Effect of hydrodynamic conditions and feedwater composition on fouling of ultrafiltration and forward osmosis membranes by organic macromolecules

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**EFFECT OF HYDRODYNAMIC CONDITIONS AND
FEEDWATER COMPOSITION ON FOULING OF
ULTRAFILTRATION AND FORWARD OSMOSIS
MEMBRANES BY ORGANIC MACROMOLECULES**

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**SCHOOL OF CIVIL AND ENVIROMENTAL
ENGINEERING**

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Effect of Hydrodynamic Conditions and Feedwater Composition on Fouling of Ultrafiltration and Forward Osmosis Membranes by Organic Macromolecules

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Summary

This study investigated the fouling of pressure-driven ultrafiltration (UF) membrane and osmotically-driven forward osmosis (FO) membrane by organic macromolecules. Protein and humic acid, two types of ubiquitous identified membrane organic foulants, were chosen as the model foulants. It was found that the hydrodynamic conditions (initial flux and cross-flow velocity) and feedwater composition (foulant concentration, pH, ionic strength, and divalent ions concentration) played a significant role on the organic fouling of these two types of membranes.

During the bovine serum albumin (BSA) ultrafiltration, drastic flux reduction was observed at high initial flux and/or low cross-flow velocity. A limiting flux existed during BSA filtration, beyond which membrane flux can not be sustained. Further increase in pressure over the limiting value did not enhance the stable flux. Foulant concentration had no effect on the stable flux, although the rate approaching to the stable flux increased proportionally with increasing foulant concentration. Fouling was most severe at the isoelectric point (IEP) of BSA (pH 4.7), where the electrostatic repulsion between foulant molecules is negligible. Membrane fouling became less severe at pHs away from the IEP. Increasing the ionic strength at pH 3.0 promoted severe fouling likely due to electric double layer (EDL) compression. On the other hand, the flux behavior was insensitive to salt concentration at pH 4.7 due to the less significance of electrostatic interaction. At a solution pH of 5.8, effect of ionic strength on long-term flux behavior was directly opposite to that on the transient behavior. While the long-term flux was lower at higher ionic strength due to EDL compression, the transient behavior was also affected by the BSA retention of the membrane.

In the FO process, the water and salt flux performance was strongly influenced by the internal concentration polarization (ICP) and also dependent on the membrane orientation. Increasing the foulant concentration, ionic strength and divalent ions concentration in the feed solution as well as salt concentration in the draw solution and lowering the pH promoted the humic acid fouling on the

porous support layer of the FO membrane, whereas the cross-flow velocity had little effect on the flux decline with the FO porous support layer towards the feed solution. In addition, humic acid fouling on the FO membrane was less severe with the active layer facing the feed solution than that with the active layer facing the draw solution.

UF and FO membrane fouling by the organic macromolecules was affected by the coupled chemical and physical aspects. Despite of different types of organic foulants and membranes, electrostatic repulsion between the foulant-foulant and foulant-membrane was one of the most significant factors affecting fouling. Foulant-membrane interaction dominated the initial flux decline, while the long-term flux behavior was governed by the foulant-foulant interaction.

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List of Articles

Qianhong She, Chuyang Y. Tang, Yi-Ning Wang, Zhenjia Zhang "The Role of Hydrodynamic Conditions and Solution Chemistry on Protein Fouling during Ultrafiltration." DESALINATION (accepted, 2009)

Chapter 1

Introduction

1.1 Problem statement

Synthetic membrane processes perform versatile functions in liquid and gaseous separations. Membrane separation is characterized by simultaneous retention of species and product flow through the semi-permeable membrane. The selectivity and rejection of a certain component might be based on its size, charge, and solubility. Most of the membrane separation processes are dependent on the applied pressure as the driven force, such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), which have received increasing popularity in recent decades. UF membranes have been used in surface water treatment (such as natural organic matter and pathogen removal), in membrane bioreactors (MBRs), in pretreatment processes for reverse osmosis (RO), and in many other industrial applications (Aoustin, Schafer et al. 2001; Durham, Bourbigot et al. 2001; Jarusutthirak and Amy 2001; Van der Bruggen, Vandecasteele et al. 2003). On the other hand, forward osmosis (FO) process, dependent on the driven force of osmotic pressure, has attracted more and more attention of membrane researchers in the recent years. It has been found to be applied in the wastewater treatment and water purification, seawater desalination, food processing, pharmaceutical applications, and power generation (Cath, Childress et al. 2006).

Membrane fouling, which is a major obstacle for the widespread use of membrane technology, is always simultaneous with the membrane separation process. Groups of foulants have been examined on the fouled membranes, such as soluble inorganic compound, collides and suspended particles, organic matter, and microorganisms (Yuan and Zydney 2000). During membrane fouling, they accumulate on the membrane surface or within the membrane pores and adversely affect both the quantity (permeate flux) and quality (solute concentration) of the product water (Zhu and Elimelech 1997; Yuan and

Zydney 2000). Protein and natural organic matter (NOM) have been identified to be main membrane foulants in the application of membrane technology (Kim, Fane et al. 1992; Yuan and Zydney 2000; Ang and Elimelech 2007; Mi and Elimelech 2008). Protein is widely found in the water treatment and wastewater reclamation as well as in the biological industry (Rebhun and Manka 1971; Saksena and Zydney 1994; Barker and Stuckey 1999; Ang and Elimelech 2007), while NOM, such as humic acid, is ubiquitous in natural waters (Collins, Amy et al. 1986; Crozes, Jacangelo et al. 1997; Buffle, Wilkinson et al. 1998) and also present in the effluents of wastewater treatment facilities (Levine, Tchobanoglous et al. 1985; Leppard, Mavrocordatos et al. 2004).

Organic fouling of pressure-driven membranes is usually distinguished between two cases. For RO, NF and “tight” UF membranes, cake layer formation is the dominant fouling mechanisms (Kim, Fane et al. 1992; Hong and Elimelech 1997; Tang, Kwon et al. 2007), while for MF and “loose” UF membranes, pore plugging by organic foulants can be an important fouling mechanism besides cake layer formation (Ho and Zydney 2000; Huisman, Pra?danos et al. 2000). Existing studies suggest that initial stages of fouling for porous membranes are likely dominated by pore plugging, while the flux behavior is probably determined by a foulant cake layer when severe fouling occurs at longer filtration duration (Kim, Fane et al. 1992; Palecek and Zydney 1994; Güell and Davis 1996; Ho and Zydney 2000; Huisman, Pra?danos et al. 2000). Systematic studies revealed that membrane fouling by organic matters was affected by the hydrodynamic conditions (applied pressure and cross-flow velocity), feedwater composition (types of foulants and foulant concentration, pH, ionic strength, hardness) together with the membrane properties (surface roughness, charge properties and hydrophilicity) (Fane, Fell et al. 1983; Palecek and Zydney 1994; Elimelech, Zhu et al. 1997; Herrero, Pra?danos et al. 1997; Chan and Chen 2001; Vrijenhoek, Hong et al. 2001; Seidel and Elimelech 2002; Ang and Elimelech 2007; Tang, Kwon et al. 2007). Hydrodynamic conditions affecting fouling is mainly through the influence of drag force, shear force and turbulence (Tarabara, Koyuncu et al. 2004; Tang, Kwon et al. 2007), whereas feedwater composition can affect the foulant – foulant and foulant – membrane

electrostatic repulsion (Jones and O'Melia 2001; Tang, Kwon et al. 2007). In general, severe fouling is observed at the isoelectric point (pI) of a protein where the electrostatic repulsive force between protein molecules is at the minimum (Fane, Fell et al. 1983; Palecek and Zydney 1994; Ang and Elimelech 2007; Mo, Tay et al. 2008). In addition, protein fouling is typically promoted by high membrane flux and/or low cross-flow velocity (Bacchin, Aimar et al. 1995; Wu, Howell et al. 1999; Ang and Elimelech 2007).

Despite of the vast number of studies on protein fouling, the effects of ionic strength and foulant concentration have been controversial in the literature. Studies on nonporous membranes (Ang and Elimelech 2007; Mo, Tay et al. 2008) reported that protein fouling was more severe at elevated ionic strength due to electrical double layer (EDL) compression. Consistent with the above studies, several research groups (Fane, Fell et al. 1983; Heinemann, Howell et al. 1988; Palecek and Zydney 1994) also reported greater protein fouling tendency for MF and UF membranes at higher ionic strength. In contrast, Chan and Chen (Chan and Chen 2001) observed lower fouling rate for MF membranes at greater background salt concentrations, which was attributed to the greater protein solubility at increase salt content. Similar observation also has been documented for UF membranes (Salgin 2007). The literature on the effect of foulant concentration is equally confusing. While many researchers have suggested that more severe fouling occurred at higher protein concentrations (Kilduff, Mattaraj et al. 2004; Bacchin, Aimar et al. 2006; Lee, Ang et al. 2006), some recent studies revealed that the quasi-steady flux at long filtration time was independent of the foulant concentrations (Cohen and Probstein 1986; Kelly and Zydney 1995; Tang and Leckie 2007). Despite of the increased fouling rate (the rate approaching to the stable flux) at greater foulant concentrations, Tang and Leckie (Tang and Leckie 2007) demonstrated that the long-term stable flux was determined by interaction forces between foulant-membrane and foulant-deposited-foulant which were largely independent of foulant concentration.

