated energy consumption must be taken into consideration when assessing the cost-effectiveness of the overall system. As compared to the MF or UF process in a conventional MBR, the FO process in the OMBR provides a much higher rejection at a lower hydraulic pressure (Achilli, Cath et al. 2009). A challenge of the technology is the salt accumulation in sludge. As membrane bioreactor is a confined volume and sludge retention time could be several-months long, high retention of influent constituents coupled with reverse diffusion of draw solute result in the salt

elevation phenomenon. Both the positive and negative effects of salinity were discussed in Lay's recent review paper (Lay, Liu et al. 2011). The elevated salinity may have impacts on various systemic aspects, including membrane performance, microbiology and physic-chemistry in the high-retention MBR.

With regard to the membrane aspects, it would reduce the effective driving force, aggravate fouling, reduce the water flux, and impair the product water quality. With regard to the physicochemical aspects, it tends to be unfavorable for oxygen transfer, density, turbidity, viscosity, salt precipitation, solute interaction and colloid chemistry. With regard to the biological aspects, increasing salt concentration changes the microbial community due to salinity selection. Generally acclimation works to sustain the BOD removal for salt concentration up to 30 g/L. Beyond that, addition of halophilic or halotolerant microorganisms should be considered. However, biological nutrients removal could be more affected by the elevated salt conditions.

Figure 2-4. Schematic diagram of OMBR system

2.2. Anaerobic membrane bioreactor (AnMBR)

2.2.1 Introduction to the membrane bioreactor (MBR)

Membrane bioreactors (MBRs) are an integrated biological wastewater treatment technology that combine membrane filtration for sludge retain and separation and biological process (Visvanathan, Ben-Aim et al. 2000; Li and Wang 2006). Since the first commercial development of MBR for ship-board sewage treatment by Dorr-Oliver back in late 1960s (Bailey et al., 1971), the development and commercialization of MBR technology keep a significant pace in recent decades and confidence in the technology grows indicated by the increase of installed MBR in number and maturity (Judd 2010).

The membrane application in bioreactors can overcome the disadvantages of the sedimentation tanks that are used in most biological treatment systems. In addition,

MBRs offer a number of advantages over the conventional activated sludge process, such as high sludge retention time and concentrated biomass as well as compacted space taken, providing better quality effluent and reduced sludge yield (Brindle and Stephenson 1996; Visvanathan, Ben-Aim et al. 2000; Rosenberger and Kraume 2003; Li and Wang 2006).

2.2.2 Anaerobic treatment

Anaerobic treatment processes remove dissolved and suspended organic chemical constituents through anaerobic digestion, as well as suspended matter through physical separation. As compared to conventional aerobic processes, anaerobic biological treatment is characterized by (Stephenson, Judd et al. 2000):

- a lower energy demand due to the absence of aeration
- slower microbial growth
- lower COD removal (generally 60–90%)
- no nitrification
- greater potential for odour generation
- longer start up (months cf. weeks)
- higher alkalinity
- lower sludge production
- biogas (methane) generation.

Anaerobic micro-organisms are known to grow and reproduce more slowly than the aerobic ones. Due to their low growth rate, biomass retention is critical for high-rate anaerobic treatment of wastewaters. Traditional way of achieving the necessary biomass retention includes granule and biofilm based technologies to enable the operation of bioreactors at high biomass concentrations (Jeison, Díaz et al. 2008) . However, under specific conditions, such as high salinities or thermophilic temperatures, biofilm and granule formations do not proceed well and are negatively

affected. Anaerobic membrane bioreactor (AnMBR) integrates anaerobic biological treatment process with membrane filtration (Judd 2010) to achieve the required sludge retention in non-conventional conditions. It can be operated at longer SRTs, not only to retain all micro-organisms, but also to fully grow and improve the anaerobic treatment significantly (Meng, Zhang et al. 2007) .

Table 2-1 summarizes the characteristic of AnMBR and makes comparison of AnMBR with conventional aerobic treatment, anaerobic treatment and aerobic MBR (Meng, Zhang et al. 2007; Lin, Peng et al. 2013). It shows that AnMBR technology combined the advantages of anaerobic treatment and MBR technology, such as total biomass retention, excellent effluent quality, low sludge production and high energy efficiency.

Table 2-1: Comparison among conventional bio-treatment processes and MBRs

Features	Conventional Aerobic Treatment	Conventional Anaerobic Treatment	Aerobic MBR	Anaerobic MBR
Organic removal	High	High	High	High
Effluent quality	High	Moderate to poor	Excellent	High
Sludge production	High	Low	High to moderate	Low
Organic loading rate	Moderate	High	High to moderate	High
Biomass retention	Low to moderate	Low	Total	Total
Energy requirement	High	Low	High	Low
Footprint	High	High to moderate	Low	Low
Temperature sensitivity	Low	Low to moderate	Low	Low to moderate
Startup time	2-4 weeks	2-4 months	<1 week	<2 weeks

Nutrient requirement	High	Low	High	Low
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2.2.3 AnMBR configuration

There are two main AnMBR process configurations: submerged or immersed and side-stream. Schematic diagrams of these two configurations are shown in Figure 2-5.

Figure 2-5. Schematic diagrams of AnMBR configurations - (1) Side stream (external) AnMBR, (2) submerged (immersed) AnMBR (Judd 2010)

Generally, the side stream configuration provides stronger and more direct hydrodynamic force over membrane surface so that enhance the control of fouling and flux performance. Membrane replacement is also easier in this configuration. However, frequent cleaning leads to high energy consumption (Le-Clech, Chen et al. 2006; Lin, Peng et al. 2013) and high cross-flow velocity could plays negative impact on biomass activities in AnMBR (Brockmann and Seyfried 1996; Choo and Lee 1996). In immersed configuration, membrane is directly placed in the mixed liquor.

The operation conditions could be mild due to the lower shear velocity and much lower energy is required to drive the process.

2.2.4 Operation condition

Operation conditions for AnMBR vary a lot and usually are freely combined to meet research or application purposes. However, anaerobic treatment is generally considered for high-strength wastewaters as low strength imply low biomass growth yield and growth rate, such that biomass concentration in the reactor is more difficult to sustain. Combination of membrane with anaerobic treatment ameliorates this problem to a large extent, such that the range of anaerobic process operation can be extended to lower limits. This is achieved by the retention of the biomass in the reactor by the membrane independently of the HRT in the same way as for aerobic systems. Hydraulic retention time (HRT) values could be as short as 2 hours to 20 days (Jeong, Kim et al. 2010; Kim, Kim et al. 2011). Longer HRT means less influent is introduced into reactor in unit time, showing a slower water production rate. On the other hand, solids retention time (SRT) could range from 18 days to 300 days or even longer (Trzcinski and Stuckey 2009). Generally, longer SRT means less wastage and disturbance of sludge, resulting in better generation of biogas (Trzcinski and Stuckey 2010; Ozgun, Dereli et al. 2013).

Most of the AnMBRs were operated under mesophilic condition, that is at around 35 °C (Jeison, Van Betuw et al. 2008; Lin, Xie et al. 2009) or at the thermophilic condition, that is around 55 °C (Jeison and van Lier 2007; Wijekoon, Visvanathan et al. 2011); Very few AnMBRs were operated under psychrophilic temperatures which is around 20 °C (Trzcinski and Stuckey 2010). Temperature is the key parameter to the AnMBR treatment efficiency. Generally the higher the temperatures are, the better are the COD removal efficiencies (Trzcinski and Stuckey 2010; Santos, Ma et al. 2011). It is also found that at thermophilic temperature, AnMBR are more

capable of coping with the higher volumetric loading rate compared to at mesophilic and psychrophilic conditions (Jeison, Van Betuw et al. 2008) . Usually, higher organic loading rate is associated with the accumulation of volatile fatty acids, high concentration of which could inhibit the microbial activity, leading to a lower COD removal efficiency (Bohdziewicz, Neczaj et al. 2008; Wijekoon, Visvanathan et al. 2011). Therefore, generally AnMBRs are considered “high-temperature friendly”.

2.2.5 Treatment efficiency

The most crucial and important requirement for the operation of AnMBR is to take influent with high organic carbon content and discharge effluent with low organic carbon content. The difference of organic carbon content between the influent and effluent is either retained within the bioreactor or utilized for growth of micro-organisms. The overall efficiency of organic removal is evaluated by the percentage of the organic carbon content in effluent over that in influent. While the COD concentration of influent may vary from 100mg/L of dilutive municipal wastewater to more than 10000 mg/L of industrial waste water (Hu and Stuckey 2006; Saddoud, Hassaïri et al. 2007; Akram and Stuckey 2008; Bohdziewicz, Neczaj et al. 2008; Jeison, Van Betuw et al. 2008; Liao, Xie et al. 2010) depending on the specific application of AnMBR, the removal efficiency also vary from as low as 76 % to up to 99%. The inconsistency of treatment efficiency is due to the difference of operation condition, quality of influent and membrane adapted (Hu and Stuckey 2006; Trzcinski and Stuckey 2010; Kim, Kim et al. 2011; Sutton, Melcer et al. 2011; Skouteris, Hermosilla et al. 2012).

For almost all types of AnMBRs, high total suspended solids (TSS) removal efficiency of more than 99% was reported (Kocadagistan and Topcu 2007; Saddoud, Hassaïri et al. 2007). In addition, total removal of pathogens such as *Escherichia coli* and *Enterococci* could be achieved.

On the other hand, the treatment efficiency would be affected by inhibitors such as ammonia and sulfite. Ammonia is an essential nutrient for the growth of microorganisms involved in anaerobic digestion, but the accumulation of ammonia in high concentration could raise the pH and forms higher levels of free ammonia, which is known as an inhibitor to methanogenic microorganisms (Jin et al., 2012). Sulfate reducing bacteria (SRB), which reduce sulfate to sulfide, play a significant role in the anaerobic digestion of complex substrates. However, it was found that SRB: i) generate sulfides which may be inhibitory and/or toxic to methane producing bacteria; ii) reduce the rate of methanogenesis; and iii) decrease the quantity of methane produced by competing for the available carbon and/or hydrogen (McCartney and Oleszkiewicz 1991).

2.2.6 Energy efficiency

Although attention paid to energy consumption of AnMBR is limited, there are still some interesting studies regarding the energy sustainability of AnMBR operation. One of them is by Jeison and van Lier (Jeison and van Lier 2007) who claimed that the cost of energy consumption for the AnMBR operation is far less compared to the membrane cost in the AnMBR, that is comparing 0.046 €/m³ to 0.5 €/m³ per treated water respectively estimated after making a series of rational assumptions. Another interesting research was done by Kim et al. in 2011 (Kim, Kim et al. 2011) who operated a conventional anaerobic reactor preceding an AnMBR. It was concluded that the total energy required for fluidization in both reactors was equal to 0.058 kWh/m³, 0.028 kWh/m³ of energy was consumed by the AnMBR out of the total energy consumption of 0.058 kWh/m³ to fully fluidize both reactor and the energy consumption could be easily covered by only 30% of the methane produced by the system.

AnMBRs utilize organics in wastewater to produce an important energy source: methane gas (CH_4) (Sutton, Melcer et al. 2011). Based on previous literature, AnMBRs could convert up to 98% of the influent COD into biogas with very small sludge production due to the low growth yield of anaerobic micro-organisms (Van Zyl, Wentzel et al. 2008). Generally the produced biogas is with excellent fuel quality, in some cases, having a composition of more than 80% of CH_4 (Hu and Stuckey 2006; Liao, Xie et al. 2010), which can then be burnt to produce electric power to cover the energy consumption of the membrane filtration (Meng, Zhang et al. 2007) and even deliver net energy for wastewater treatment plant (Van Zyl, Wentzel et al. 2008). In some cases the composition of CH_4 would be lower to around 70%. This is due to the nature and complexity of the degraded organics in mix liquor which may lead to various CO_2/CH_4 ratio (Chernicharo 2007). Organic wastes rich in carbohydrates would increase the biogas production and percentage of CH_4 (Zhou, Li et al. 2012).

CHAPTER 3: ORGANIC FOULING OF THIN-FILM COMPOSITE AND CELLULOSE TRIACETATE FORWARD OSMOSIS MEMBRANE BY OPPOSITELY CHARGED MACROMOLECULES

3.1. Introduction

Forward Osmosis (FO) process is driven by osmotic energy, which is arisen from the osmotic difference between draw solution and feed solution across the membrane due to their concentration difference. Under this osmotic driving force, water flows spontaneously through the membrane from the low-concentration feed solution to the high-concentration draw solution side. Implied lower energy consumption and higher retention of membrane lead to a growing interest in applying FO process into wastewater treatment and seawater desalination as well as other water treatment field (Cath, Childress et al. 2006; McCutcheon, McGinnis et al. 2006; Holloway, Childress et al. 2007; Andrea, Tzahi Y. et al. 2010).