While the mechanism of membrane fouling has been extensively investigated in the pressure-driven membrane process, only a few publications reported the membrane fouling in the FO process. Cornelissen et al. (Cornelissen, Harmsen

et al. 2008) investigated the active sludge on the FO membrane fouling in the osmotic membrane bioreactor, nevertheless, neither reversible nor irreversible membrane fouling was found. They ascribed this to their operation of low flux conditions, probably below the critical flux for membrane fouling. Mi and Elimelech (Mi and Elimelech 2008) made systematic research on FO membrane fouling by protein, humic acid and alginate. They revealed that the FO fouling is governed by the coupled influence of chemical and hydrodynamic interactions. However, the limitedly existing studies on membrane fouling were based on the membrane active layer facing the feed solution. The fouling behavior on the side of support layer was less investigated. In addition, FO membrane character and performance, which might be related to the membrane fouling, are always an interesting research scope. Furthermore, the implying relationship of membrane fouling mechanisms between the pressure-driven membrane separation process and the osmotically-driven membrane separation process was less investigated in the previous researches.

Therefore, it is important to systematically study the hydrodynamic conditions and feedwater composition on the pressure-driven UF membrane fouling and osmotically-driven FO membrane fouling by the typical organic foulants – protein and humic acid, and to further understand the fouling mechanisms in these two types of membrane filtration process, which could provide effective suggestions for the fouling control.

1.2 Hypotheses

According to the literature study and tentative experiments, the major hypotheses are summarized as follows:

- 1) It is hypothesized that the long-term membrane fouling will not be affected by the foulant concentration during the protein ultrafiltration.
- 2) The rate of BSA fouling on the UF membrane will not be promoted at high ionic strength while the solution is at certain pH value.

- 3) Fouling of FO membrane will be more pronounced while the FO membrane porous support layer faces the feed solution.
- 4) Water flux will not increase linearly while increasing the draw solution concentration.

1.3 Objectives

Based on the above statement and considerations, the objectives of this research herein are to:

- 1) Systematically investigate how the hydrodynamic conditions and feedwater composition affect the fouling of UF and FO membranes by organic macromolecules – protein and humic acid.
- 2) Utilize the existed limiting flux model to analyze the fouling behavior in UF membrane fouling, and develop simply conceptual physical and mathematical model to further explain the fouling behavior.
- 3) Characterize the properties of UF and FO membranes.
- 4) Test the performance of FO membranes and simulate the flux behavior in FO process.
- 5) Compare the fouling behavior between the pressure-driven membrane and osmotically-driven membrane.

Chapter 2

Literature Review

2.1 Membrane separation process

Osmosis is a physical phenomenon that has been exploited more than two hundred years' ago (Singh 2006) and extensively studied by scientists in various disciplines of science and engineering. Osmosis is the transport of water across a selectively permeable membrane from a region of higher water chemical potential to a region of lower water chemical potential (Cath, Childress et al. 2006). The automatic transport of water through the membrane is caused by the osmotic pressure which is due to the difference in solute concentrations across the membrane. Membrane technology is developed from the osmosis phenomenon.

Of all the membrane separation processes, a large group is the pressure-driven membrane process – reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) – which utilizes additional hydraulic pressure as the driving force, while another group is osmotically-driven membrane process, such as forward osmosis (FO) and pressure-retarded process (PRO), which adopts the osmotic pressure to drive the water transportation. Both of the two types of membrane processes are developed from a physical phenomenon – osmosis.

2.1.1 pressure-driven membrane process

Pressure-driven membrane process – reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) – use hydraulic pressure as driving force on the solution at one side of the membranes to separate it into a permeate and a retentate. The permeate is usually pure water, while the retentate is solute concentrated solution (Van der Bruggen, Vandecasteele et al. 2003). These membrane technologies have become increasingly popular in the industrial application, such as seawater desalination, wastewater purification, food processing, biological industry and so on (Keith Brindle 1996; Van der Bruggen, Vandecasteele et al. 2003). RO and NF membranes have the relatively smaller

pore size and higher rejection in comparison to UF and MF membranes. RO membranes is mostly used for sea water desalination and wastewater reclamation due to its high efficiency of salt rejection, while NF membranes are more permeable and able to reject divalent and multivalent ions, colloids and some dissolved organic matters but allow the monovalent ions to pass through them. Unlike RO and NF membranes, UF and MF membranes are porous structure and need lower operational pressure. While MF membranes can remove particles, turbidity and microorganisms from surface water, ground water and effluent of wastewater, UF membranes also allow the remove of a variety of waterborne viruses and much of the dissolved organic matter (such as humic acid and proteins) (Jonsson and Tra?ga?rdh 1990; Rautenbach and Mellis 1995; Yuan and Zydney 2000). In addition, UF membranes are widely used in the pretreatment process for RO (van Hoof, Hashim et al. 1999; Pearce 2008).

Specifically, UF membrane process can be defined as between NF and MF with pore size ranging from 1 to 100 nm (0.001 to 0.1 μm). Separation of UF membrane is typically characterized by the nominal molecular weight cut off (MWCO). A loosely defined term of MWCO is generally taken to mean the molecular weight of the globular protein molecule that is 90% rejected by the membrane. Ideally, any species above the MWCO will not pass through the membrane; however, in addition to the molecular size, there are other factors which affect the retentivity of membranes such as shape of the molecule, presence of other solutes, adsorption of solutes, solution chemistry (pH, ionic strength), module configuration (flat sheet, hollow fiber) and membrane material (Van der Bruggen, Vandecasteele et al. 2003).

Flux through a UF membrane is defined by Darcy's law of flow through porous materials as:

$$J = A(\Delta P) \dots \dots \dots (1)$$

where A is the membrane permeability constant and ΔP is the transmembrane pressure. The value of A is a function of membrane porosity, pore size, and

membrane thickness, and varies from $0.5 \text{ m}^3/\text{m}^2\cdot\text{day}\cdot\text{bar}$ for dense membranes to $5 \text{ m}^3/\text{m}^2\cdot\text{day}\cdot\text{bar}$ for more open membranes (Singh 2006).

2.1.2 Osmotically-driven membrane process

Forward osmosis (FO) and pressure-retarded osmosis (PRO) are the main types of osmotically-driven membrane processes. They use the osmotic pressure differential ($\Delta\pi$) across the selectively permeable membrane (which allows passage of water, but rejects most solute molecules or ions), rather than hydraulic pressure differential (as in RO), as the driving force for transport of water through the membrane. In FO process, the membrane active layer faces the feed solution and no additional pressure is applied in either side of the feed solution or draw solution. However, in PRO process, the membrane active layer is placed against the draw solution and additional hydraulic pressure which is lower than the osmotic pressure is applied in the opposite direction of the osmotic pressure gradient (similar to RO). The general equation describing water transport in FO, PRO and RO is (Cath, Childress et al. 2006)

$$J = A(\sigma\Delta\pi - \Delta P) \dots\dots\dots(2)$$

where J is the water flux, A the water permeability constant of the membrane, σ the reflection coefficient, and ΔP is the applied pressure. For FO, ΔP is zero; for RO, $\Delta P > \Delta\pi$; and for PRO $\Delta\pi > \Delta P$.

Due to the osmotically-driven principles, using of forward osmosis has exhibited unparalleled advantages compared with pressure-driven membrane process - it operates at low or no hydraulic pressures, it has higher rejection of a wide range of contaminants, and it may have lower membrane fouling propensity (Cath, Childress et al. 2006). As a result, FO received increasing popularity of studies on a range of applications. In the recent decades, the application of FO can be found in various fields, such as in wastewater treatment and water purification (concentration of dilute industrial wastewater, concentration of landfill leachate (York, Thiel et al. 1999), direct potable reuse of wastewater in advanced life support systems for space applications (Beaudry and Herron 1997; Cath, Gormly et al. 2005), concentration of digested sludge liquids (Holloway, Cath et al. 2005), and source water purification, in seawater

desalination, in food processing, and in pharmaceutical industry. Additionally, PRO has been tested and evaluated as a potential process for power generation. PRO uses the osmotic pressure difference between seawater and fresh water to pressurize the saline stream, and thus convert the osmotic pressure of seawater into a hydrostatic pressure which can produce electricity (McGinnis, McCutcheon et al. 2007).

2.2 Membrane material and properties

Synthetic membranes can be made from a large number of materials. A list of common polymers used in membrane separations is given in table 2.1 (Singh 2006). The materials used to synthesize UF membranes are limited. Polysulphone (PS) is the most widely used polymer in the UF membrane manufacture, however, other type of materials are still received wide application, such as poly(ether sulfone) (PES), poly(vinylidene fluoride) (PVDF), polyacrylonitrile (PAN), poly(vinyl chloride)-polyacrylonitrile copolymers (PVC-PAN), cellulose acetate (CA), and some aromatic polyamides (Baker 2004).

Referring to the methods for membrane manufacture, Table 2.2 gives several common methods of manufacturing synthetic membranes (Singh 2006). Each method produces different membrane morphology, different porosity, pore size distribution, and ultrastructure. UF membranes are usually asymmetric and heterogeneous structures and manufactured through Loeb-Sourirajan (phase-inversion) process (Baker 2004; Jung 2004). Typically, they are comprised of a finely porous surface layer or skin supported on a much more open microporous substrate. The finely porous surface layer performs the separation; the microporous substrate provides mechanical strength. UF and MF are related processes – the distinction between the two lies in the pore size of the membrane. MF membranes have larger pores and are used to separate particles in the range of 0.1 – 10 μm , while UF is generally considered to be limited to membranes with pore diameters from 0.001 – 0.05 μm .

Table 2.1 Characteristics of common polymeric membrane materials

Polymer	Glass transition temp (°C)	Melting temp (°C)
Polyethylene	-60 – 90	137 – 143.5
Poly (vinylidene fluoride)	-40	160 – 185
Polypropylene	-10	167 – 170
Polycarbonate	150 – 155	240
Teflon	-113	327
Cellulose acetate	69	230
Poly (ether sulphone)	225	NA
Polysulphone	190	NA
Poly (vinyl alcohol)	65 – 85	228 – 256
Polyacrylonitrile	80 – 104	319
Poly (phenylene sulphide)	85	285
NA: Not available		

Table 2.2 Synthetic membrane manufacturing methods

Process	Materials
Phase inversion:	
Solvent evaporation	CA, PA;
Temperature change	PP, PA;
Precipitant addition	PS, nitrocellulose
Stretching sheets of partially crystalline polymers	PTFE
Irradiation and etching	Polycarbonate, polyester
Moulding and sintering of fine grain powders	Ceramics, metal oxides, PTFE, PE

The physiochemical properties of the surface layer can essentially determine the permeate flux and rejection performance of the membranes. In general, more hydrophilic membranes are more fouling-resistant than those with the completely hydrophobic materials. Therefore, water-soluble polymers such as poly(vinyl pyrrolidone) or poly(vinyl methyl ether) are often added to the

membrane casting solutions used for hydrophobic polymers such as PE or PVDF for the purpose of making the membrane surface hydrophilic (Baker 2004).

In addition, the zeta potential of the membrane is another key factor that can influence the performance of permeate flux and solute rejection. Most of the colloidal materials have a slightly negative charge from carboxyl, sulfonic or other acid groups. If the membrane surface also has slight negative charge, adhesion of the colloidal gel layer to the membrane is reduced, which can help to maintain a high flux and inhibit membrane fouling (Baker 2004). Membrane surface charge can affect the protein-membrane interactions in the initial stages of filtration and thus affect the permeate flux and protein transmission (Huisman, Pra?danos et al. 2000). Mehta and Zydney used series of positively charged membranes modified by chemical attachment of a quaternary ammonium group to the free hydroxyls in the glucose rings of cellulose membranes to demonstrate the importance of electrostatic interactions in ultrafiltration and further quantitatively investigated the effects of membrane charge density on protein transport and membrane hydraulic permeability (Mehta and Zydney 2006). Specifically, for PAN composite membranes, previous researches have reported that they are negatively charged within the normal pH ranges from 3 to 10 and the charge are decreasing with increasing pH values, suggesting that PAN membrane holds a priority of repulsing the negatively charged foulants, such as colloids or molecules, mitigating their deposition on the membrane surface (Jung 2004; Kang, Subramani et al. 2004; Ecaterina Stela Dragan 2005).

Other properties, such as membrane morphology and pore structure, play an important role on membrane performance and fouling. Chia-Chi and Zydney pointed out that the more likely protein fouling of membranes with straight-through pores occurred by pore blockage, the rate of which was a function of the membrane porosity, whereas membranes with interconnected pores fouled more slowly (Ho and Zydney 1999). Elimelech and co-workers revealed that thin-film composite membranes have higher fouling rate compared to those cellulose acetate membranes, which is attributed to surface roughness that is inherent in interfacially polymerized aromatic polyamide composite membranes

(Elimelech, Zhu et al. 1997). Kang et al. used a novel polyacrylonitrile (PAN) UF membrane to incorporate the amphiphilic comb copolymer additive, polyacrylonitrile-graft-polyethylene oxide (PAN-g-PEO), to investigate the change of membrane fouling behavior. Results indicate that the blend membrane exhibits the antifouling character, which is attributed to the surface segregation and local orientation of PAN-g-PEO molecules at the membrane surface and pore walls during membrane casting, creating a dense PEO brush layer that provides a steric barrier to protein adsorption (Kang, Asatekin et al. 2007).

With reference to FO process, any dense, non-porous, selectively permeable material can be used as a membrane for it. Although RO membranes can be used as FO modal process (Cath, Childress et al. 2006), results shows that the product water flux is quite lower than expected (McCutcheon, McGinnis et al. 2005; Cath, Childress et al. 2006). Recently, Wang et al. applied the polybenzimidazole (PBI) nanofiltration hollow fiber membrane in the forward osmosis process. Results showed that desirable permeation flux and high rejection to divalent ions were achieved while PBI membrane applied in the FO process, and MgCl_2 was verified to be a considerable draw solution for FO process (Wang, Chung et al. 2007).

At present, there is only one type of FO membrane produced by Hydration Technologies, Inc. (Albany, OR) used in the commercially application, such as water purification for military, emergency relief, and recreational purposes. The solely commercially used FO membranes in the current days are made of cellulose triacetate (CTA). The FO membrane has a thickness of less than 50 μm and contains two layers: the active layer with high density for high solute rejection and a support layer with embedded polyester mesh providing mechanical support. Unlike RO membranes, it is likely due to the relative thinness of the membrane and the lack of a fabric support layer that the FO membranes can be well performed in the forward osmosis process.

Membrane structural properties have been demonstrated to greatly influence the performance of the FO process. Through modeling the water flux in forward osmosis, McCutcheon and Elimelech suggest that possible improvements in

flux behavior and recovery can be realized by designing membranes specifically for FO or PRO processes (McCutcheon and Elimelech 2007). These improvements may include making the support layer thinner or more porous (McCutcheon and Elimelech 2007). Ng et al. used two types of RO membrane and a FO membrane to test the performance of FO process (Ng, Tang et al. 2006). Results showed that the FO membrane was able to achieve the higher water flux compared to RO membranes under the same experimental conditions, concluding that an ideal FO membrane should consist of a thin dense selective layer without any loose fabric support layer (Ng, Tang et al. 2006). Membrane support layer hydrophobicity has also been proved to significantly hinder water flux in osmotically driven membrane processes (McCutcheon and Elimelech 2008). McCutcheon and Elimelech found that lack of sufficient support layer wetting not only exacerbates internal concentration polarization phenomena, but also disrupts water continuity within the membrane, thereby reducing the pathways for water transport (McCutcheon and Elimelech 2008). Improved wetting of the support layer has been shown to increase water flux, especially for pressure-retarded osmosis applications with dilute feed solutions (McCutcheon and Elimelech 2008).

With the summary of the advantages and disadvantages of membranes used in FO process, the desired characteristics of membranes for FO would be high density of the active layer for high solute rejection, a thin membrane with minimum porosity of the support layer for low internal concentration polarization, and therefore, higher water flux; hydrophilicity for enhanced flux and reduced membrane fouling; and high mechanical strength to sustain hydraulic pressure when used for PRO (McCutcheon, McGinnis et al. 2005; Cath, Childress et al. 2006).

2.3 Membrane fouling

2.3.1 Types of foulant

During the membrane filtration process, membrane fouling is strongly related to the types of foulant in the feed water. Generally, four types of foulant are characterized in the membrane fouling, i.e., soluble inorganic compounds,

colloids and suspended solids, organic matter, and microorganism. Figure 2.1 illustrates the different types of foulants during membrane fouling.

Figure 2.1: Different types of foulants during membrane fouling.

Scaling by soluble inorganic compounds

Sparingly soluble compounds can precipitate and form scales, such as metal hydroxides, when their concentration exceeds the solubility limit. The scales accumulate on the membrane surface or attach within the membrane pores. Some commonly encountered problematic compounds include BaSO_4 , CaSO_4 , CaF_2 , CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$, SiO_2 (Tang 2007).