Fouling can severely deteriorate membrane performance during water/wastewater treatment (Jarusutthirak and Amy 2006; Lay, Zhang et al. 2011; Tang, Chong et al. 2011). Existing FO fouling studies have focused on the effects of permeate flux level (Mi and Elimelech 2008; Tang, She et al. 2010; Zou, Gu et al. 2011; She, Jin et al. 2012), membrane orientation (Tang, She et al. 2010; Wang, Wicaksana et al. 2010; Zhao, Zou et al. 2011), and DS type (Zou, Gu et al. 2011; She, Jin et al. 2012). Investigations on FO fouling mechanisms often involve single type of model foulant (Mi and Elimelech 2008; Tang, She et al. 2010; Zhao, Zou et al. 2011; She, Jin et al. 2012). On the other hand, literature on FO fouling by mixed foulants is still lacking (Liu and Mi 2012). Systematic study is still required to understand the role of the

interactions between the different foulant species on FO fouling behavior in mixed foulants systems.

The effect of FO membrane materials on fouling is also of great interest. An ideal FO membrane shall possess high water permeability, high solute rejection and as well as good chemical stability (Wang, Shi et al. 2010). Due to the dominance of cellulose triacetate (CTA) FO membranes in the commercial market (Wei, Qiu et al. 2011), most existing FO fouling studies were performed with CTA membranes (Mi and Elimelech 2008; Tang, She et al. 2010; Wang, Wicaksana et al. 2010; Zhao, Zou et al. 2011; She, Jin et al. 2012). On the other hand, recent developments in thin film composite (TFC) polyamide FO membranes show these membranes can have significantly higher water flux and better solute rejection compared to CTA FO membranes (Wang, Shi et al. 2010; Yip, Tiraferri et al. 2010; Wei, Qiu et al. 2011). In addition, TFC membranes are also superior to CTA membranes in terms of their better pH stability and resistance to hydrolysis and biological degradation (Vos, Burris et al. 1966; Mulder 1996; Geise, Lee et al. 2010). Despite the great potential of TFC membranes for FO applications, their fouling behavior is rarely reported in the literature. Thus, there is a critical need to assess fouling performance of TFC FO membranes and to compare it with that of CTA FO membranes.

The objectives of this study were 1) to understand fouling of forward osmosis membrane by two oppositely charged organic macromolecules. 2) to compare the flux performance and foulant deposition differences between the CTA membrane and TFC membrane.

3.2. Methods and experiments

3.2.1 Membrane parameters

Two membranes were used in the current study, including a commercially available CTA FO membrane supplied by Hydration Technology Inc. (HTI, Albany, OR) and a polyamide TFC FO membrane synthesized in-house according to Wei et al. (2011). The properties of these membranes are summarized in Table 3-1.

Table 3-1. FO membrane properties

Membrane	Water permeability, A (10^{-12} m/s·Pa)	Salt permeability, B (10^{-8} m/s)	NaCl rejection (%)	Contact Angle ($^{\circ}$) ^d	Zeta potential at pH 6 (mV) ^d	RMS surface roughness ^d (nm)
CTA	2.8 ± 0.1 ^a	17.5 ± 0.5 ^a	89.5 ^a	77 ± 1 ^b	-2.1 ± 0.3 ^b	30 ± 6
TFC	5.0 ± 0.7 ^c	9.4 ± 1.9 ^c	93.4 ^c	45 ± 4 ^c	-10 ± 5	105 ± 11

- a. A, B values, NaCl rejection of CTA membrane are obtained from She et al. (2012b)
b. Contact angle and zeta potential of CTA membrane are obtained from Jin et al. (2012)
c. Characterization of TFC membrane are obtained from Wei et al. (2011)
d. Measured for active layer of both membranes

The TFC membrane was formed by interfacial polymerization of m-phenylenediamine and trimesoyl chloride on a polysulfone substrate with straight finger-like pores to minimize its mass transfer resistance (Wei et al., 2011). As compared to the CTA membrane, the TFC membrane has a higher water permeability and a lower salt permeability (i.e., better salt rejection). The TFC membrane rejection layer is also more hydrophilic (contact angle $\sim 45^{\circ}$) and more negatively charged (zeta potential ~ -10 mV at pH 7) compared to the CTA membrane (contact angle $\sim 77^{\circ}$ and zeta potential ~ -2 mV). The surface roughness of the TFC membrane (~ 105 nm) is significantly higher than that of CTA membrane (~ 30 nm) based on the root-mean-square roughness measurements by atomic force microscopy (AFM). Figure 3-1 shows the surface morphology of both CTA and TFC

membrane measured by AFM (Park Systems XE-100). Graphs were obtained using non-contact head mode with a scanned membrane size of $5 \times 5 \mu\text{m}$ and digitized with a resolution of 256×256 pixels.

(a)

(b)

Figure 3-1. Surface morphology of membrane under atomic force microscopy: (a) CTA membrane; (b) TFC membrane

3.2.2 Foulants

Lysozyme (LYS, Fluka 62971) and sodium alginate (ALG, Sigma A2158) were chosen as model foulants in the current study to represent proteins and polysaccharides with opposite charge. The molecular weights of LYS and ALG are 14.3 kDa and 12-80 kDa, respectively (Wang and Tang 2011). Within the test pH range (pH 5 - 8), LYS is positively charged and ALG is negatively charged (Wang and Tang 2011; Wang and Tang 2011). Both foulants were received in powder form with purity above 98%. They were freshly dissolved in ultrapure water (resistivity of 18.2 MΩ.cm, Millipore Integral 10 Water Purification System) prior to fouling tests.

3.2.3 FO submerged setup and fouling test

The schematic layout of the experimental setup is shown in Figure 3-2.

Figure 3-2 Schematic diagram of experimental setup

The membrane cell with effective membrane area of 80 cm^2 was fully submerged into a 6-L feed solution (FS) tank. Air bubbles were introduced into the FS by an air diffuser for FS mixing and fouling control. A diamond-shaped spacer was placed in the draw solution (DS) channel (width of 5 cm and depth of 2 mm), and a peristaltic pump was used to recirculate the DS at a crossflow velocity of 16.7 cm/s . The weight of the DS tank (3L) was measured by a digital balance that is connected to a computer data acquisition system.

For each FO experiment, a new membrane coupon was used with its active layer facing the FS (i.e., the AL-FS membrane orientation). NaCl solutions of 3.0 M and 2.2 M were used as DS for experiments conducted using the CTA membrane and the TFC membrane, respectively, in order to achieve an identical initial flux of $25 \text{ L/m}^2\text{h}$. Membrane coupon was first equilibrated with background electrolytes (FS without

the addition of foulants) for 20 mins. The flux after the equilibration stage was recorded as the initial flux. Foulants were then added into the feed tank to initiate membrane fouling, and each fouling test was performed for 220 min. The effects of foulant composition, solution pH, ionic composition and membrane properties on FO fouling were investigated by varying one parameter at each time while keeping the others constant. Baseline tests were performed to evaluate the membrane flux behavior without the presence of foulants in feed solution. Unless otherwise specified, the following reference fouling test conditions were applicable:

- The total foulant concentration in feed solution was 100 mg/L, and only the mass ratio of LYS:ALG was varied to study the effect of feed composition;
- Feed solution pH was adjusted to 7 using NaOH/HCl solution unless the effect of pH was tested, and the total ionic strength was 10 mM by the addition of NaCl and/or CaCl₂;
- Temperature was maintained at 23 ± 1 °C.

3.2.4 Foulant mass deposition evaluation

After each fouling test, the fouled membrane coupon was analyzed for foulant mass deposition (Wang and Tang 2011; Wang and Tang 2011). Briefly, sodium dodecyl sulfate (SDS, 5%) solution and NaOH solution (pH 11) were used to extract LYS and ALG, respectively. Membrane disks (area of 1.267 cm²) were cut from the fouled coupon and were soaked in 5 ml extraction solution for 1 hr and vortexed for 5 min. The concentration of LYS extractant was analyzed using a protein assay kit (Sigma, QuantiPro BCA Assay Kit, 0.5-30 µg/mL) at UV of 562 nm (Brown, Jarvis et al. 1989; Wang and Tang 2011), and that of ALG extractant was analyzed using phenol-sulfuric acid method at UV of 485 nm (Dubois, Gilles et al. 1956; Wang and Tang 2011). Calibration curves were prepared using standard solutions with water chemistry matrix identical to the extraction solution to minimized analysis errors.

3.3. Results and discussion

3.3.1 Effect of foulant composition

This section reports the effect of foulant composition in the FS on flux behavior (Figure 3-3a) and foulant deposition (Figure 3-3b) during FO fouling of the CTA membrane. While the total foulant concentration was fixed at 100 mg/L, the feed composition was changed by varying LYS content from 0% to 100%. In Figure 3-3a, slight water flux decline was observed for the baseline condition where foulant was absent in the feed. This was due to the concentration of FS and dilution of DS (Tang et al., 2010), both led to a loss of osmotic driving force across the membrane (McCutcheon and Elimelech 2006; Mi and Elimelech 2008). The degree of fouling can be assessed by comparing the water flux curve of a fouled membrane to the baseline.

In Figure 3-3a, the flux profiles corresponding to pure ALG (i.e., 0% LYS) and pure LYS (i.e., 100% LYS) were almost overlapping with the baseline, indicating that there was negligible membrane fouling caused by ALG or LYS alone. This was further confirmed by the small amount of foulant mass deposited on the membrane surfaces under these conditions (Figure 3-3b). For cases that the FS contained mixed foulants of LYS and ALG, a significant flux decline was observed relative to the baseline even if one of the foulant components was present in relatively small amount (e.g., 10% LYS or 90% LYS). Foulant deposition in the presence of mixed foulants also increased significantly. This was likely due to the electrostatic attraction between the positively charged LYS and negatively charged ALG molecules. More severe flux decline was observed when comparable amount of LYS and ALG were present in the FS (50% or 70% LYS), under which conditions the foulant mass deposition also increased significantly.

(a)

(b)

Figure 3-3. Effect of foulant composition in feed solution on FO fouling of CTA membrane. (a) flux performance; (b) foulant deposition on membrane. Test conditions: total ionic

strength of 10 mM (NaCl), total foulant concentration of 100 mg/L, pH 7, and temperature at $23 \pm 1^\circ\text{C}$. Error bars in (b) were based on 2 replicates under the identical fouling conditions.

Fouling tests were also performed with the TFC FO membrane and the feed compositions of 0%, 50% and 100% LYS were evaluated. Flux performance and mass deposition results are presented in Figures 3-4a and 3-4b, respectively. Similar trends were observed for the TFC membrane: (1) both flux reduction and foulant mass deposition were more severe for the feed containing mixed foulants (50% LYS); and (2) flux was more stable under single foulant conditions (either 0% or 100% LYS in the feed). Nevertheless, the TFC membrane experienced obvious flux decline and foulant deposition even when the feed only contained LYS or ALG. The differences in TFC and CTA membrane fouling will be discussed in detail in Section 3.3.2.

(a)

(b)

Figure 3-4. Effect of foulant composition in feed solution on FO fouling of TFC membrane. (a) flux performance; (b) foulant deposition on membrane. Test conditions: total ionic strength of 10 mM (NaCl), total foulant concentration of 100 mg/L, pH 7, and temperature at $23 \pm 1^\circ\text{C}$. Error bars in (b) were based on 2 replicates under the identical fouling conditions.

It is interesting to note that, for the CTA membrane fouling by mixed foulants (Figure 3-3b), the deposited LYS mass was significantly more than the ALG mass on the fouled membrane. Considering the case of 10% LYS in the feed solution, although the concentration of ALG in solution was nine times of that of LYS, the amount of LYS deposited on the membrane surface was 67% more than the deposited ALG mass. Similarly, more LYS was found in the foulant cake layer compared to ALG for feed solutions containing 30-90% of LYS. The preferential deposition of LYS may be explained by the charge properties of LYS and ALG. Presumably, a more stable foulant cake layer is formed when the overall charge of the cake layer is neutral or nearly neutral ((Wang and Tang 2011), also see further discussion in Section 3.3.3). Since ALG is significantly more charged compared to

LYS (zeta potential values of ALG and LYS are -65 and 11 mV, respectively, at pH 7 in 10 mM NaCl) (Wang and Tang 2011), greater amount of positively charged LYS is needed to neutralize the negatively charged ALG deposited on the fouled membrane.

Figure 3-5 plots the percentage of LYS in the foulant cake layer versus that in the FS. The data obtained for a nanofiltration (NF) membrane fouled under constant pressure (Wang and Tang 2011) is also included for comparison within the data obtained for the CTA and TFC membranes under FO conditions. As expected, only one type of foulant was detected on the membrane surface when the feed only contained LYS or ALG. However, the cake layer LYS content (m_{LYS}) was within a relatively narrow range of 60-95% when the feed LYS content changed from 10% to 90%. In particular, when both LYS and ALG were present in the feed at relatively high concentrations (30-70% LYS in feed), a nearly constant m_{LYS} of ~ 75 - 80% was found in the foulant cake layer. Furthermore, the cake layer composition was not affected by the membrane type (CTA versus TFC) nor the testing mode (pressure-driven NF mode versus osmosis-driven FO mode). These observations seem to suggest that the foulant cake composition was mainly governed by the interaction(s) between the different foulant species, while the foulant-membrane interaction(s) and hydrodynamic conditions had negligible influence. As long as both foulants were present in the FS in sufficient amounts (30-70% LYS), the FS foulant composition barely had any influence on the composition of foulant cake layer (at a fixed mass ratio m_{LYS}/m_{ALG} of ~ 1:4). This phenomenon is analogous to scaling formation (e.g., Ca^{2+} to SO_4^{2-} ratio is fixed at 1:1 in gypsum scaling ($CaSO_4 \cdot 2H_2O$) regardless of their relative abundance in the solution), and it can be attributed to the tendency to attain a thermodynamically most stable state (i.e., the minimum free energy state) (Wang and Tang 2011). The relationship between the “thermodynamically stable” m_{LYS}/m_{ALG} incorporation ratio and inter-foulant-species interaction is further

provided in Section 3.3.3. When the m_{LYS}/m_{ALG} composition in the feed solution (e.g., 10% LYS or 90% LYS in the feed) was very different from the stable cake composition (75-80%), the formation of the cake layer can be limited/retarded due to kinetic factors to assume a cake composition different from the stable composition. This kinetic consideration also explains why the CTA membrane was most severely fouled by the feed containing 70% LYS (Figures 3-3a and 3-3b) – this feed composition matched most closely with the stable cake composition.