Fouling by colloids and suspended solids

Colloidal particles are ubiquitous in natural waters, covering a wide range size ranging from a few nanometers to a few micrometers. Normally, aquatic colloids include clay minerals, colloidal silica, iron, aluminum, and manganese oxides, organic colloids and suspended matter, and calcium carbonate precipitates. In the pH range of natural waters, most colloids carry a negative surface charge, reflecting their surface chemical properties and the chemical composition of natural waters. During membrane filtration, colloidal fouling is caused by the accumulation of particles on the membrane surface in a so-called cake layer for RO, NF and tight UF membranes, whereas pore plugging by colloidal particles can be an important fouling mechanism for MF and loose UF membranes, in addition to particle accumulation on the membrane surface (Zhu and Elimelech 1997).

Fouling by organic matter

Organic matters have been identified to be a major part of foulant contributing to membrane fouling. These organic foulants contain a wide range of organic matter from low to high molecular weight compounds, such as proteins, polysaccharides, amino-sugars, nucleic acids, humic and fulvic acids, and cell components (Ang and Elimelech 2007). They can accumulate on the membrane surface to form cake layer and especially adsorbed into the UF and MF membrane pores, which induces the flux decline during the membrane filtration process.

Fouling by microorganisms

Biofouling has long been recognized as one of the most problematic types of fouling during membrane filtration process, which is due to the microbial attachment and subsequent colonization. When bacteria attach to the membrane, they start to multiply and produce extracellular polymeric substances (EPS) to form a viscous, slimy, hydrate gel, and eventually form a mature biofilm on the membrane surface to prevent the water pass through the membrane. The situation is aggravated with poor anti-fouling strategies that tend to target only the microorganisms but not the EPS, which is the foundation of a biofilm.

2.3.2 Membrane fouling and flux decline

1. Concentration polarization

In the liquid-phase membrane filtration processes such as MF, UF, NF, RO and FO, solutes and/or particles transfer to the membrane surface with the solvent by convection, the concentration of solutes and/or particles near the membrane surface inevitably increases due to the rejection of these species by the membrane. The retention of rejected species results in the formation of a secondary or a dynamic membrane (boundary layer) due to the mass balance between the convective flow of solutes and/or particles to the membrane surface and the back diffusion of the solutes and/or particles to the bulk feed solution. The build up in concentration in this boundary layer region is referred to as concentration polarization (CP) (Singh 2006).

Concentration polarization resulting in substantial decline in flux is undesirable in the membrane filtration process due to the following reasons. For one thing,

osmotic pressure near the membrane surface is increased due to the higher solute concentration, which in turn reduce the net pressure that can act as the driving force and therefore flux will decline unless additional pressure is applied to compensate for the increasing osmotic pressure. For another, effect of CP often leads to fouling, which is irreversible and can only be rectified by cleaning. The accumulated solutes, such as Ca^{2+} and CO_3^{2-} , form insoluble salts when the solubility limit is exceeded; or particles like silica colloids transit from the solution phase (particle polarization layer) to the solid phase (deposit layer) on the membrane surface.

CP in the osmotic-driven membrane processes (FO processes) is more complicated than that in the pressure-driven membrane processes. Since most of the FO membranes currently used are asymmetric, CP is divided into two cases based on the location of the occurrence of CP in FO processes: (1) external concentration polarization (ECP), which occurs near the membrane surface; (2) internal concentration polarization (ICP), occurring inside of the porous support layer of the FO membranes. For the two cases, CP not only occurs on the feed sides of the membrane similar to the pressure-driven membrane processes, but also occurs on the permeate side of membrane. On feed solution side, CP refers to concentrative CP, while dilutive CP occurs in the draw solution side. Existing researches reported that the ICP was more pronounced on the water and salt flux decline than the ECP (McCutcheon and Elimelech 2006; McCutcheon and Elimelech 2007; Tan and Ng 2008).

2. Pore blocking and restriction

During the membrane filtration process, solutes or particles with the size less than the membrane pore size can be adsorbed onto the membrane internal pore surface due to electrostatic interaction with the membrane pores, narrowing/blocking the pores, decreasing the porosity and increasing the resistance of membrane, especially for those MF and UF membranes which have large pore sizes compared with NF and RO membranes. In addition, those larger solutes or particles which can not pass through the membranes can be adsorbed onto the membrane surface, directly covering and blocking the pores. In general, nearly no pore adsorption occur on NF and RO membranes since

their fine pore size or even non-porous structure on some RO membranes. Typically, pore blocking is the dominant mechanism in the initial stage of filtration and lead dramatic flux decline if the initial flux is high enough (normally above the critical flux) (Herrero, Pra?danos et al. 1997; Ho and Zydney 2000; Huisman, Pra?danos et al. 2000).

3. Cake/gel layer formation

While pore blocking mainly occurs due to the foulant-membrane interaction at the initial membrane filtration stage, cake layer is formed on the membrane surface as a result of the interaction between foulant and deposited-foulant at later filtration stage. In the later filtration stage, foulant in the feed water continues to deposit on the membrane surface which has totally covered by former adsorbed foulant to form the cake/gel layer and flux continues to decline. The cake/gel layer may act as a filter and remove small particles and/or solutes or it may compact over time. The foulant will not deposit until the flux reaches the limiting value (Tang and Leckie 2007).

The above mechanisms for membrane fouling are illustrated in Figure 2.2. This figure proposes one possible method to categorize membrane fouling mechanisms, including pore restriction, pore blocking, and cake layer formation.

Figure 2.2: Schematic diagram for membrane fouling mechanisms.

2.3.3 Model foulant – bovine serum albumin (BSA) and humic acid

During the membrane filtration processes, membranes can be fouled by a variety of dissolved and suspended organic matters with molecular weights ranging from below one hundred to several million. Natural organic matter

(NOM), proteins and polysaccharides have been classified and identified as important components in the secondary effluents and soluble microbial products (SMP) in wastewater treatment (Rebhun and Manka 1971; Manka, Rebhun et al. 1974; Barker and Stuckey 1999). Additionally, NOM are also widely found in the surface and ground waters which can be used as the source of drinking water by the membrane treatment, and proteins are the main the materials in the biophaceutical industry where membrane technologies are popularly used. Groups of researchers have investigated the membrane fouling by NOM, proteins and polysaccharides, since these kinds of substance can typically represent the foulants in the membrane filtration processes (Kim, Fane et al. 1992; Kelly and Zydney 1997; Lee, Ang et al. 2006; Tang, Kwon et al. 2007; Mi and Elimelech 2008). Palecek and Zydney used five kinds of protein in their research and revealed that the steady-state permeability for each of the protein deposits was minimum at the protein isoelectric pH and decreased with increasing salt concentration at pH both above and below the isoelectric point (Palecek and Zydney 1994). Jones and Melia investigated the adsorption of protein and humic acid onto hydrophilic membrane surfaces and pointed that adsorption decreased as pH increased (Jones and O'Melia 2000). They further pointed out that increased salt concentration reduces electrostatic repulsion between like-charged material (increasing adsorption) and decreases electrostatic attraction between oppositely charged material (decreasing adsorption). In the FO processes, alginate, BSA and Aldrich humic acid (AHA) were found to be model organic foulants whose fouling behaviors were strongly affected by the coupled chemical and hydrodynamic interactions (Mi and Elimelech 2008).

Many researchers choose BSA as the model proteins and humic acid as the model NOM for their researches (Yuan and Zydney 2000; Chan and Chen 2001; Kang, Asatekin et al. 2007; Mi and Elimelech 2008). BSA is approximate ellipsoidal (14 x 4 x 4 nm), with a molecular weight of ~ 67 kDa (Palecek and Zydney 1994). It has an amphoteric charge behavior due to the presence of both amine and carboxylic groups (Ang and Elimelech 2007). The isoelectric point is pH 4.7 (Peters Jr, C.B. Anfinsen et al. 1985). Humic acid comprises heterogenous and recalcitrant polymeric organic degradation products and is

only soluble at $\text{pH} > 2$. The typical molecular weight spans from a few thousand to a few hundred thousand Daltons with a great dependence on their sources (Chin, Aiken et al. 1994; Vermeer, Van Riemsdijk et al. 1998; Hur and Schlautman 2003). Humic acid is negatively charged over a wide pH range due to deprotonation of carboxylic and phenolic functional groups. The charge density increases at higher pH (Hong and Elimelech 1997). For both of humic acid and BSA, increasing ionic strength can increase the charge density slightly, but also shields the charges due to increased concentration of counter ions, leading to a net reduction in the electrostatic repulsion between molecules. Calcium has a strong affinity to carboxylic groups. Therefore, it is able to complex with humic acid and BSA and partially neutralizes their charges.

2.3.4 Factors affecting fouling

Flux decline caused by membrane fouling is unavoidable in the membrane filtration processes. It is widely agreed that rate of fouling is affected by membrane properties (hydrophilicity/hydrophobicity, surface charge, roughness, and porosity), solution chemistry (concentration, pH, ionic strength, and hardness), and hydrodynamic conditions (applied pressure and cross-flow velocity). Solution chemistry can affect the charge density of the solute and thus influence the interaction between solute and solute or solute and membrane surface, while hydrodynamic conditions have effects on the convective flow of solutes and the shear force paralleling to the membrane surface. Membrane properties mainly affect the interaction between membrane and solutes, and thus affect fouling behavior.