Figure 3-5. Comparison of cake layer foulant composition and feed solution foulant composition. Data for NF270 membrane is obtained from Wang and Tang (2011b). FO test conditions: total ionic strength of 10 mM, total foulant concentration of 100 mg/L, pH 7 and temperature at $23 \pm 1^\circ\text{C}$; NF test conditions: ionic strength of 10 mM (NaCl), total foulant concentration of 20 mg/L, initial flux of 75 L/m²h, crossflow velocity of 9.5 cm/s, pH 7 and

temperature at $23 \pm 1^\circ\text{C}$. Error bars were based on 2 replicates under the identical fouling conditions.

3.3.2 Effect of membrane types

The fouling behaviors of CTA and TFC membranes are presented in Figure 3-3 and Figure 3-4, respectively. To aid a direct comparison, the relevant fouling data (flux and foulant mass deposition) for 0%, 50%, and 100% feed LYS content are re-plotted in Figure 3-6.

Figure 3-6. Comparison of flux behavior and foulant deposition between CTA and TFC membranes. (a) flux performance with 0% LYS in feed; (b) flux performance with 50% LYS in feed; (c) flux performance with 100% LYS in feed; (d) foulant deposition on membranes. Test conditions: feed solution contains 10 mM NaCl, total foulant concentration of 100 mg/L, pH 7, and temperature at $23 \pm 1^\circ\text{C}$. Error bars in (d) were based on 2 replicates under the identical fouling conditions.

In the absence of membrane fouling, similar baselines were observed for the CTA and TFC membranes. The slightly lower water flux of CTA membrane can be attributed to its higher solute permeability over water permeability (B/A) ratio, which causes more severe reverse diffusion of solute from the draw solution into the feed solution and thus accelerated flux decline (Tang, She et al. 2010; Xiao, Tang et al. 2011; Zou, Gu et al. 2011).

For feed solutions containing either ALG alone (0% LYS) or LYS alone (100% LYS), it is evident that the TFC membrane was more prone to fouling compared to the CTA membrane: (1) The TFC membrane showed more severe flux decline compared to the CTA membrane; (2) While the CTA membrane experienced little fouling deposition ($< 50 \mu\text{g}/\text{cm}^2$) for FSs containing a single foulant type, the TFC membrane had a deposited foulant mass of $\sim 200 \mu\text{g}/\text{cm}^2$ for the ALG feed and that of $\sim 100 \mu\text{g}/\text{cm}^2$ for the LYS feed. The low fouling tendency of the CTA membrane confirms prior literature reports that CTA based commercial FO membranes have low fouling tendency (Mi and Elimelech 2010; Jin, She et al. 2012; She, Jin et al. 2012). In addition, the higher fouling tendency of the TFC membrane is also consistent with the past experience in the reverse osmosis (RO) field - TFC RO membranes are more prone to fouling compared to cellulose acetate RO membranes (Tang, Chong et al. 2011). The greater fouling propensity of the TFC FO membrane is most likely attributed to its much greater surface roughness (Table 1 and Supporting Information S1). Existing literature reports that the ridge-and-valley roughness structure of TFC membranes has a great tendency to promote foulant deposition (Vrijenhoek, Hong et al. 2001; Li, Xu et al. 2007; Tang, Fu et al. 2007; Wang and Tang 2011). As surface roughness and hydrophobicity are two important factors determining the solute/membrane non-electrostatic affinity, the current study also seems to suggest that the surface roughness plays a more dominant role over surface hydrophilicity in membrane fouling, noting that the TFC membrane was more hydrophilic than the CTA membrane (Table 3-1).

When the feed solution contained the mixture of LYS and ALG (50% LYS in feed), both the CTA and the TFC membranes experienced severe flux decline and the final flux values towards the end of fouling tests were similar ($\sim 15 \text{ L}/\text{m}^2\text{h}$ for CTA and $13 \text{ L}/\text{m}^2\text{h}$ for TFC). In addition, the deposited foulant mass and composition for the two membranes were nearly identical. In both case, the unfavorable interaction

between the foulant species in the feed solution (i.e., the electrostatic attraction between LYS and ALG) led to a large amount of foulants depositing onto the membrane surface, which caused severe flux loss. The reduced importance of membrane properties on fouling under this condition can be explained by the dominance of foulant-fouled-membrane interaction. It is hypothesized that for an unstable feed solution, a foulant cake layer could be formed on membrane by severe fouling (Tang, Kwon et al. 2006; Tang, Kwon et al. 2009; Wang and Tang 2011). Consequently, the membrane properties are largely governed by the foulant layer (Tang, Kwon et al. 2006), such that the deposition of additional foulant is largely governed by the interaction between foulant in the solution and the already deposited foulant on the membrane surface. In contrast, foulant-membrane interaction governs the fouling behavior under mild foulant conditions (e.g., for feed containing LYS or ALG) such that fouling was more membrane dependent.

Results from the current study suggest that: (1) Under mild FO fouling conditions, TFC FO membranes can have greater fouling tendency compared to CTA FO membranes due to their greater surface roughness; (2) Under severe FO fouling conditions, membrane surface properties play a less important role; (3) Although FO is believed to have superior fouling resistance in the AL-FS orientation, severe fouling can occur even at moderate flux levels, especially for TFC membranes or for unstable feed solutions. With the shift towards the use of TFC membranes (Wei, Qiu et al. 2011) and the development of new applications that involves complicated feed compositions (e.g., FO based MBRs (Achillia, Cathb et al. 2009; Lay, Zhang et al. 2011)), FO fouling remains as an important operational issue that deserves attention from the membrane community.

3.3.3 Effect of solution chemistry

Effect of solution chemistry was investigated by varying the FS pH or the addition of calcium to the FS (Figure 3-7). In this series of fouling tests, the CTA membrane was used and the FS contained 50 mg/L LYS and 50 mg/L ALG. The change of solution chemistry did not have significant effect on the baseline flux profile. Figure 3-7a shows less flux decline at pH 8 compared to those at pH 5 and 7 when there was no Ca^{2+} present in the FS. Correspondingly, Figure 3-7b shows reduced alginate deposition at higher pH. As discussed in Section 3.3.1, foulant cake composition was primarily governed by the inter-foulant-species interaction. For the pH range over 5-8, the zeta potential of ALG remained nearly constant (~ -70 mV), whereas LYS became significantly less positively charged at higher pH (Wang and Tang 2011). The reduced positive charge of LYS weakens the electrostatic interaction between ALG and LYS; it also requires less ALG to “neutralize” LYS in the foulant cake layer. This explains the more stable flux and reduced foulant mass deposition at pH 8.

The effect of Ca^{2+} on FO fouling was also illustrated in Figures 3-7a and 3-7b. The feed solutions either contained 0 or 1 mM Ca^{2+} with a fixed total ionic strength of 10 mM and solution pH of 7. Slightly more severe fouling was observed at 1 mM Ca^{2+} , especially at the beginning of the fouling tests. The presence of Ca^{2+} also increased the amount of ALG in the deposited foulant cake layer. As reported in literatures (Wang and Tang 2011), Ca^{2+} has a strong ability to interact with ALG by forming Ca^{2+} -ALG complex, which reduces the negative charge of ALG. As a result, more ALG is required to “neutralize” LYS in the foulant cake layer.

The above discussion reveals a strong dependence of foulant cake layer composition on the FS chemistry (such as pH and divalent ion concentration), which results from the shift in inter-foulant-species interaction when changing solution chemistry. For

oppositely charged foulants like LYS and ALG, the electrostatic interaction between the different foulant species plays a dominant role.

(a)

(b)

Figure 3-7. Effect of feed solution chemistry on FO fouling of CTA membrane. (a) flux performance; (b) foulant deposition on membrane. Test conditions: total ionic strength of 10 mM, foulants consist of 50 mg/L lysozyme and 50 mg/L alginate, and temperature at $23 \pm 1^\circ\text{C}$. Error bars were based on 2 replicates under the identical fouling conditions.

Figure 3-8 plots foulant mass deposition ratio ($m_{\text{LYS}}/m_{\text{ALG}}$) as a function of their charge properties (specifically, the ratio of zeta potential value of ALG over LYS, $|\xi_{\text{ALG}}/\xi_{\text{LYS}}|$). Data for NF270 membrane is obtained from Wang and Tang (Wang and Tang 2011). A clear correlation can be observed between the cake foulant mass ratio and the charge ratio, confirming the dominant role of electrostatic interaction between LYS and ALG in regulating the foulant cake composition. Nevertheless, the experimental data points deviated from the 1:1 linear correlation (the condition corresponding complete charge neutralization), suggesting that the cake composition may also be affected by other factors (such as geometries of foulant molecules). It is also worthwhile to note that many mixed foulant systems can be also affected by

non-electrostatic interactions such as van der Waals interaction and acid-base interactions (Tang, Chong et al. 2011).

While the current study has focused on the effect of FS chemistry on FO flux behavior and foulant layer composition, it is worthwhile to note that FO fouling can also be strongly affected by the draw solution chemistry and the ability of draw solutes to diffuse through the FO membrane into the feed water (Zou et al., 2011; She et al., 2012a). Further studies on the effect of reverse diffusion of draw solutes on FO foulant cake layer composition are required.

Figure 3-8. Cake layer foulant composition as a function of charge properties of foulants (the ratio of zeta potential of alginate over that of lysozyme). FO test conditions: total ionic strength of 10 mM. foulants consist of 50 mg/L lysozyme and 50 mg/L alginate, and temperature at $23 \pm 1^\circ\text{C}$; NF test conditions: ionic strength of 10 mM, foulants consist of 10 mg/L lysozyme and 10 mg/L alginate, initial flux of 75 L/m²h, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Zeta potentials of alginate and lysozyme are obtained from Wang and Tang (Wang and Tang 2011). Error bars were based on 2 replicates under the identical fouling conditions.

While the current study has focused on the effect of FS chemistry on FO flux behavior and foulant layer composition, it is worthwhile to note that FO flux behavior and fouling can also be strongly affected by the draw solution chemistry and the ability of draw solutes to diffuse through the FO membrane into the feed water (Zou et al., 2011; She et al., 2012a). Further studies on the effect of reverse diffusion of draw solutes on FO flux and foulant cake layer composition are required.

3.3.4 Effect of foulant mass deposition on flux performance

Figure 3-9 presents the flux reduction (compared to the corresponding baseline values) as a function of the total foulant mass deposition for various fouling testing conditions. A reasonable correlation is observed, although the TFC FO membrane appeared to suffer slightly greater flux decline compared to the CTA membrane. This was likely due to the relatively lower membrane resistance of the TFC membrane (Table 3-1), such that the same amount of foulant deposition will cause a greater percentage increase in the fouled membrane resistance. On the other hand, the lower membrane resistance of the TFC membrane also means a smaller driving force is needed to achieve the targeted initial flux (a draw solution of 3 M NaCl for CTA versus 2.2 M NaCl for TFC for an initial flux of 25 L/m²h).

Figure 3-9. Flux reduction versus total foulant mass deposition at various fouling testing conditions. Test conditions: total ionic strength of 10 mM, total foulant concentration of 100 mg/L, and temperature at $23 \pm 1^\circ\text{C}$.

3.4. Summary

The organic fouling by two oppositely charged macromolecules of two different types of forward osmosis membrane has been systematically studied in submerged mode. For both types of membrane, the foulant ratio of two foulants deposited on membrane will approach to the charge density ratio regardless of foulant composition in feed solution and most severe fouling occurs when foulant composition in solution is most similar to the charge density ratio. Thin film composite membrane has a better flux performance with absence of foulant but prone to be attached by organic foulants due to high surface roughness. For single foulant

condition, CTA membrane undergo very little fouling but more severe fouling could be observed for TFC membrane. Severity of fouling is increased with decrease of PH and addition of Ca in ambient solution. Feed solution chemistry has great effect on the foulant deposition ratio on membrane.