Basically, proteins and humic acid are neutrally charged at their isoelectric point (IEP) and their charges increase with the pH values deviating from the IEP (Palecek and Zydney 1994; Hong and Elimelech 1997). The salt ions can compress the electrical double layer of charged proteins and humic acid, and have effect of charge shielding on them as well. Calcium ions can complex with the carboxylic groups in protein and humic acid molecules and reduce the charge density. When the charge density of protein and humic acid decrease, the intermolecular electrostatic force is reduced, indicating that protein and humic acid are more easily aggregated together and enhancing the fouling during membrane filtration processes (Hong and Elimelech 1997; Huisman,

Pra?danos et al. 2000; Tang and Leckie 2007). Tang and co-workers investigated the humic acid fouling in the RO and NF membranes and observed that the severe flux reduction occurred at high initial flux, low pH, and high calcium concentration (Tang, Kwon et al. 2007). Similar effects of those factors on the membrane fouling were observed during ultrafiltration of humic acid (Yuan and Zydney 2000). Chan and Chen pointed out in their study of effects of chemical solution on MF membrane fouling that the BSA fouling were the product of a balance between electrostatic, solubility and hydrophobic effects which were manifested in protein-protein and protein-membrane interactions (Chan and Chen 2001).

Increasing the applied pressure can increase the collide efficiency between solutes and solute-membrane and thus increasing rate of fouling (Herrero, Pra?danos et al. 1997; Seidel and Elimelech 2002; Tang and Leckie 2007). However, Tang and Leckie pointed out that the limiting fluxes were unaffected by the applied pressure, indicating the extent of fouling is independent of initial flux at long time (Tang and Leckie 2007). Cross flow can dilute the concentrated solution near the membrane surface and further alleviate the effect of concentration polarization (Song and Elimelech 1995; Goosen, Sablani et al. 2005). In addition, an increase in the shear rate (cross-flow velocity) mitigates the extent of fouling by reducing the accumulation of foulant on the membrane and arresting the growth of the fouling layer (Seidel and Elimelech 2002).

Besides solution chemistry and device conditions are generally considered as key factors affecting membrane fouling among membrane researchers, reports on the effects of membrane surface properties are still well documented. It is traditionally believed that fouling tends to be greater for more hydrophobic membranes (Josson and Josson 1995; Bartels, Wilf et al. 2005). Meanwhile, researches revealed that protein adsorption is somewhat reduced on more hydrophilic membranes, with less than monolayer adsorption for BSA (Bowen and Gan 1991) and β -lactoglobulin (Persson, Capannelli et al. 1993) on hydrophilic polyvinylidene fluoride membranes. Additionally, membrane surface charge and zeta potential are also believed to be important to membrane fouling. In general, membrane surface are more negative charged due to deprotonation of the carboxylic groups at higher pH or adsorption of anionic

species (Deshmukh and Childress 2001). Therefore, those foulants with negative charges are not easily fouling on the negatively charged membranes due to the repulsive electrostatic interaction between foulant and membrane (Goosen, Sablani et al. 2005). In addition, membrane roughness and porosity still have significant on fouling. It is generally recognized that membranes with higher roughness and more porous structure lead to severe fouling. Elimelech et al. indicated that higher fouling rate for the thin-film composite membranes is attributed to surface roughness which is inherent in interfacially polymerized aromatic polyamide composite membranes (Elimelech, Zhu et al. 1997). Ho and Zydney pointed out that membranes with interconnected pores fouled more slowly since the fluid could flow around the blocked pores through the interconnected pore structure (Ho and Zydney 1999).

2.3.5 Limiting flux

The concept of critical flux has been well developed and documented over the last decade, which was defined by Field et al. “a flux below which a decline of flux with time does not occur; above it fouling is observed” (Field, Wu et al. 1995), and currently can be generally defined as the “first” permeate flux at which fouling become noticeable (Bacchin, Aimar et al. 2006). If the adsorption is negligible, and the non-deposition and fouling condition is reversible, the observed critical flux is defined as the strong form of critical flux, whereas, in the presence of adsorption, fouling would occur even with a nil flux, in which case, mass deposition by convection can occur in addition to adsorption, and the particular value of flux below which such deposition would cease may be viewed as the weak form of the critical flux (Bacchin, Aimar et al. 2006).

Numerous researches also demonstrated that a limiting flux existed during the membrane filtration process. Most of the early publications on limiting flux were based on the theory of mass transfer through a thin film, which indicated that the limiting flux was dependent on the solute concentration (Aimar, Taddei et al. 1988; Field and Aimar 1993; Song 1998). However, lots of experimental observation revealed that additional increase in the concentration and hydraulic applied pressure could not increase the final stable flux in the membrane filtration process (Cohen and Probstein 1986; Kelly and Zydney 1997; Seidel

and Elimelech 2002; Tang and Leckie 2007). Recently, Tang and Leckie redefined the limiting flux to be a flux beyond which the membrane flux cannot be sustained (Tang and Leckie 2007). They pointed out that the limiting flux was independent of the membrane properties, foulant concentration and applied pressure, but strongly dependent on the feedwater composition, such as types of foulants, pH, ionic strength, and divalent ions (Tang and Leckie 2007).

Chapter 3

Methodology

3.1 Chemicals and materials

3.1.1 General chemicals

Unless otherwise specified, all reagents and chemicals used in the study are analytical grade with purity over 99%. Ultrapure water, supplied from an ELGA purification system (UK) with a resistivity of 18.2 Mohm.cm, was used for preparing all reagents and working solutions. Sodium chloride, calcium chloride, sodium hydroxide, and hydrochloric acid purchased from Sigma-Aldrich (St. Louis, MO) were used to adjust the ionic composition of working solution (pH, ionic strength, and calcium concentration). Sodium chloride, magnesium chloride and sodium sulphate were purchased from VWR to be used as the draw solution in forward osmosis process.

3.1.2 Model foulant – Bovine Serum Albumin (BSA) and Purified Aldrich Humic Acid (PAHA)

Bovine serum albumin (BSA) with a purity of 98% purchased from Sigma-Aldrich was used as one of model foulants in this study. It is approximate ellipsoidal (14 x 4 x 4 nm), with a molecular weight of ~ 67 kDa (Peters 1985; Palecek and Zydney 1994). BSA has more than 200 titratable sites, and it is amphoterically charged due to the presence of both amine and carboxylic functional groups (Tanford, Swanson et al. 1955; Peters 1985; Ang and Elimelech 2007). The isoelectric (IEP) point is pH 4.7 (Palecek and Zydney 1994). Immediate upon receiving, the powder-form BSA was stored in a cold room at 4—5 °C. BSA working solution was prepared by dissolving the powder at desired pH and ionic strength. The solution was then stirred for 24 hours prior to a fouling test. The concentration of the BSA was quantified by total organic carbon (TOC) (Shimadzu, Tokyo, Japan), which was shown in chapter 4.

Sodium salt of humic acid was obtained from Sigma-Aldrich (H16752, technical grade, St. Louis, MO). Aldrich® humic acid (AHA) is a terrestrial

peat-derived humic material with larger weight-averaged molecular weight (M_w) compared to typical aquatic humic (Chin, Aiken et al. 1994; Hur and Schlautman 2003). M_w was reported ranging from 4000 to 23,000 Da (Chin, Aiken et al. 1994; Vermeer, Van Riemsdijk et al. 1998; Hur and Schlautman 2003). AHA has an estimated elemental composition of: 55% C, 38.9% O, 4.6% H, and 0.6% N (Vermeer, Van Riemsdijk et al. 1998). The total acidity is about 5 mmol/g (5 meq/g), with an estimated carboxylic acidity of 3.4 mmol/g (3.4 meq/g) (Hong and Elimelech 1997). AHA is easily obtainable and well characterized, thus it has been found to be a widely used model foulant by a variety of membrane researchers (Hong and Elimelech 1997; Yuan and Zydney 2000; Seidel and Elimelech 2002).

Prior to use, AHA was pretreated extensively to remove fulvic, metal, and ash content based on a slightly modified method from the International Humic Substances Society (Swift 1996). Hydrochloric acid was added to AHA to give a final concentration of 0.1 g dry AHA/ml solution and a final pH of 1.0. The suspension was shaken for one hour and centrifuged. The residue from centrifugation was adjusted to 0.1 g dry AHA/ml at pH~13 with NaOH. The mixture was shaken and centrifuged. The supernatant was filtered twice through a 0.2 μm polyethersulfone filter under a nitrogen headspace. The filtered solution was acidified to pH 1.0 with 6 N HCl, allowed to settle overnight, and then centrifuged. The residue was transferred to Spurr 7 dialysis tubes (molecular weight cutoff of 1000 Dalton, Fisher Scientific, Santa Clara, CA) and dialyzed in a large MilliQ water bath. The dialyzing water was changed every few hours initially and then daily. Dialysis was stopped when the conductivity of the dialyzing water became lower than 1 $\mu\text{S/cm}$. The purified Aldrich humic acid (PAHA) was freeze dried and stored in the dark at 4 °C.