CHAPTER 4: DEVELOPMENT OF ANAEROBIC OSMOSIS MEMBRANE BIOREACTOR FOR LOW-STRENGTH WASTEWATER TREATMENT

4.1. Introduction

Membrane bioreactor (MBR) combines activated sludge process and membrane filtration for biomass retention into one single integrated system (Brindle and Stephenson 1996; Le-Clech, Chen et al. 2006). In a conventional MBR, a porous microfiltration (MF) or ultrafiltration (UF) membrane is used to retain suspended solids in bioreactor (Judd 2010). Where waste water reuse is targeted, further treatment such as nanofiltration (NF), reverse osmosis (RO), or advanced oxidation may be necessary after the MBR to further improve the effluent water quality (Lawrence, Adham et al. 2003; Achilli, Cath et al. 2009). Compact space usage and consistent effluent quality make MBR technology superior to other wastewater treatment options (Brindle and Stephenson 1996; Baker 2004).

Anaerobic membrane bioreactor (AnMBR) integrates anaerobic biological treatment process with membrane filtration (Judd 2010). Merits of AnMBR include lower sludge yield and energy requirement achieved by eliminating the need for aeration and producing energy in the form of methane (Choo and Lee 1996; Hu and Stuckey 2006; Judd 2010). AnMBR has generally been used to treat high-strength wastewaters especially industrial wastewaters. There are some recent advances demonstrating the technical feasibility of AnMBR systems for treating low-strength wastewaters (Hu and Stuckey 2006; Huang, Ong et al. 2013); however the process involves more difficulties. Moreover, due to the limitation of membrane rejection, soluble organics and trace organic pollutants will end up in the treated effluent inevitably.

In recent years, there is growing research interest in applying high-retention membranes into bioreactors (Goh, Zhang et al. ; Phattaranawik, Fane et al. 2008; Lay, Liu et al. 2010). Smaller size contaminants such as hydrolyzed organic matter could be effectively retained by membrane, prolonging their residence time in reactor and potentially leading to an improved biodegradation efficiency and effluent quality. One highlight among those high-retention MBRs is osmotic membrane bioreactor (OMBR) combining forward osmosis (FO) process with MBR (Cornelissen, Harmsen et al. 2008; Lay, Zhang et al. 2011; Wang, Chen et al. 2014). FO is a membrane separation process in which water flows from a low-osmotic-pressure feed solution (FS) to a high-osmotic-pressure draw solution (DS) across a semi-permeable membrane (Cath, Childress et al. 2006; Zhao, Zou et al. 2012). With seawater used as DS in an open loop to avoid the need for DS regeneration, FO requires no additional energy input to drive the filtration process compared to conventional pressure-driven separation processes such as reverse osmosis (RO) and nanofiltration (NF). In the case where pure water is required as a final product, i.e. water reclamation, an extra step of recovery of pure water from draw solution and the associated energy consumption must be taken into consideration when assessing the cost-effectiveness of the overall system. Previous studies on OMBR have focused on wastewater treatment under aerobic conditions (Lay, Zhang et al. 2011; Alturki, McDonald et al. 2012; Zhang, Loong et al. 2012). Utilizing FO membrane in the anaerobic bioreactor to retain and concentrate soluble organics, a novel anaerobic osmosis membrane bioreactor (AnOMBR) is expected to achieve high treatment efficiency of dilutive domestic wastewater, high effluent quality, low energy demand and high methane yield in one integrated system.

In the current study, feasibility of the AnOMBR for treating low-strength wastewater at mesophilic condition was evaluated. Specific objectives of the study include: 1) to study the FO membrane performances including flux level, draw solute back

transport and nutrient removal rate; 2) to evaluate the efficiency of bioprocess including sludge bioactivity and biogas production rate of the system.

4.2. Materials and methods

4.2.1 Batch test

In the initial stage of the study, performances of both cellulose triacetate (CTA) and thin film composite (TFC) polyamide FO membranes were evaluated under the batch mode for a time span of 14 days. The detailed description of the batch test and results are obtained in appendix I. Results show that CTA membrane could sustain a more stable flux which is the key to the stability of the bioreactor. The treatment efficiency and biogas conversion rate were also promising. On the other hand, the TFC membrane suffered from the severe membrane fouling due to the high complexity of mixed liquor within the reactor. The operation and bioactivity could not be continued due to the extreme low flux rate. The results were in line with the findings in Chapter 3 that TFC has higher fouling tendency compared to CTA membrane and the flux could hardly be sustained with the increase of both the complexity of aqueous environment and time span.

4.2.2 Membranes

Therefore, the membrane adopted in this study was the CTA membrane produced by Hydration Technology Inc. (HTI, Albany, OR). The CTA membrane has a water permeability of 3.1×10^{-12} m/s Pa, salt permeability of 20.2×10^{-8} m/s at 35 °C.

4.2.3 Synthetic nutrients

The composition of the synthetic feed wastewater used in this study was modified from literature (Hu and Stuckey 2006) and summarized in Table 4-1. The wastewater

had a total sCOD value of 460 mg/L. The derived sCOD:N:P ratio was 100:10:1. The conductivity and pH of the wastewater were 1.1 ± 0.1 mS/cm and 7 ± 0.1 , respectively.

Table 4-1. Synthetic nutrients composition

Organic		Inorganic	
	Concentration (mg/L)		Concentration (mg/L)
Glucose	275	NH₄Cl	25
Peptone	100	NaHCO₃	100
Meat Extract	100	KH₂PO₄	20
Urea	10	CaCl₂•6H₂O	10
		MgCl₂•2H₂O	5

4.2.4 Experimental setup and operation

The schematic diagram is shown in Figure 4-1. Membrane cell with effective membrane area of 250 cm² was fully submerged into a 3.6 L bioreactor. Active layer-facing-feed (sludge) orientation was adopted. A peristaltic pump was used to recirculate DS at a cross flow velocity of 8.3 cm/s (equivalent to flow rate of 400 ml/min). Coarse bubbles were introduced by recycling gas in the headspace back to the bottom of reactor at constant rate of 2 L/min for sludge mixing and membrane fouling control. Conductivity, temperature, pH, oxidation–reduction potential (ORP) value, pressure and water level in the reactor were monitored by a data logging system continuously. The constant mesophilic temperature of 35 °C was achieved by wrapping heating belt on outer surface of reactor. The reactor was kept at atmospheric pressure using pressure release valve and extra gas would be exerted out of the tank and collected by liquid-displacement method. Sludge volume in

reactor was monitored by a level sensor and was maintained constant by topping up with feed wastewater.

The effective volumes of draw solution (DS) tank were 2 L. 0.5 M sodium chloride (NaCl) solution was used as DS (representing the case of seawater based DS). The concentration in the DS tank was monitored by an online conductivity probe, and its concentration was maintained constant by dosing a 5 M NaCl stock solution to avoid DS dilution by permeate water over time. The membrane flux was acquired by measuring the combined mass of the DS and the 5 M NaCl stock solution.

The seed sludge was collected from the digester of a local municipal water reclamation plant (Ulu pandan WRP). The digester is to break down the organic substances in the sludge at mesophilic temperature. The sludge was stabilized in the reactor for two months. The seed sludge was first diluted to targeted MLSS value with the synthetic wastewater. Air in the reactor was first replaced with nitrogen gas and the mixed liquor was continuously stirred by circulating the gas at headspace of reactor to the bottom of reactor. The circulation continued for 12 hours per day and the halted for the rest of day to allow rest and sedimentation of the sludge. Before restarting the gas-mixing on the next day, supernatant in the reactor was discharged and reactor was fed with fresh synthetic wastewater to keep an HRT of 14 hours. Same procedure was repeated for two months until sludge was fully stabilized and constant gas production could be observed. Mesophilic temperature was well kept throughout the whole stabilization.

After the stabilization, the AnOMBR operation was started and continued for 120 days at sludge retention time (SRT) of 90 days. The initial total suspended solids (TSS) and volatile suspended solids (VSS) of sludge in reactor were 3 g/L and 2.5 g/L respectively. The initial hydraulic retention time (HRT) of reactor was 15 hours. Due to the constant concentration of draw solution and concentration built-up of feed

solution caused by retention of salts and draw solute back diffusion, driving force was lost and flux declined with time, leading to a prolonged HRT of around 40 hours. To allow membrane fouling analysis, the system was running in two-week cycles, and fouled membrane coupons were taken-out at the end of each cycle for further analysis. In the meantime, sludge was settled and supernatant was discharged after each cycle to control the salt accumulation in the reactor.

Figure 4-1. Schematic diagram of the AnOMBR system

4.2.5 Analytical methods

pH, conductivity and temperature of both sludge and permeate were measured by probes connected with electrometers (Mettler-Toledo M200 system). Total solids

(TS) and volatile solids (VS) were measured as described in standard methods (APHA 1999). Mixed liquor was centrifuged at 4000 rpm for 10 mins and supernatant was used to determine the sCOD, total nitrogen (TN), Ammonia (N-NH_4^+) and total phosphorous (TP) concentration by USEPA Reactor Digestion Method (HACH 2125915/ 2415815), Persulfate Digestion Method (HACH 2714100/2672245), AmVer Salicylate method (HACH 2606945) and Molybdovanadate Method (HACH 2767245) respectively. Particle size distribution of sludge mixed liquor was analyzed by Mastersizer 2000 and morphology was observed under inverted microscope (Olympus IX51). Adenosine triphosphate (ATP), an excellent indicator of microbial activity was extracted using tris-EDTA solution (Chen 2000) and was measured by HPLC system with C18 column and UV detection at 254 nm (Natalio, Pleše et al. 2011). Concentration of volatile fatty acid was measured by HPLC with cation exchange column at UV 210 nm. The composition of biogas was determined using a Shimadzu GC-TCD fitted with J&W 113-4362 column (0.32 mm $\times$ 60 m, 0 μm) and Agilent 19095P-MS6 column (0.53 mm $\times$ 30 m, 50 μm).

4.3. Results and discussion

4.3.1 Flux performance, salt accumulation and fouling

Figure 4-2a shows the mix liquor conductivity in the reactor and the flux performance of the CTA membrane in reactor versus time is plotted in Figure 4-2b. Both the flux and conductivity showed good repetition comparing among different cycles. The flux decreases from a nearly identical initial flux of around 10 $\text{L/m}^2\text{h}$ to a final flux of around 3 $\text{L/m}^2\text{h}$. Correspondingly, the conductivity increases from 1.1 mS/cm to around 20 mS/cm over time. The increase of conductivity is due to accumulation of salts from the influent wastewater as well as the solutes diffused through the membrane from the high concentration draw solution into the bioreactor

(Lay, Zhang et al. 2011; Xiao, Tang et al. 2011). The build-up of conductivity would lead to the reduced driving force across the membrane, therefore contributing to the observed flux decline. The effect of salt accumulation in the bioreactor can be assessed using the FO flux model with measured salt concentrations of the DS and the FS (see Appendix II). In Figure II-1, both the experimental flux and modeled flux (accounting for salt accumulation but assuming no fouling) are presented. In general, the modeled flux profile followed closely with the experimental flux profile, revealing salt accumulation as the dominant mechanism leading to flux decline. This observation agreed well with prior investigations on aerobic OMBRs (Lay, Zhang et al. 2011; Xiao, Tang et al. 2011), suggesting a strong need for salinity management for OMBR reactors. Nevertheless, the experimental flux was consistently lower than the modeled flux, which can be attributed to additional flux loss due to membrane fouling (Zou, Gu et al. 2011).

The mix liquor pH in the reactor versus time is plotted in Figure 4-2c. Generally the pH increases from 7 to 7.7 and it also shows good repetition among cycles. As FO membrane has good rejection to carbon bicarbonate, the alkalinity in the wastewater could be retained and accumulated in reactor, leading to the slow rise of pH. The neutral to slight alkaline environment could facilitate methane production and prevent the failure caused by acidification of anaerobic environment (Lay, Li et al. 1997).

Figure 4-2. Basic operation condition of reactor. (a) Water flux across the membrane; (b) Conductivity of the bulk mixed liquor; HRT varied from 14 hrs to 40 hrs depending on the flux, SRT = 90 d, Temperature at 35°C.

Visual inspection and electron microscopy were performed for fouled FO membrane coupons. Visual examination of virgin membrane and fouled membrane taken out from reactor after one cycle are illustrated in Figure 4-3a and 4-3b. Generally fouling on membrane surface appeared to be mild, which seems to be consistent with the notion that membrane flux reduction was mainly driven by salt accumulation (Figure II-1). By flushing the membrane with tap water, the foulant layer could be easily removed from membrane surface, which confirms the low fouling nature of CTA membrane (Mi and Elimelech 2010; Jin, She et al. 2012). SEM images (Fig. 4-3(c) and (d)) show the presence of both biofouling and crystal deposition. Consistent with SEM results, the EDX results (Fig. 4-3(e)) show that carbon (43.1%), oxygen (26.3%), nitrogen (18.1%), calcium (6.5%) and phosphorous (4.3%) were the most abundantly presented elements in the foulant layer. Since the virgin CTA membrane does not contain nitrogen, a high nitrogen content together with the presence of

calcium and phosphorous at much lower concentration supports the co-existence of biofouling and inorganic scaling.