The purified Aldrich® humic acid was freeze dried and stored in the dark at 4 °C. Stock solutions of 1 g/L at pH ~7.5 were prepared from freeze dried PAHA and stored at 4 °C in dark. PAHA working solutions were prepared from the stock solution and stirred about 12 h before use.

3.1.3 UF and FO membranes

The UF membrane, denoted MW, used in the current study was a commercial hydrophilic polyacrylonitrile (PAN) composite membrane, which was donated by the GE Osmonics. MW membrane was supplied and stocked as dry flat coupons in the dark. According to the manufacturer, the molecular weight cutoff of the membrane is 100 kDa, and the tolerant pH range at 25 °C is from pH 1 to 10. It has been reported that the MW membrane had been modified by the manufacturer to possess a highly hydrophilic surface with minimal surface roughness (~ 0.4 nm) (Kang, Asatekin et al. 2007). The zeta potential of MW membrane was measured using an Electro Kinetic Analyzer (EKA, Anton Paar GmbH, Graz, Austria) and reported in Chapter 4.

Forward osmosis membrane used in this study was gained from Hydrowell Filter System Filter, which is a commercial FO product purchased from Hydration Technologies, Inc. The Hydrowell Filter System Filter was first flushed with ultrapure water several times to dissolve and dilute the syrup sticking to the FO membrane. Then, FO membrane housed in the system was cut into small pieces and soaked in the ultrapure water. The soaked membrane was stored in the dark at 4 °C. Prior to use, FO membrane was taken out and cut to the desired dimensions. It is reported that the active layer of the FO membrane is made of cellulose triacetate (CTA) (Cath, Childress et al. 2006). Other properties of the FO membrane are reported in Chapter 5.

3.2 Characterization methods

3.2.1 Membrane fouling test

3.2.1.1 Test setup

UF membrane fouling experiments were conducted in a laboratory-scale cross flow test unit (Mode C10-T, Nitto Denko, Japan) (Figure 3.1). The effective membrane area housed in the acrylic cross flow test cell was approximately 60 cm². A gear pump was used to deliver the feedwater to the test cell. The pressure and cross flow rate in the cell were adjusted by a pressure regulation valve and a needle valve, respectively. Permeate flux was determined gravimetrically by weighing the mass of permeate water collected at

predetermined time intervals by a digital balance, and the flux data were recorded to a personal computer for further analysis.

Figure 3.1: Schematic diagram of the crossflow membrane test unit.

With reference to FO membrane fouling test, figure 3.2 shows the schematic diagram of the bench-scale FO system. The FO cross-flow setup was modified from previous UF cross-flow setup. The pressurized pump was replaced by the variable speed peristaltic pump. Two peristaltic pumps were connected to the feed solution side and draw solution side respectively to recirculate the feed and draw solutions and generate the cross-flows. The FO membrane was installed in the modified membrane cell (Mode C10-T, Nitto Denko, Japan) that has symmetric channels on both sides of the membrane. The effective membrane surface area was 60 cm². Mesh spacers were placed in each of the feed and draw channel to support the membrane and enhance mixing. The feed solution and draw solution were mixed by the flow of the recirculated solution. The feed solution was placed on a digital mass balance and its weight changes of predetermined time intervals were logged into a computer to record the permeate flux. Prior to each experiment, all the required solutions and membrane were placed in the airconditioned room with a temperature of 22 – 24 °C for overnight to maintain the consistent temperature for the whole system.

Figure 3.2: Schematic diagram of bench-scale forward osmosis (FO) system.

3.2.1.2 Fouling test procedures

A clean MW UF membrane coupon was used for each UF membrane fouling test. The coupon was soaked in ultrapure water for 24 hours before being loaded into the test cell. It was then precompacted with ultrapure water under the desired pressure for 1h to reach a stable permeate flux. The membrane was subsequently allowed to equilibrate for ½ hour with background electrolytes at the desired pH. Precompaction and equilibration with electrolytes were necessary to ensure that changes in flux after the addition of foulant were solely due to membrane fouling, not any structural changes caused by membrane compaction or swelling (Tang and Leckie 2007). Finally, BSA working solution with the same ionic composition and pH was added to the feed reservoir to make a 5 L feed solution, and the fouling test was continued under the same pressure used for precompaction and equilibration stages. The typical fouling test duration was 2 hours except where the effect of ionic strength and protein concentration was investigated. The feedwater temperature was maintained at 22 - 24 °C for all the tests, and permeates were recycled back to the feed tank to maintain constant feed tank concentration. Unless otherwise specified, the following reference test conditions were used: applied pressure

100 kPa (14.5 psi), cross flow velocity 27.8 cm/s, BSA concentration 20 mg/L, pH 5.8, and 10 mM NaCl as background electrolytes.

In the FO process tests, pure water experiments and PAHA fouling experiments were performed. The conductivity in the feed water was measured at the predetermined time intervals to indicate the salt flux in each experiment. For PAHA fouling experiments, membrane were precompacted and equilibrated for 0.5h under the desired ionic strength and pH to eliminate the effect of membrane swelling and compaction on the flux decline. Then, the desired PAHA with the identical ionic strength and pH was added into the feed solution to perform the membrane fouling test. The water flux was determined by the weight changes in the feed solution which was measured by a digital mass balance connected to a personal computer. The typical fouling test duration was lasted for 8 hours. Unless otherwise specified, the following reference conditions were applied in the whole study: draw solution concentration of 2 M NaCl, 10 mg/L PAHA, 10 mM NaCl, and pH 6.0 in the feed solution composition, and cross-flow velocity of 27.8 cm/s on both draw and feed side.

Baseline tests of the feed solution with the same ionic strength and pH were also conducted to indicate the flux decline due to the decrease of osmotic driving force during the fouling experiments resulting from the continuous dilution of the draw solution by the permeate water.

3.2.2 Characterization of virgin and fouled membranes

3.2.2.1 Pure water flux and foulant rejection

Membrane permeability and solute rejection was evaluated through the test setup described in Section 3.2.1.1. As described in Section 3.2.1.2, the reference conditions for the UF membrane fouling test were applied pressure 100 kPa (14.5 psi), cross flow velocity 27.8 cm/s, BSA concentration 20 mg/L, pH 5.8, and 10 mM NaCl as background electrolytes, while in the FO membrane fouling test, the reference conditions were draw solution concentration of 2 M NaCl, 10 mg/L PAHA, 10 mM NaCl, and pH 6.0 in the feed solution composition, and cross-flow velocity of 27.8 cm/s on both draw and feed side. Prior to the membrane filtration test, UF membranes were thoroughly rinsed with ultrapure water and soaked in the ultrapure water for 24

hours. Then the soaked UF membranes and FO membranes were performed pre-compaction, equilibration and fouling test in the cross flow membrane filtration test unit. The pure water flux was determined as the flux at the end of the compaction period. The foulant rejection in the UF membrane fouling test was determined by measuring the TOC in the permeate with predetermined time intervals, whereas in the FO process, the foulant rejection was determined by measuring the concentration of humic acid in the draw solution through the ultraviolet spectrophotometer (UV-1700 shimadzu).

3.2.2.2 Scanning Electron Microscopy (SEM)

Both clean and fouled membrane coupons were characterized by a scanning electron microscope (SEM, Zeiss Evo®). Fresh membrane samples were rinsed with ultrapure water and subsequently dried naturally in the air for the UF membranes or in a freeze drier (CHRIST ALPHR 1-4 LD, Germany) for the FO membranes for more than 8 hours. On the other hand, fouled membrane samples were first rinsed with ultrapure water to remove any labile BSA and then dehydrated in a freeze drier for at least 8 hours. Prior to imaging by SEM, samples were coated with a uniform layer of gold in a sputter coating chamber (Emitech SC7620). All samples were imaged at an accelerating voltage of 15kV.

3.2.2.3 Atomic Force Microscopy (AFM)

Membrane samples used for the AFM microscopy were dried in the freeze drier (CHRIST ALPHR 1-4 LD, Germany) overnight. Tapping Mode® AFM micrographs of virgin membrane coupons were obtained with a MultiMode® SPM equipped with a J type piezoelectric scanner and a NanoScope® III controller (Santa Barbara, California) on a scan size of 3 x 3 microns. The Version 5.12 of the Nanoscope control software was used for image acquisition. Single crystal etched silicon probes (Santa Barbara, California) were oscillated at 98% of its resonant frequency to yield a 2 V rms amplitude before engagement. Once engaged, the rms signal was adjusted to 0.9 – 1.4 V for optimal imaging quality. The manufacturer specified resonance frequency and spring constant for the probes were 265-309 kHz and 20-80 N/m, respectively. The actual resonance frequency determined using the auto-tune function of the

control software was very close to 300 kHz. Typical scan rate used was 0.3-1.0 Hz.