ATR-FTIR spectra of virgin membrane and fouled membrane are presented in Fig. 4-3(f) and (g), respectively. As compared to the virgin membrane, the fouled membrane had three distinct bands at about 1632 cm^{-1} , 1525 cm^{-1} and 1240 m^{-1} , which were attributed to the protein secondary structure (corresponding to Amides I (C–O stretching), II (N–H in plane), and III (C–N stretching), respectively). This reveals the presence of proteins in the foulant layer. There was also a broad peak at 1025 cm^{-1} , suggesting the presence of C–O bonds and attributed to the presence of polysaccharides or polysaccharide-like substances in the MBR. Through the FTIR spectra, it was evident that biological macromolecules including both proteins and polysaccharides were present in foulants.

Figure 4-3. Surface morphology of FO membrane. (a) virgin membrane; (b) fouled membrane at day 14; (c) and (d) fouled membrane under SEM; (e) fouled membrane under EDX spectrometry. (f) ATR-FTIR spectra of virgin membrane; (g) ATR-FTIR spectra of fouled membrane.

4.3.2 Reactor performance

- **Reactor pH**

The mixed liquor pH in the reactor is plotted against time in Figure 4-4. In each cycle, pH increased from 7 up to 7.6 over a 14-day period. The gentle increase in pH can be attributed to the retention of alkalinity and its subsequent accumulation in the reactor, in a way similar to salt accumulation. Indeed, a comparison between Figure 4-4 and Figure 4-2(a) shows very similar trend between the conductivity increase (due to salt accumulation) and pH raise (due to alkalinity accumulation). It is worthwhile to point out that such alkalinity accumulation is not possible in conventional anaerobic membrane bioreactors in which porous membranes are used. Since acidification of anaerobic bioreactors (and thus the inhibition of methanogens) can be an important practical issue (Lay, Li et al. 1997), AnOMBR can be potentially advantageous over conventional anaerobic MBRs by avoiding low pH conditions in the bioreactor. Nevertheless, long term pH stability in AnOMBR reactors needs to be systematically investigated in future studies.

Figure 4-4. Evolution of pH of the bulk mixed liquor. HRT varied from 15 hrs to 40 hrs depending on the flux, SRT = 90 d, Temperature at 35°C.

- **Soluble Chemical oxygen demand (sCOD) removal**

Figure 4-5 shows the evolution of sCOD concentration in influent, bulk reactor and in permeate as well as the sCOD percentage removal rate. With inflow sCOD around 460 mg/L, the sCOD concentration in the bulk varied within the range of 100 mg/L to 250 mg/L. In comparison, permeate sCOD concentration was quite low, generally under 30 mg/L. Overall, the system showed good sCOD removal rate of more than 95% at most of the time. An even higher removal rate was observed at longer operation, possibly due to more stable biological process and microbial growth. The current study demonstrates that the sCOD rejection of AnOMBR can be better than conventional anaerobic membrane bioreactors.

Volatile fatty acids (VFA) are important components of the sCOD and are important intermediate compounds in the metabolic pathway of methane fermentation (Buyukkamaci and Filibeli 2004). They are good indicators of process imbalance in anaerobic digesters (Ahring, Sandberg et al. 1995). From Figure 4-6, it could be found that in this study, the concentration of VFA in the reactor was extremely low (below 1.2 mg/L) throughout the experiment and only acetate could be detected. This may be due to the efficient conversion of VFA during the methane production

process. The other possible reason could be the dilute nature of wastewater, leading to the concentration of propionate, butyrate and other forms of VFAs under the detectable limit.

Figure 4-5. Evolution of the sCOD concentrations in the feed, bulk and the permeate (left axis) and the sCOD removal percentage (right axis). HRT varied from 14 hrs to 40 hrs depending on the flux, SRT = 90 d, Temperature at 35°C.

Figure 4-6. Evolution of the VFA concentrations in the feed, bulk and the permeate. HRT varied from 14 hrs to 40 hrs depending on the flux, SRT = 90 d, Temperature at 35°C. Measured by HPLC with cation exchange column at UV 210nm.

- **Ammonia and total nitrogen (TN) removal**

Figure 4-7a and 4-7b show the evolution of total nitrogen (TN) and ammonia concentration in inflow wastewater, bulk reactor and in permeate. As compared to the inflow TN concentration of around 45 mg/L and inflow ammonia concentration of around 15 mg/L, the corresponding bulk concentrations in the bioreactor were much higher (TN concentration ranging from 50 – 100 mg/L and ammonia concentration ranging from 30-90 mg/L), indicating significant accumulation of both. Furthermore, although ammonia concentration was less than 50% of the TN in the influent wastewater, the bulk ammonia concentration in the bulk reactor was very similar to the bulk TN concentration (with ammonia accounting for ~85% of the TN concentration). This result may indicate that most of the total nitrogen in the bulk was converted and presented in the form of ammonia as a result of biodegradation of organic N sources like proteins derived from the raw wastewater or even cell debris. Concentration of TN and that of ammonia in permeate water both ranged from 0-30 mg/L. Indeed, these concentrations were nearly identical, suggesting that ammonia was the main form of nitrogen permeating through the FO membrane while non-ammonia based nitrogen can be well rejected by the FO membrane.

It is interesting to note that the permeate ammonia concentration was higher than that in the influent wastewater in some cases, i.e., negative ammonia removal was observed sometimes. This peculiar phenomenon arises due to the combined effects of: (1) the conversion of TN to ammonia in the bioreactor and (2) the accumulation of ammonia in the reactor due to FO membrane retention. Both effects led to an elevated bulk ammonia concentration (30 – 90 mg/L) that was several times higher than the influent ammonia concentration (on the order of 15 mg/L), which negatively impacts the permeate quality (i.e., increases ammonia concentration in the permeate water). In the current study, it is important to differentiate the overall removal efficiency of the AnOMBR and the FO membrane rejection rate. The former is

defined by comparing the permeate concentration ($C_{permeate}$) to the influent concentration ($C_{influent}$), while the latter is defined by comparing $C_{permeate}$ to the bulk reactor concentration ($C_{reactor}$). Thus, the overall removal efficiency ($\eta_{overall}$) can be related to the membrane rejection rate ($R_{membrane}$) by:

$$C_{permeate} = (1 - \eta_{overall}) C_{influent} = (1 - R_{membrane}) C_{reactor} \quad (1a)$$

$$\text{Or} \quad \eta_{overall} = 1 - f_c (1 - R_{membrane}) \quad (1b)$$

where f_c is the concentration factor, i.e., the ratio of $C_{reactor} / C_{influent}$. Equation 1(b) clearly shows that $\eta_{overall}$ can be negative in the presence of a large concentration factor despite a high membrane rejection.

In the current study, the ammonia rejection by the FO membrane was relatively high (around 70 to 80%) and was in line with existing literatures (Holloway, Childress et al. 2007; Cath, Hancock et al. 2010). Nevertheless, the overall ammonia removal rate was poor (or even negative) in the absence of ammonia removal mechanism. Future studies need to consider the integration of nitrogen removal (e.g., biological nitrogen removal (Chen, Yin et al. 2005; Zhu, Peng et al. 2008) or nutrient recovery in the form of struvite (Zhang, She et al. 2014)) with AnOMBR in order to enhance nitrogen removal.

Figure 4-7. Evolution of the ammonia and total nitrogen (TN) concentrations in the feed, bulk and the permeate. (a) TN; (b) ammonia; HRT varied from 14 hrs to 40 hrs depending on the flux, SRT = 90 d, Temperature at 35°C.

• Total phosphorous (TP) removal

Figure 4-8 shows the evolution of total phosphorous (TP) concentration in inflow wastewater, bulk reactor and in permeate. Inflow TP concentration is stable at around 5mg/L and it gradually accumulated in bulk solution within one operation cycle. Maximum value of around 20 mg/L was reached in the middle of one cycle and following by a slight concentration decline. Referring to the EDX analysis of the foulant layer composition on membrane (Figure 4-3d), the abundant presence of phosphorous, calcium and other ions could be an indication of phosphorous based

inorganic scaling that was precipitated on the membrane at high phosphorous concentration. Similar phenomenon was also observed in other researches. Trzcinski and Stuckey (Trzcinski and Stuckey 2009) investigated the morphology and structure of the inorganic precipitate in an AnMBR, suggested that high amount of phosphorus existed in the precipitate could either be di-calcium phosphate dehydrate ($\text{Ca}_2\text{H}_2(\text{PO}_4)_2$) or amorphous calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). Furthermore, struvite (MgNH_4PO_4) precipitation is prevalent at sludge digestion process (Doyle and Parsons 2002). Proper scaling control is thus an important aspect of reactor operation. Meanwhile, proper recovery of struvite may also present a good opportunity for nutrient recovery in addition to scaling control (Verstraete, Van de Caveye et al. 2009; Zhang, She et al. 2014).

Figure 4-8 Evolution of the total phosphate concentrations in the feed, bulk and the permeate. HRT varied from 14 hrs to 40 hrs depending on the flux, SRT = 90 d, Temperature at 35°C.

4.3.3 Sludge morphology

Sludge morphology was analyzed by particle size analysis and microscopic observation. Figure 4-9a shows the particle size distribution of sludge from the AnOMBR at day 120. The majority of particles was larger than 10 μm , with the peak

volume fraction occurred at slightly higher than 100 μm . A small amount of fine particles with diameter 1-10 μm was also present in the mixed liquor. Figure 4-9b shows that the mean flocs size (D50) of sludge increased gradually from the initial point of 85 μm , and a stable size of around 110 μm was achieved after about 60 days of reactor operation. Flocs tend to form bigger aggregates with longer and more stable operation. Figure 4-9c demonstrates the microscope observation of the sludge mixed liquor at day 0 and day 120. It could be clearly observed that macro-flocs were formed and abundantly presented in the mixed liquor at both day 0 and day 120. Small particles such as dispersed bacteria and fine flocs were less dominant. Prior studies have revealed that larger flocs are generally correlated with lower fouling potential (Lencki and Riedl 1999; Lin, Xie et al. 2009). Thus, the growing in floc size could be potentially beneficial to the reactor operation. Nevertheless, systematic studies are needed to further investigate the role of floc size on AnOMBR reactor fouling.

(a)

(b)

(c)

Figure 4-9. Sludge morphology. (a) Typical particle size distribution of the bulk sludge liquor at day 120 of the sludge; (b) Evolution of mean flocs size (d50); (c) Microscopic observation of the sludge mixed liquor at day 0 and day 120. HRT varied from 14 hrs to 40 hrs depending on the flux, SRT = 90 d, Temperature at 35°C.

4.3.4 Bioactivity and gas production

Adenosine triphosphate (ATP) content of anaerobic digesters is a direct biomass activity measurement. ATP in volatile suspended solids was measured and expressed as specific ATP content (mg / gVSS). Figure 4-10 plots the specific ATP in the

reactor along with time. It could be observed that at most of the time, the specific ATP contents varied within 0.1 mg / gVSS to 0.4 mg / gVSS, which is within the acceptable range for conventional anaerobic MBR (Chen 2000; Natalio, Pleše et al. 2011). Unlike the regular change of conductivity in reactor from 1.1 mS/cm to 20 mS/cm every 14-days cycle, the specific ATP values are almost random and there was little correlation between conductivity and specific ATP content could be observed, showing that the elevated salt concentration has little effect on the bioactivity of sludge.

Figure 4-10. Specific ATP content of sludge in reactor. ATP is extracted using tris-EDTA solution and was measured by HPLC with C18 column and UV detection at 254 nm.

For biogas production, stable biogas composition was observed throughout the experiment with the changes of conductivity. Methane and carbon dioxide compositions achieved concentrations of around 70%–80% and 20%–28%, respectively. Figure 4-11 presents the methane yield of the reactor expressed as liters of methane produced per gram of sCOD digested. The initial methane yield was 0.2 L CH₄/g sCOD digested and the value increased to 0.25 L CH₄/g sCOD digested after one week. The yield was stable in the range of 0.25 - 0.3 L CH₄/g sCOD

digested at longer operation duration. As compared to conventional AnMBR, the methanogens in AnOMBR was exposed to a high salinity environment (10 mM~200 mM NaCl equivalent) throughout the operation as a result of salt accumulation in the reactor (Section 4.3.1). Nevertheless, the methane yield measured in the current study was promising compared to the methane yield ranges from 0.2-0.35 L CH₄/g sCOD digested reported in conventional AnMBR studies treating municipal wastewater (Gao, Lin et al. 2010; Trzcinski and Stuckey 2010; Wijekoon, Visvanathan et al. 2011), indicating that methanogens had strong endurance to the gradually built-up high salinity environment such that the bioactivity was not significantly affected. The observed methane yield was lower than the theoretical value of 0.395 L/g sCOD at 35°C, which could be due to the ineligible solubility of methane gas during gas recirculation and loss of dissolved methane in effluent (solubility of methane at 35°C is about 19.4 mg/L). The current results show that gas production of AnOMBR system is achievable while optimization of gas production rate still requires further investigation.

Figure 4-11. Evolution of methane production rate. HRT varied from 14 hrs to 40 hrs depending on the flux, SRT = 90 d, Temperature at 35°C.

4.4. Implications and perspectives

The AnOMBR system enjoys many advantages. A dense FO membrane can be used to retain organic waste (including sCOD) in dilute wastewater and to prolong their retention time in the reactor. This can potentially enable efficient anaerobic treatment of dilute wastewater (e.g., municipal wastewater). Although it is not investigated in the current study, the dense FO membrane is presumably able to retain trace organic pollutants such as pharmaceutically active compounds and endocrine disrupting compounds (Jin, Shan et al. 2012; Lay, Zhang et al. 2012; Xie, Price et al. 2012; D'Haese, Le-Clech et al. 2013), which allows greater exposure time for their biological removal. Thus, the permeate water through FO can have a high quality to allow direct disposal. Moreover, with a carefully selected draw solution and its regeneration scheme, AnOMBR has the potential to achieve water reclamation and energy recovery (in the form of methane gas) simultaneously for municipal wastewater treatment. Anaerobic treatment of municipal wastewater also means reduced sludge production and the avoidance of excess energy consumption for aeration (Judd 2010; Ozgun, Dereli et al. 2013).

In the current study, we observed alkalinity accumulation and nutrient accumulation in the reactor in addition to the commonly reported salt accumulation. Although it did not have severe impact on the bioactivity and methane production of the reactor, salt accumulation was the main contributing factor responsible for membrane flux decline. Thus, it is critical for future studies to develop salinity management strategies along with fouling control strategies to avoid excessive flux loss. Alkalinity accumulation seems to be beneficial in avoiding reactor acidifications, although long term pH stability in the reactor still need to be assessed. Finally, accumulation of ammonia in the bioreactor can adversely impact its removal by AnOMBR, despite the relatively high rejection by the FO membrane. Future studies

may consider integrate nutrient removal or recovery with AnOMBR for improved permeate water quality.

4.5. Summary

In this chapter, a novel anaerobic osmosis membrane bioreactor (AnOMBR) was developed and its feasibility for treating dilute wastewater was evaluated. The bioreactor was operated for a period of 120 days at SRT of 90 days at mesophilic conditions:

- Flux through membrane gradually declined due to both feed conductivity build-up and membrane fouling. The fouling was mild but both organic fouling and inorganic scaling were observable.
- The AnOMBR showed good and stable sCOD removal and nearly complete total phosphorous removal. The FO membrane had relative good membrane rejection rate for total nitrogen and ammonia. Nevertheless, the system removal rate was limited due to total nitrogen and ammonia accumulation in the bioreactor.
- The elevated salt environment had severe effect on bioactivity in the AnOMBR. Promising methane production of 0.25 - 0.3 L CH₄/g sCOD digested was obtained.

CHAPTER 5: COMPARISON OF USING A SUBMERGED ANAEROBIC OSMOSIS MEMBRANE BIOREACTOR AT ROOM TEMPERATURES WITH AT MESOPHILIC TEMPERATURE TO TREAT LOW-STRENGTH WASTEWATER

5.1. Introduction

It's widely reported that temperature has significant effects on the biological process and lower temperature is known to lead to a decrease of nutrient utilization rate and microbial growth (Lettinga, Rebec et al. 2001; Martinez-Sosa, Helmreich et al. 2011). Under mesophilic conditions (35 °C), a COD removal efficiency of over 90% could be easily achieved while the number would drop when the temperature drops to ambient temperature around 24 °C based on the study carried by Kettunen and Rintala, who applied an on-site UASB reactor to treat landfill leachate (Kettunen and Rintala 1998). Low temperatures were also reported to affect biogas production, methanogenic activity and microbial community composition. In recent researches of submerged anaerobic membrane bioreactor, at mesophilic temperatures the methane production is around 0.25 L CH₄/g COD digested while at psychrophilic temperatures, the value drops to 0.16-0.2 L CH₄/g COD digested (Trzcinski and Stuckey 2010; Martinez-Sosa, Helmreich et al. 2011; Chen, Gu et al. 2014).

On the other hand, the ambient environment could not always meet the energy requirement for anaerobic reactor to operate under the mesophilic condition, even in tropical area like Singapore. To achieve it, additional energy and capital expenditure would be unavoidable for heating up of anaerobic reactors, leading to the increase of capital cost and overall energy inefficiency. Therefore, it could be significant to study the effect of temperature on the performance of the AnOMBR and whether the favorable efficient digestion of wastewater at lower temperature could be achieved.

In this chapter, comparisons between the performance of the laboratory-scale AnOMBR system fed with low-strength wastewater operated at mesophilic temperature (35 °C) and room temperature (25 °C) were carried out. Report includes the performance on water flux, reverse salt transport, nutrient removal and gas production.

5.2. Materials and methods

5.2.1 Membranes

Membrane adopted in this study was the CTA membrane produced by Hydration Technology Inc. (HTI, Albany, OR). The CTA membrane has a water permeability of 2.8×10^{-12} m/s Pa, salt permeability of 17.5×10^{-8} m/s at 25 °C and water permeability of 3.1×10^{-12} m/s Pa, salt permeability of 20.2×10^{-8} m/s at 35 °C.

5.2.2 Synthetic nutrients

The composition of the synthetic feed wastewater could refer to section 4.2.3.

5.2.3 Experimental setup and operation

Two identical reactors with same specs were operated in parallel. At the initial stage, for both reactors they share the same seed sludge which was collected from an anaerobic digester at local domestic sewage treatment plant (Ulu Pandan WTP) and was stabilized for two months. After which the AnOMBR operation was started and continued for 120 days at sludge retention time (SRT) of 90 days. The initial total suspended solids (TSS) and volatile suspended solids (VSS) of sludge in both reactors were 3 g/L and 2.5 g/L respectively. Two membrane coupons cut from same piece of virgin membrane were applied in each reactor, making sure they have similar initial flux and salt rejection. Therefore, the initial hydraulic retention time

(HRT) for both reactors was 15 hours based on the initial flux level. Due to the constant concentration of draw solution and concentration built-up of feed solution caused by retention of salts and draw solute back diffusion, driving force was lost and flux declined with time, leading to a prolonged HRT of around 40 hours. To allow membrane fouling analysis, the two reactors were running in cycles of 14 days and 21 days at mesophilic and room condition respectively. Fouled membrane coupons were taken-out at the end of each cycle for further analysis. In the meantime, sludge was settled and supernatant was discharged after each cycle to control the salt accumulation in the reactors.

The schematic diagram and detailed description of the reactor could refer to section 4.2.4. Membrane cell with effective membrane area of 250 cm² was fully submerged into a 3.6 L bioreactor. Active layer-facing-feed (sludge) orientation was adopted. A peristaltic pump was used to circulate DS at a cross flow velocity of 8.3 cm/s (equivalent to flow rate of 400 ml/min). Coarse bubbles were introduced by recycling gas in the headspace back to the bottom of reactor at constant rate of 2 L/min for sludge mixing and membrane fouling control. Conductivity, temperature, pH, oxidation–reduction potential (ORP) value, pressure and water level in the reactor were monitored by a data logging system continuously. The constant mesophilic temperature of 35 °C was achieved by wrapping heating belt on outer surface of reactor. The constant room temperature of 25 °C was achieved by the 24-hour room air-conditioning in the lab, leave the reactor unheated. The reactor was kept at atmospheric pressure using pressure release valve and extra gas would be exerted out of the tank and collected by liquid-displacement method. Sludge volume in reactor was monitored by a level sensor and was maintained constant by topping up with feed wastewater.

Both reactors were fed by the same nutrient tank and draw stock tank. The effective volumes of draw solution (DS) tank were 2 L. A 0.5 M Sodium chloride (NaCl)

solution osmotic pressure of which equivalent to seawater was used as DS and the concentration in the DS tank was measured by conductivity probe. The shared draw stock of 5 M NaCl was dosed into draw solution tanks of both reactors to eliminate the diluting effect by permeate and keep the the DS concentration constant. The membrane flux was acquired by mass balance to account for the mass of 5M NaCl dosing into the draw solution tank, and then normalised for the membrane area.

5.2.4 Analytical methods

pH, conductivity and temperature of both sludge and permeate were measured by probes connected with electrometers (Mettler-Toledo M200 system). Total solids (TS) and volatile solids (VS) were measured as described in standard methods (APHA 1999). Mixed liquor was centrifuged at 4000 rpm for 10 mins and supernatant was used to determine the sCOD, total nitrogen (TN), Ammonia (N-NH_4^+) and total phosphorous (TP) concentration by USEPA Reactor Digestion Method (HACH 2125915/ 2415815), Persulfate Digestion Method (HACH 2714100/2672245), AmVer Salicylate method (HACH 2606945) and Molybdovanadate Method (HACH 2767245) respectively. Particle size distribution of sludge mixed liquor was analyzed by Mastersizer 2000 and morphology was observed under inverted microscope (Olympus IX51). The composition of biogas was determined using a Shimadzu GC-TCD fitted with J&W 113-4362 column (0.32 mm $\times$ 60 m, 0 μm) and Agilent 19095P-MS6 column (0.53 mm $\times$ 30 m, 50 μm).

5.3. Results and discussion

5.3.1 Flux performance and salt accumulation

Figure 5-1a compares the flux performance of the CTA membrane versus time and Figure 5-1b compares the conductivity in mixed liquor of the two reactors. At room

temperature, similar trend of flux change occurred in mesophilic condition could be observed. Generally the flux of membrane decreased from around 9.5 L/m²h to 3.5 L/m²h and conductivity increased from 1.1 to around 20 mS/cm within the time interval of around 22 days (one cycle). The repetition of cycles was due to the discharge and replacement of supernatant with nutrients at the end point in order to lower the conductivity back to 1.1 mS/cm. To have a direct view, performance change of membrane at room temperature between day 47 and day 69 could be compared to the performance change of membrane at mesophilic temperature between day 42 and day 58. Within one cycle, compared the result at room temperature with mesophilic condition, the initial flux was almost the same (9.5 L/m²h) and it could be found that the flux decrease and conductivity increase were quite comparable, however, at a slower speed, reflected as the longer operation cycle. Instead of 22 days, it took only 16 days for flux of membrane in reactor at mesophilic condition to drop from 10 L/m²h to 3 L/m²h and conductivity increased from 1.1 to around 20 mS/cm.

As explained in previous section, the increase of conductivity was due to accumulation of salts resulting from both the accumulation of ions in wastewater and draw solute back diffusion through membrane from draw solution. At comparable flux level, the amount of inflow ions from feed nutrients retained within the reactor was similar. What made the difference was the amount of draw solute back diffusion. The difference could be attributing to the effect of temperature on the permeability coefficients of solute B. B value is positively correlated with the diffusion coefficient of solute D which is also positively correlated with temperature. As salt permeability coefficient value B increased with temperature, the diffusion rate of draw solute through membrane becomes faster at 35 °C compared to at room temperature, leading to the faster increase of conductivity.

It is also worth noting that the durability of membrane also seems to be stronger at room temperature compared to mesophilic condition. In the batch test under mesophilic condition, the rejection of salt was weakened after 15 days operation. While at room temperature, the membrane shows good stability in terms of good rejection of draw solute within all the 22-days cycles. This could be attributing to the nature of low temperature tolerance of CTA membrane, which could be easily hydrolyzed at high temperature especially at 35 °C or above. Based on this promising result, a membrane cleaning was carried out after one cycle (the end of day 77) by washing the membrane surface with tap water to remove the deposited visible foulant layer. At the same time, the supernatant was discharged until the conductivity down to 1.1 mS/cm. A flux recovery of more than 90% could be observed (day 78) compared to the initial flux at day 47. This could be possibly due to the smooth membrane surface and loosely attached fouling. This result is aligning with previous research findings that FO systems could achieve a 90% recovery of flux level after cleaning (Mi and Elimelech 2010). However, after the cleaning, the conductivity of the mixed liquor sharply increased from 1.1 to 20 mS/ cm within 6 days. This could be attributed to the absence of other more readily biodegradable carbon sources during the membrane cleaning, forcing the microorganisms to utilize the CTA material as the carbon source for survival. The membrane was therefore degraded and salt rejection was deteriorated (Lay, Zhang et al. 2011).

(a)

(b)

Figure 5-1. Comparisons of the flux performance of the CTA membrane versus time and conductivity in mixed liquor at room and mesophilic temperatures.

5.3.2 Treatment Efficiency

- **Soluble Chemical oxygen demand (sCOD) removal**

Figure 5-2 below compares the sCOD removal rate and sCOD concentration in supernatant at room and mesophilic temperature. It shows that at room temperature, the sCOD overall removal rate was generally above 95% corresponding to the

influent sCOD concentration of around 460 mg/L. This COD removal rate was comparable to the sCOD removal rate at mesophilic temperature. The concentration in permeate was below 20 mg/L at most of time, which is much lower than the previously reported result in conventional AnMBR (Sutton, Be'ube' et al. 2004). This could be contributed by the high retention advantage of non-porous FO membrane over the other porous membranes such as ultra-filtration and micro-filtration.

At both temperatures, the supernatant sCOD followed similar pattern but generally the concentration was higher at room temperature than mesophilic temperature. The supernatant sCOD generally increased at the initial phase of one cycle which could be due to the high retention of sCOD by FO membrane and release of soluble microbial products (SMP). The biomass could not fully utilize and degrade the sCOD completely and the residues accumulated in mixed liquor. The concentration became relatively stable at the last few days of the cycle due to the prolonged HRT which facilitate the degradation of sCOD over longer time. Generally the supernatant sCOD concentration was not high while at room temperature the value was still slightly higher than at mesophilic temperature at most of time. This could be due to the reason that some of the particulate sCOD could not be hydrolyzed at lower temperature to be converted to methane (Trzcinski and Stuckey 2010). The difference of methane production at two temperatures will also be discussed in later session.