3.2.2.4 Contact Angle by Sessile Drop Method

In this study, fresh FO membrane samples were cleaned and dried with the same methods described in Section 3.2.2.2. Then contact angles of FO membranes were measured with a FTA 200 Contact Angle Analyzer (OCA, LMS Technologies PTE LTD) using the sessile drop method following procedures similar to those reported by Kwon (Kwon, Tang et al. 2006). Briefly, a droplet of 5 μ l of ultrapure water was delivered onto a dry membrane surface, and a static image of the droplet in equilibration with the membrane surface is taken with a CCD camera. Image analysis and contact angle computation were performed using the FTA software assuming a circular profile of the droplet. For any given membrane type, contact angle measurements were performed for at least 16 different locations, with a left angle and a right angle reading at each location.

3.2.2.5 Zeta potential

Zeta (ζ) potential measurement of the fresh membrane surface was performed using an Electro Kinetic Analyzer (EKA, Anton Paar GmbH, Graz, Austria). Zeta potentials for the membrane samples were calculated from the measured streaming potentials using the Helmholtz-Smoluchowski equation (Childress and Elimelech 1996).

The EKA is comprised of external pH and conductivity electrodes, an automatic pH titrator, an asymmetric flow cell with a platinum electrode on each end of flow cell, and a control system connected to a computer. In this work, zeta potentials were measured using a single piece of sample mounted to a reference poly (methyl methacrylate) (PMMA) channel plate for the asymmetric cell, which is different from conventional measuring cells where two identical flat samples are mounted face to face and separately by a channel spacer such as a piece of Teflon.

Fresh membrane samples were rinsed using ultrapure water and soaked in the ultrapure water for 24 hours prior to performing zeta potential measurement. The EKA system was cleaned by rinsing with 2 liters each of the following

solution in order without recirculation: ultrapure water, 1 mM NaOH, ultrapure water, 1 mM HCl, and ultrapure water. After mounting the membrane samples, the system was flushed with 2 liters of 10 mM NaCl at pH 3. In the whole measurement, a constant concentration of 10mM NaCl aqueous solution was used as background electrolyte solution and the pH of the solution adjusted by manual addition of the HCl and/or NaOH was ranged from 3 to 10 at room temperature (22 – 24 °C). The background electrolyte was degassed at pH 3 before analysis, and a nitrogen headspace was maintained to eliminate potential artifacts from the presence of carbon dioxide. Solution pH was increased in small steps by adding aliquots of 1N sodium hydroxide with the automatic pH titrator. The equilibration time at each pH was at least 15 minutes.

The measured zeta potential (ζ_{TOT}) is derived half from the sample zeta potential (ζ_s) and half from the zeta potential of reference channel plate (ζ_{PMMA}):

$$\zeta_{TOT} = \frac{1}{2}(\zeta_s + \zeta_{PMMA}) \quad (3.1)$$

The PMMA reference zeta potential can be determined by mounting the PMMA channel plate to the cell with out sample.

3.2.2.6 Foulant Accumulation on Membrane Surfaces

BSA accumulation on the UF membrane surfaces and PAHA accumulation on the FO membrane surfaces were extensively measured. Fouled membranes were rinsed with ultrapure water to remove the labile foulant on the membrane surfaces. Then, 5 – 10 samples (a total area of 9 – 11.3 cm²) were taken from multiple locations of a fouled membrane coupon and then transferred into a 50 ml polyethylene tube for BSA extraction and 15 ml polyethylene tube for PAHA extraction. For the BSA extraction, about 20 – 30 ml sodium dodecyl sulfate (SDS) was added into the tube. Then the tube was shaken overnight on an orbital shaker before the extractant was collected for further analysis. Similar extraction procedures were applied for PAHA extraction except that extractant was 5 – 10 ml of 0.1 N sodium hydroxide. The BSA and PAHA concentration in the extractant was measured through ultraviolet adsorption at

562 nm and 254 nm respectively. UV_{562} and UV_{254} was measured by a UV spectrophotometer (UV-1700 shimadzu).

Chapter 4

The Role of Hydrodynamic Conditions and Solution Chemistry on Protein Fouling during Ultrafiltration¹

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4.1 Introduction

Ultrafiltration (UF) has received increasing popularity in the recent decades. UF membranes have been used in surface water treatment (such as natural organic matter and pathogen removal), in membrane bioreactors (MBRs), in pretreatment processes for reverse osmosis (RO), and in many other industrial applications (Aoustin, Schafer et al. 2001; Durham, Bourbigot et al. 2001; Jarusutthirak and Amy 2001; Van der Bruggen, Vandecasteele et al. 2003). Similar to other types of pressure-driven membranes, UF membranes are prone to fouling – the accumulation of inorganic colloids, organic macromolecules, and biological entities on membrane surfaces or inside membrane pores, which directly reduces the productivity and increases the operational costs.

Protein has been identified as one of the major membrane foulants in wastewater treatment and reclamation applications (Schneider, Ferreira et al. 2005; Shon, Vigneswaran et al. 2006; Ang and Elimelech 2007; Li, Xu et al. 2007). Fouling of non-porous membranes (nanofiltration and RO membranes) is likely dominated by cake layer formation in addition to concentration polarization (Ang and Elimelech 2007; Tang, Kwon et al. 2007; Tang and Leckie 2007). In contrast, the permeability loss of porous microfiltration (MF) and UF membranes might be attributed to a combination of pore blockage and cake layer formation (Kim, Fane et al. 1992; Güell and Davis 1996; Ho and Zydney 2000). Existing studies suggest that initial stages of fouling for porous membranes are likely dominated by pore plugging, while the flux behavior is probably determined by a foulant cake layer when severe fouling occurs at longer filtration duration (Kim, Fane et al. 1992; Palecek and Zydney 1994; Güell and Davis 1996; Ho and Zydney 2000; Huisman, Pradanos et al. 2000). Numerous studies have also demonstrated that membrane fouling by organic macromolecules are affected by hydrodynamic conditions (such as membrane flux and cross-flow velocity) (Wu, Howell et al. 1999; Chan and Chen 2001; Ang and Elimelech 2007), feed water characteristics (foulant concentration, pH, and ionic compositions) (Fane, Fell et al. 1983; Palecek and Zydney 1994; Palecek and Zydney 1994; Chan and Chen 2001; Ang and Elimelech 2007; Mo, Tay et al. 2008), as well as the membrane properties (membrane hydrophobicity, roughness, and porosity) (Palecek and Zydney 1994; Li, Xu et al. 2007). In

general, severe fouling is observed at the isoelectric point (pI) of a protein where the electrostatic repulsive force between protein molecules is at the minimum (Fane, Fell et al. 1983; Palecek and Zydney 1994; Ang and Elimelech 2007; Mo, Tay et al. 2008). In addition, protein fouling is typically promoted by high membrane flux and/or low cross-flow velocity (Bacchin, Aimar et al. 1995; Wu, Howell et al. 1999; Ang and Elimelech 2007). Such phenomenon is consistent with the critical flux concept (Bacchin, Aimar et al. 1995; Wu, Howell et al. 1999) which states that little flux decline occurs when the membrane flux is below a threshold value, i.e., the critical flux. On the other hand, severe fouling can occur above the critical flux (Bacchin, Aimar et al. 1995; Wu, Howell et al. 1999).

Despite of the vast number of studies on protein fouling, the effects of ionic strength and foulant concentration have been controversial in the literature. Studies on nonporous membranes (Ang and Elimelech 2007; Mo, Tay et al. 2008) reported that protein fouling was more severe at elevated ionic strength due to electrical double layer (EDL) compression. Consistent with the above studies, several research groups (Fane, Fell et al. 1983; Heinemann, Howell et al. 1988; Palecek and Zydney 1994) also reported greater protein fouling tendency for MF and UF membranes at higher ionic strength. Similar effect of EDL compression has been suggested for natural organic matter, alginate, and inorganic colloids (Zhu and Elimelech 1997; Lee and Elimelech 2006; Tang and Leckie 2007). In contrast, Chan and Chen (Chan and Chen 2001) observed lower fouling rate for MF membranes at greater background salt concentrations, which was attributed to the greater protein solubility at increase salt content. Similar observation also has been documented for UF membranes (Salgin 2007). The literature on the effect of foulant concentration is equally confusing. While many researchers have suggested that more severe fouling occurred at higher protein concentrations (Kilduff, Mattaraj et al. 2004; Bacchin, Aimar et al. 2006; Lee, Ang et al. 2006), some recent studies revealed that the quasi-steady flux at long filtration time was independent of the foulant concentrations (Cohen and Probstein 1986; Kelly and Zydney 1995; Tang and Leckie 2007). Despite of the increased fouling rate (the rate approaching to the stable flux) at greater foulant concentrations, Tang and Leckie (Tang and Leckie 2007) demonstrated

that the long-term stable flux was determined by interaction forces between foulant-membrane and foulant-deposited-foulant which were largely independent of foulant concentration.