(a)

(b)

Figure 5-2. Comparison of the the sCOD removal percentage and sCOD concentrations in the bulk and the permeate at room and mesophilic temperatures.

- **Ammonia and total nitrogen (TN) removal**

Figure 5-3a and 5-3b compares the evolution of ammonia (NH_4^+) and total nitrogen (TN) concentration in bulk reactor and in permeate. With an inflow ammonia concentration of around 20 mg/L, at both temperatures, the bulk concentration was

much higher than the inflow, indicating the accumulation of ammonia in bulk mixed liquor. Similar phenomenon was also observed for TN.

However, at room temperature, the supernatant concentration of ammonia and TN were generally higher than at mesophilic concentration. The peak concentration of TN and ammonia are around 100 mg/L and 85 mg/L at mesophilic temperature versus 115 mg/L and 100 mg/L at room temperature. One possible reason is the higher activity of the anaerobes at higher temperature, facilitating the degradation and utilization of the nitrogen source. The other possible reason is the easier formation of ammonia calcium/magnesium phosphate at higher temperature so that the peak concentration of ammonia and TN is limited.

Comparing between Figure 5-3a and b, it could be found that at both temperatures, concentration of TN and ammonia in permeate water were the same, showing that ammonia is the only form of nitrogen which existing in permeate. The concentration of ammonia in permeate was around 10 to 30 mg/L at both temperature and the membrane rejection rate of ammonia at both temperatures were similar around 70 to 80 percent, which is quite promising and in line with previous literature (Holloway, Childress et al. 2007; Cath, Hancock et al. 2010).

(a)

(b)

Figure 5-3. Comparisons of the ammonia and total nitrogen (TN) concentrations in the bulk and the permeate. (a) TN; (b) ammonia at room and mesophilic temperatures.

• Total phosphorous (TP) removal

Figure 5-4 compares the total phosphorous (TP) removal efficiency at room temperature and at mesophilic temperature. Inflow TP concentration was stable at around 5mg/L and it gradually accumulated in bulk solution within one operation cycle at both temperatures. Similar to sCOD and total nitrogen, the concentration of TP in supernatant at room temperature was generally higher compared to at

mesophilic condition. Similar to mesophilic condition, the peak TP concentration appeared in the middle of one cycle followed by a slight concentration decline observed at room temperature also, however, at a higher level. It shows that phosphorous based precipitation was formed at room temperature but not as easy as at mesophilic condition unless a high TP concentration in bulk was reached. This could be attributed to the specific property that the solubility level of calcium phosphate becomes lower as temperature increases. At mesophilic condition, the bulk temperature is higher, leading to the precipitation at lower TP concentration. No TP could be detected in permeate, showing that the FO membrane has perfect rejection to any form of phosphorous and temperature doesn't affect the rejection of TP.

Figure 5-4. Comparison of the total phosphate concentrations in the, bulk and the permeate at room and mesophilic temperatures. HRT varied from 14 hrs to 40 hrs depending on the flux, SRT = 90 d.

5.3.3 Sludge morphology

Sludge morphology was analyzed by particle size analysis and microscopic observation. Figure 5-5a is the particle size distribution of sludge from both reactors at day 120 and it could present the typical particle size distribution pattern of sludge along the operation. Both distributions had a unimodal pattern and at room temperature, flocs with size around 60 μm took up the highest percentage volume and at mesophilic condition it was 110 μm instead. Generally the particle size at room temperature was much smaller than at mesophilic condition as the whole curve was at the smaller size region. Higher percentage of fine particles with diameter 1-10 μm presented in the mixed liquor could be found at room temperature as well. According to Carman-Kozeny equation in a conventional filtration, specific cake resistance (α) is a function of particle diameter (d_p), porosity of the cake layer (ϵ) and particle density (ρ):

$$\alpha = \frac{180 (1 - \epsilon)}{\rho * d_p^2 * \epsilon^3}$$

In general, the smaller the particle size, the greater the cake resistance. This distribution could pose higher tendency of fouling at room temperature as smaller particles are more likely to be convected to the membrane by the imposed flux, leading to membrane fouling (Li, Fane et al. 1998; Zhang, Chua et al. 2006). Figure 5-5b shows that at both temperatures, the mean flocs size (D50) of sludge increased gradually with time. Flocs tended to form bigger aggregates with longer and more stable operation. Figure 5-5c demonstrates the microscope observation of the sludge mixed liquor at day 120 at both temperatures. It could be clearly observed that at room temperature, floc size were much smaller than at mesophilic temperature. Presence of macro-flocs was also not as abundant but small particle such as dispersed bacteria and fine flocs were detectable. All these findings may indicate a possible

higher fouling tendency of the nature of mixed liquor at room temperature. However, it doesn't reflect to the membrane flux in this study and further study may be required.

(a)

(b)

(c)

Figure 5-5. Comparison of sludge morphology at room and mesophilic temperatures. (a) Typical particle size distribution of the bulk sludge liquor at day 120 of the sludge; (b) Evolution of mean flocs size (d50); (c) Microscopic observation of the sludge mixed liquor at day 120. HRT varied from 14 hrs to 40 hrs depending on the flux, SRT = 90 d

5.3.4 Gas production

Figure 5-6 presents the methane production of the two reactors. At room temperature, the production of methane was detectable throughout the whole operation, indicating the active methanogenesis despite the elevated salinity environment in mixed liquor. In the first week, gas collection could not be optimized due to instability of the anaerobic liquor environment and limitation of the gas collection system. The biogas production measurable was starting from 0.14 L CH₄/g sCOD digested and production rate increased to around 0.2 L CH₄/g sCOD digested after one week. The average specific methane production rate was around 0.21 L CH₄/g sCOD digested. As compared to the theoretical methane yield of 0.38 L CH₄/g sCOD at 25 °C, it is around 55% of the theoretical value. Similarly, at mesophilic temperature, an

average methane yield of 0.3 L CH₄/g sCOD was achievable, taking up about 75% of the theoretical value (0.395 L CH₄/g sCOD at 35 °C).

Although both reactor suffered from the built-up of salinity in bulk (10 mM~0.2M NaCl equivalent) throughout the operation, which posed threat to the bioactivity of methanogens, the promising results show that methanogens have some endurance to the gradually built high salt environment. It still could be noticeable that at room temperature, the larger difference between the experimental methane yield and theoretical value could be due to the incomplete hydrolyzation of sCOD to convert into methane by methanogens at lower temperature and it is more vulnerable to the inhibited effect caused by the high salinity environment. In addition, according to Arrhenius temperature-dependence equation, degradation at 25 °C should proceed half as fast as at 35 °C. As the HRT of the reactor was not long enough, the slower sCOD degradation rate may also limit the production of methane. The results show that gas production at both temperatures was achievable while at lower temperature, the efficiency of methane production was also lower. Optimization of gas production rate still requires further investigation.

Figure 5-6. Comparison of specific methane production at mesophilic and room temperatures.

5.4. Summary

In this chapter, the performance of two submerged AnOMBRs operating at room and mesophilic temperature were investigated. CTA membrane was applied in the bioreactor and operated for a period of 120 days at SRT of 90 days:

- Flux through membrane gradually declined due to both the feed conductivity build-up and membrane fouling. At room temperature, the flux decrease and conductivity increase were both at a slower speed than at mesophilic temperature. Membrane cleaning by tap water was practical at room temperature and 90% flux recovery was achievable. However, the strength of membrane also weakened after the cleaning.
- The AnOMBR at room temperature showed good and stable sCOD removal of more than 95% and perfect total phosphorous removal contributed by the high retention FO membrane. The nutrient utilization efficiency within the mixed liquor was not as efficient as at mesophilic temperature, reflected as the higher supernatant concentration of COD, TN and TP.
- Methane yield at room temperature was stable and promising however 50% lower than mesophilic temperature. This may be due to the inhibited effect of elevated salinity in mixed liquor, incomplete hydrolyzation and slower degradation rate of sCOD at lower temperature.

CHAPTER 6: CONCLUSIONS

6.1. Major findings and conclusions

6.1.1 Differences of fouling behavior between TFC and CTA membrane

Organic fouling of TFC and CTA FO membranes by the oppositely charged macromolecules was systematically studied using a submerged FO membrane system. FO fouling experiments were performed using alginate and lysozyme as model foulants with a total feed foulant concentration of 100 mg/L and under the same initial flux of 25 L/m²h:

- For feed water containing mixed foulants, the foulant cake layer composition was controlled by the inter-foulant-species interaction and was strongly correlated to the charge properties of the foulants. In contrast, the cake layer composition during mixed organic fouling was not affected by the membrane type or the testing mode.
- Under mild fouling conditions, the TFC membrane was more prone to fouling due to its much rougher membrane surface. However, membrane surface properties played a less important role under severe fouling conditions due to the dominance of foulant-foulant interaction.

6.1.2 Feasibility of using AnOMBR to treat low-strength wastewater

An anaerobic osmosis membrane bioreactor (AnOMBR) is developed and feasibility of using such system to treat low-strength wastewater is evaluated.

CTA membrane was applied in the bioreactor and operated for a period of 120 days at SRT of 90 days:

- The flux, conductivity and pH of the reactor were stable and show good repetition among cycles. Flux through membrane gradually declined due to both (1) the feed conductivity build-up as a result of the gradual increase of the mixed liquor conductivity contributed both by the back diffusion of draw solution and accumulation of salts from influent and (2) membrane fouling which is mild but still both organic fouling and inorganic scaling were observable after membrane characterization.
- The AnOMBR shows good and stable sCOD removal rate of around 95% at most of the time. It also achieved total phosphorous removal at all time. The FO membrane has good membrane removal rate for total nitrogen and ammonia.
- The elevated salt environment has little effect on bioactivity in terms of the VFA and ATP concentration and methane production of AnOMBR system is comparable to conventional AnMBR.

6.1.3 Effect of temperature on the operation of AnOMBR

Comparisons between the performance of the laboratory-scale FOAnMBR system fed with synthetic wastewater operated at mesophilic temperature (35 °C) and room temperature (25 °C) were carried out:

- At room temperature, the flux decrease and conductivity increase are both at a slower speed than at mesophilic temperature. The membrane durability is also better and tap water cleaning is practical at room temperature with 90% flux recovery.
- There is no noticeable difference in terms of nutrient removal for reactors operating at two temperatures. However, the differences in the nutrient

concentration in supernatants indicate a slower and less efficient nutrient degradation of microbial at room temperature.

- Methane production rate at mesophilic temperature is significant higher than at room temperature.

6.1.4 CTA membrane provides a more sustainable flux and biogas production in AnOMBR

In terms of water permeability and salt rejection, performance of CTA membrane is not as satisfying compared to TFC membrane. The story changes when applying both membranes in the AnOMBR due to the higher fouling propensity of TFC membrane. The dramatic flux decline of TFC could not sustain a stable MBR operation in long term. Stable biogas production was able to be detected using CTA membrane while collection of produced biogas was difficult when using TFC membrane, which may be due to the low organic loading and prolonged HRT caused by the low flux of TFC membrane.

6.2. Implimentations

The AnOMBR integrates FO and anaerobic treatment in a single membrane bioreactor, with the FO serving the dual purposes of concentrating wastewater and retaining biomass and soluble organic matters for enhanced biological treatment. The complete biomass retention by the FO membrane is especially beneficial in an anaerobic process to overcome the slow growth rate of methanogens. Smaller size contaminants such as hydrolyzed organic matter could also be effectively retained by membrane, prolonging their residence time in reactor and potentially leading to an improved biodegradation efficiency and effluent quality. AnOMBR has the potential to achieve drastic energy saving and performance enhancement for sewage treatment. In the case seawater was used as a naturally available draw solution, the

diluted draw solution (the mixture the high quality FO permeate and seawater) will be disposed without need for further treatment. Temperature has limited effect on the treatment efficiency of the AnOMBR in terms of COD, nitrogen and phosphorous removal thanks to the high rejection of the FO membrane, but the degradation rate and efficiency in the mixed liquor of the biomass would be affected and methane gas production rate would be greatly reduced due to the lower operating temperature. On the other hand, lower temperature could benefit to the CTA membrane durability due to the vulnerability of CTA membrane on high temperature. The draw solute back-diffusion is also reduced in speed so that the salt accumulation within the MBR mixed liquor is slower which has positive effect on both the sustainability of membrane flux and bioactivity. With the currently available FO membranes on hand, thin film composite membrane has a better flux performance with absence of foulant but prone to be attached by organic foulants due to high surface roughness. When applying in AnOMBR, the dramatic flux decline of TFC membrane could not sustain a stable operation in long term, which makes it a less favorable choice over CTA membrane. However, with the rapid development of TFC membrane and limitations of CTA membrane such as low resistance to hydrolysis and biological degradation, the future application of TFC membrane in AnOMBR could be expected.

6.3. Suggestion to Future Research

There would be challenges associated with the use of FO-AnMBR systems, especially in the aspects of the membrane, salinity control and the permeate recovery/supernatant disposal.

As stated before, the CTA membrane had a low tolerance to both the high temperature solution and the biological attachment, hence the uncertainty of the stability of membrane made it difficult to sustain the operation for a long time. As

the TFC membrane adopted in this study was prone to fouling and weak in mechanical strength, with the recent development of commercial available, high flux TFC membranes, feasibility of applying TFC membrane in AnOMBR needs to be further evaluated and more research efforts are required in selection and development of an optimized FO membrane for the AnOMBR system.

Additionally, the steady level of salinity in the reactor was not observed during the study. As the increasing salinity might reduce the effective driving force, yield unfavorable parameters for salt precipitation, and aggravate the membrane fouling (Lay et al., 2010), with more confidence of the AnOMBR performance under high salinity and the development of FO membrane with smaller B/A value, further study on SRT optimization is necessary to achieve salinity steady-state in the MBR and to understand and alleviate the salinity effects on the physico-biological performance of AnOMBR system.

Furthermore, accumulation of ammonia in the bioreactor can adversely impact its removal by AnOMBR, despite the relatively high rejection by the FO membrane. Future studies may consider integrate nutrient removal or recovery with AnOMBR for improved permeate water quality. With respect to the inorganic-rich (e.g. nitrogen, phosphorous and metals) supernatant discharging from the reactor, this might limit the post-treatment technology or the reuse. Therefore, future work should focus on exploiting a suitable process to dispose or reuse the inorganic-rich supernatant.

Last but not least, more research efforts are required when applying AnOMBR for water reclamation, which was not covered in this study. In such a case, a suitable draw solute which is abundantly available and easily recovered needs to be identified and suitable method to recover FO permeate from its mixture with draw solution

such as membrane distillation needs to be investigated to achieve the cost effectiveness and high energy efficiency.

LIST OF PUBLICATIONS

Yangshuo Gu, Lin Chen, Jing-Wen Ng, Changsoo Lee, Victor W.-C. Chang, Chuyang Y. Tang. Development of anaerobic osmotic membrane bioreactor for low-strength wastewater treatment at mesophilic condition. *Journal of Membrane Science*, 2015, Volume 490, Pages 197-208

Yangshuo Gu, Yi-Ning Wang, Jing Wei, Chuyang Y. Tang. Organic fouling of thin-film composite polyamide and cellulose triacetate forward osmosis membranes by oppositely charged macromolecules. *Water Research*, Volume 47, Issue 5, 1 April 2013, Pages 1867-1874

Lin Chen, Yangshuo Gu, Chuqing Cao, Jun Zhang, Jing-Wen Ng, Chuyang Tang. Performance of a submerged anaerobic membrane bioreactor with forward osmosis membrane for low-strength wastewater treatment. *Water Research*, 2014, Volume 50, Pages 114-123

Shan Zou, Yangshuo Gu, Dezhong Xiao, Chuyang Y. Tang. The role of physical and chemical parameters on forward osmosis membrane fouling during algae separation. *Journal of Membrane Science*, 2011, Volume 366, Issues 1–2, Pages 356-362

Xue Jin, Chuyang Y. Tang, Yangshuo Gu, Qianhong She, and Saren Qi. Boric Acid Permeation in Forward Osmosis Membrane Processes: Modeling, Experiments, and Implications. *Environmental Science and Technology*, 2011, Volume 45, Issues 6, Pages 2323–2330

APPENDIX I: BATCH TEST TO IDENTIFY THE SUITABLE MEMBRANE APPLIED IN ANOMBR

This batch test aims to identify the suitable membrane to apply into the AnOMBR.

Materials and methods

1. Membranes

Two membranes were used in the current study, including a commercially available CTA FO membrane supplied by Hydration Technology Inc. (HTI, Albany, OR) and a polyamide TFC FO membrane synthesized in-house according to Wei et al. (2011). Detailed membrane properties please refer to section 3.2.1.

2. Synthetic nutrients

The composition of the synthetic feed solution used in this study is listed in Table I-1. Synthetic wastewater was close to real sewage and had a reference total COD value of 600 ppm (soluble COD around 200ppm). The derived COD:N:P ratio was 60:6:1. The conductivity and pH of the synthetic feed solution were 1.1 ± 0.1 mS/cm and 7 ± 0.1 , respectively. Ten times concentrated feed was prepared and diluted by tap water before entering the reactor.

Table I-1. Synthetic nutrients composition

Organic		Inorganic	
	Concentration(mg/L)		Concentration(mg/L)
Glucose	200	NH ₄ Cl	30
Peptone	160	Na-acetate	250
Meat Extract	110	KH ₂ PO ₄	40
Urea	30	CaCl ₂ •6H ₂ O	20
		FeSO ₄	20

3. Experimental setup and operation

Batch test was operated for 15 continuous days for both membranes at SRT of 90 days. As the water flux in FO process is not constant, the HRT of reactor kept changing from 40 hours at initial state to 100+ hours, determined by both the membrane flux and SRT. The initial TSS and VSS of sludge in reactor were 2.5g/L and 1.7g/L respectively. The system mainly comprised a bioreactor, the feed supply, a draw solution circulation loop, the auto-dosing of draw stock and a central monitoring and controlling system. The schematic diagram is shown in section 4.2.4.

The effective volumes of bioreactor and draw tank were 3.6 L and 2 L respectively. The membrane cell was made up of three square hollow plates. Two pieces of membrane coupons with an effective area of 10cm x 5 cm were placed at the two sides of the middle plates to form a closed draw solution channel. Active layer facing feed orientation was adopted. The peristaltic pump was used to recirculate draw solution at a flow rate of 16.7 cm/s (500 ml/min). The membrane cell was completely submerged in the reactor during experiment so that the outer surface (active surface) of membrane was in direct contact with ambient feed solution. Coarse bubbles were introduced at the bottom of reactor at constant rate of 1.5L/min using peristaltic pump to mix sludge homogenously and to avoid excessive membrane fouling. The constant mesophilic temperature of 35 °C was achieved by wrapping heating belt on outer surface of reactor. Conductivity, temperature, pH, pressure and water level in the reactor were monitored by the central system at all time.

0.5 M Sodium chloride(NaCl) was used as draw solution and the concentration in the draw solution tank was measured by conductivity probe. Draw stock of 5M NaCl was dosed in constantly to eliminate the diluting effect by permeate and keep the concentration constant. In the meantime, extra volume of draw solution which was contributed both by the flux and the draw stock dosing would overflow into the permeate tank on the balance for flux acquisition.

4. Analytical methods

pH, conductivity and temperature of both sludge and permeate were measured by probes connected with electrometers (Mettler-Toledo M200 system). Total solids (TS), volatile solids (VS), mixed were measured as described in standard methods (APHA 1999). Chemical Oxygen Demand (COD) were determined by USEPA Reactor Digestion Method (HACH 2125915/ 2415815). The composition of biogas was determined using a Shimadzu GC-TCD fitted with J&W 113-4362 column (0.32 mm $\times$ 60 m, 0 μ m) and Agilent 19095P-MS6 column (0.53 mm $\times$ 30 m, 50 μ m).

Results and discussion

1. pH and conductivity change

The mix liquor conductivity and pH in the reactor versus time for both CTA and TFC membrane are plotted in Figure I-1. Generally, for both membrane, pH is stable between 6.9 -7.1 but the conductivity keeps increasing with time, showing a accumulation of ions in the mixed liquor. The accumulation of salts come from unbalance between inflow and outflow salt loads, which is contributed both by the retain of ions in influents by membrane and the salt back diffusion through membrane from draw solution. Within the 14-days experiment, the mixed liquor conductivity for reactor using CTA and TFC membrane increased from 1.6 mS/cm to 16.3 mS/cm and 11.9 mS/cm. The different ending point of conductivity may be due to the better salt rejection of TFC membrane but it also may relate to the flux level of two systems.

The sudden building up of conductivity happened in CTA membrane reactor at day 15 may due to the weakening of membrane due to membrane hydrolyzation. The

breakage is predictable as CTA membrane is known for poor resistance to hydrolysis and biological degradation.

Figure I-1a. Conductivity and pH change versus time of reactor using CTA membrane

Figure I-1b. Conductivity and pH change versus time of reactor using TFC membrane

2. Flux performance

Figure I-2a shows the flux performance of the CTA membrane during the 15 days experiment and the first 24 hour flux performance is enlarged on the top right corner. Within the first 24 hours of experiment, the flux decreased by 20% from 10.8 L/m²h to 8.2 L/m²h and the flux further declined to 3.7 L/m²h in the following 14 days of experiments. However, the slope of flux profile was much milder compared to the 1st day decline. The decline of flux could be contributed both by the salt concentration build-up in mixed liquor and membrane fouling.

By using TFC membrane, similar trend of flux decline was observed, however in a bigger percentage. From figure I-2b it shows that the initial flux of TFC membrane is actually higher than CTA membrane, with a 12.5 L/m²h versus 10.8 L/m²h. However, within the first 24 hours of experiment, the flux declined to 7.8 L/m²h so

that the advantage of higher initial flux was eliminated after the 1st day running. The flux of TFC membrane keeps decline at a higher speed and it ends up at around less than 2 L/m²h at the end of the test. One interesting finding from the TFC flux profile is the flux is approaching to a stable state when flux is at level of 2 L/m²h. This could be explained by critical flux phenomenon in FO processes (Zou, Gu et al. 2011). The fouling severity of FO membrane is closely related to the operation flux level. At flux level above the critical flux, the membrane fouling could be noticeable for osmotic-pressure driven FO process. The flux reduction could be significant under the fouling condition until the flux drops below the critical flux level.

Figure I-2a: Flux profile of CTA membrane under 14 days batch test

Figure I-2b: Flux profile of TFC membrane under 14 days batch test

3. Chemical oxygen demand removal (COD)

Figure I-3 shows the COD level in inflow nutrients, in bulk reactor and in permeate for both reactors. The two reactors share lots in common in terms of COD removal. With stable inflow SCOD around 600 mg/L, the COD concentrations in the bulk of both reactors increase from 200 mg/L at the early few days to 230 mg/L at the end of the experiments. This is due to the retention of influent COD and temporary sCOD build-up by microbial hydrolysis in the bulk. Permeate sCOD concentration was quite low, generally under 30 mg/L. Overall, the system showed good sCOD removal rate of more than 95% at most of the time. An even higher removal rate could be expected at long term operation with more stable biological process and microbial growth. It shows that the COD rejection of OMBR adopting both TFC and CTA FO membrane could be comparable or even better than conventional membrane bioreactor.

Figure I-3a: Evolution of the sCOD concentrations in the inflow, bulk and the permeate (left axis) and the sCOD removal percentage (right axis) for reactor using CTA membrane

Figure I-3b: Evolution of the sCOD concentrations in the inflow, bulk and the permeate (left axis) and the sCOD removal percentage (right axis) for reactor using TFC membrane

4. Gas production

The gas and methane production of reactor using CTA membrane is plotted in Figure I-4. In the first few days no gas was detectable until the 4th day of experiment. Around 0.3 L/g COD digested of gas was produced and among it, 0.1L/g COD was methane. This production sustained for the following days. Although the methane composition and production rate is lower than literature reported, it is still a promising result to be found as the batch test is preliminary and the experiment time span is quite short.

Unfortunately, although methane gas was detected in the upper chamber of the reactor when using TFC membrane, the production of gas was too little to be collectable. This may be due to the low organic loading and prolonged HRT caused by the low flux of TFC membrane. The small volume and the low strength nature of influent wastewater lead to the limited bulk COD which could be utilized by biomass for gas production. In addition, the biogas generated is partially soluble and the prolonged HRT could lead to further lost of produced gas in bulk solution, making the detection of gas production more difficult.

Figure I-4: Flux profile of CTA membrane under 14 days batch test

APPENDIX II: COMPARISON OF FLUX UNDER THE EFFECT OF FEED CONDUCTIVITY BUILD-UP AND FLUX IN BIOREACTOR

Feed conductivity build-up is an important factor affecting the flux in bioreactor (Xiao, Tang et al. 2011). The effect of salt accumulation alone on water flux can be assessed by applying the FO water flux model:

Referring to the previous derivation work done by Lee et al. (Lee, Baker et al. 1981) and Loeb et al. (Loeb, Titelman et al. 1997), for active layer facing feed solution, the flux could be modeled as:

$$J_v = K_m \ln \left(\frac{A\pi_{draw} - J_v + B}{A\pi_{feed} + B} \right)$$

where J_v is the volumetric flux of pure water, π is the osmotic pressure, A is the water permeability coefficient of the clean membrane, B is the salt permeability coefficient of the clean membrane, and K_m is the mass transfer coefficient defined as the ratio of solute diffusion coefficient D over membrane structural parameter S .

The comparison of the modeled flux (accounting for the effect of feed conductivity build-up but without considering fouling) and actual experimental flux in bioreactor are plotted in Figure II-1. The two sets of data points followed a similar trend, but experimental flux was always below modeled flux. This result shows that salt accumulation was a major contributor to flux decline, but the effect of membrane fouling was not negligible.

Figure II-1: Comparison of modeled baseline flux of AnOMBR with experimental flux

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