The study aims to systematically investigate the influence of hydrodynamic conditions and solution environment on protein fouling for an UF membrane. The effect of membrane flux, cross flow velocity, protein concentration, pH, and ionic strength were thoroughly investigated through constant pressure fouling tests. The results from the current study may help us better understand the coupled effects of solution chemistry and hydrodynamic conditions.

4.2 Materials and methods

4.2.1 Chemicals and materials

Ultrapure water, supplied from an ELGA purification system (UK) with a resistivity of 18.2 Mohm.cm, was used for preparing all reagents and working solutions. The ionic composition and solution pH were adjusted by drop-wise addition of analytical grade sodium chloride, calcium chloride, sodium hydroxide, and hydrochloric acid (Sigma-Aldrich, St. Louis, MO).

Bovine serum albumin (BSA, 98% purity, A7906, Sigma-Aldrich) was used as a model protein foulant. It is approximate ellipsoidal (14 x 4 x 4 nm), with a molecular weight of ~ 67 kDa (Peters 1985; Palecek and Zydney 1994). BSA has more than 200 titratable sites, and it is amphoterically charged due to the presence of both amine and carboxylic functional groups (Tanford, Swanson et al. 1955; Peters 1985; Ang and Elimelech 2007). The isoelectric (IEP) point is pH 4.7 (Palecek and Zydney 1994). Immediate upon receiving, the powder-form BSA was stored in a cold room at 4 – 5 °C. BSA working solution was prepared by dissolving the powder at desired pH and ionic strength. The solution was then stirred for 24 hours prior to a fouling test.

A commercial hydrophilic polyacrylonitrile (PAN) composite UF membrane (MW, GE Osmonics, Minnetonka, MN) was used for all fouling experiments. MW membrane was supplied and stocked as dry flat coupons in the dark. According to the manufacturer, the molecular weight cutoff of the membrane is 100 kDa. It has been reported that the MW membrane had been modified by

the manufacturer to possess a highly hydrophilic surface with minimal surface roughness (~ 0.4 nm) (Kang, Asatekin et al. 2007). The zeta potential of MW membrane was measured using an Electro Kinetic Analyzer (EKA, Anton Paar GmbH, Graz, Austria) with a procedure similar to Tang and coworkers (Tang, Fu et al. 2006; Tang, Kwon et al. 2007). The MW membrane was negatively charged over a wide range of pH values (pH 3 – 10), and the measured zeta potential was ~ -20 mV at circumneutral pHs in a background electrolyte of 10 mM NaCl (Figure 4.1).

Figure 4.1: Zeta potential of the MW membrane as a function of pH. A background electrolyte of 10 mM NaCl was used during measurement.

4.2.2 Membrane fouling experiments

A laboratory-scale cross flow test unit (Mode C10-T, Nitto Denko, Japan) was used for the fouling experiments (Figure 4.2). The effective membrane area housed in the acrylic cross flow test cell was approximately 60 cm^2 . A gear pump was used to deliver the feedwater to the test cell. The pressure and cross flow rate in the cell were adjusted by a pressure regulation valve and a needle valve, respectively. Permeate flux was determined gravimetrically by weighing the mass of permeate water collected at predetermined time intervals by a digital balance, and the flux data were recorded to a personal computer for further analysis.

A clean membrane coupon was used for each fouling test. The coupon was soaked in ultrapure water for 24 hours before being loaded into the test cell. It was then precompacted with ultrapure water under the desired pressure for 1h to reach a stable permeate flux. The membrane was subsequently allowed to equilibrate for ½ hour with background electrolytes at the desired pH. Precompaction and equilibration with electrolytes were necessary to ensure that changes in flux after the addition of foulant were solely due to membrane fouling, not any structural changes caused by membrane compaction or swelling (Tang and Leckie 2007). Finally, BSA working solution with the same ionic composition and pH was added to the feed reservoir to make a 5 L feed solution, and the fouling test was continued under the same pressure used for precompaction and equilibration stages. The typical fouling test duration was 2 hours except where the effect of ionic strength and protein concentration was investigated. The feedwater temperature was maintained at 22 – 24 °C for all the tests, and permeates were recycled back to the feed tank to maintain constant feed tank concentration. Unless otherwise specified, the following reference test conditions were used: applied pressure 100 kPa (14.5 psi), cross flow velocity 27.8 cm/s, BSA concentration 20 mg/L, pH 5.8, and 10 mM NaCl as background electrolytes.

Figure 4.2: Schematic diagram of the crossflow membrane test unit.

A small amount of feedwater and permeate water was also sampled at predetermined time interval to evaluate BSA rejection by the membrane. The BSA concentrations were determined by a total organic carbon (TOC) Analyzer (Shimadzu, Tokyo, Japan) calibrated over 0 - 100 mg BSA/L ($R^2 > 0.99$), and were further checked by BCA protein assay measurements (QPBCA, Sigma-Aldrich).

4.2.3 Scanning electron microscopy (SEM)

Both clean and fouled membrane coupons were characterized by a scanning electron microscope (SEM, Zeiss Evo®). Fresh membrane samples were rinsed with ultrapure water and subsequently naturally dried in the air. On the other hand, fouled membrane samples were first rinsed with ultrapure water to remove any labile BSA and then dehydrated in a freeze drier for at least 8 hours. Prior to imaging by SEM, samples were coated with a uniform layer of gold in a sputter coating chamber (Emitech SC7620). All samples were imaged at an accelerating voltage of 15kV.

4.3 Results and Discussion

4.3.1 Effect of hydrodynamic conditions

The effect of applied pressure and crossflow velocity on the BSA fouling is systematically investigated in this section. Figure 4.3(a) shows the flux performance of the MW membrane at various applied pressures ranging from 20 – 500 kPa. The feed composition was fixed at pH 5.8, 10 mM NaCl, and 20 mg/L BSA. In a typical run, membrane experienced rapid initial flux decline in the first 15 minutes of the test. Subsequent flux decline was much milder, and stable flux was achieved within two hours. Increasing applied pressure significantly increased BSA fouling. While greater initial flux was observed at increased pressure, the corresponding flux reduction was much more drastic. The flux reductions were 70.4%, 81.6%, and 92.2% at 100kPa, 200kPa, and 500kPa, respectively, compared to only 28.5% reduction at 20 kPa. This observation was consistent with many existing studies (Palecek and Zydney 1994; Hong and Elimelech 1997; Wu, Howell et al. 1999; Chan and Chen 2001; Bacchin, Aimar et al. 2006; Tang, Fu et al. 2006; Tang and Leckie 2007) that greater applied pressure (thus greater initial flux) has the tendency to promote

fouling. Drastic fouling may occur at elevated flux due to its greater throughput for the same fouling duration – the amount of foulant material brought towards the membrane surface is proportional to the throughput (Hong and Elimelech 1997). More importantly, greater permeate flux may result in severe concentration polarization (Goosen, Sablani et al. 2004) and increased drag force acting on the foulant molecules towards the membrane surface (Palecek and Zydney 1994; Tang and Leckie 2007), both of which can lead to severe flux reduction.

A useful normalization is to compare the flux reduction at the same throughput as discussed by Elimelech and coworkers (Hong and Elimelech 1997). A similar approach was adopted in the current study by normalizing the flux reduction against the foulant mass (M_f) convected towards the membrane surface per unit membrane area (Figure 4.3(b)). The total foulant convected is proportional to the membrane throughput (V_p / A_m) for a fixed foulant concentration C_f :

$$M_f = V_p C_f / A_m \quad (1)$$

where V_p and A_m denote the total permeate volume and the membrane area, respectively. Since the membrane throughput can be determined integrating permeate flux J over time τ ,

$$M_f = \int_0^t C_f J d\tau \quad (2)$$

The feedwater concentration term was included in the normalization such that the effect of foulant concentration (Section 4.2) and that of throughput can be treated in a unified way.

Figure 4.3: Effect of applied pressure and initial flux on BSA fouling. Other experimental conditions: 20 mg/L BSA, pH 5.8, 10 mM NaCl, cross-flow velocity of 27.8 cm/s, and feed solution temperature at 25 °C.

Figure 4.3(b) presents the flux reduction as a function of total convected foulant. As expected, flux was reduced initially with increasing throughput. As the membrane flux was reduced at longer filtration time, however, further flux reduction was much milder. Considering the test at 200 kPa, little flux reduction occurred when the flux reached 100 L/m²hr. This might suggest little additional foulant attachment onto the membrane despite of the significant further increase in convected foulant mass towards the membrane surface (from 2000 to 5000 mg/m²). In addition, throughput alone would not explain the greater flux reduction at higher applied pressure. For example, the percentage flux reduction was much greater at 500 kPa than that at 100 kPa for the same convected foulant mass of 3000 mg/m² (a throughput of 150 L/m²). Rather, the significant role of flux on fouling was apparent in Figure 4.3(b) – drastic flux decline was observed only when permeate flux was greater than 100 L/m²hr. Tang and coworkers (Tang, Kwon et al. 2007; Tang and Leckie 2007) suggested that the rate of foulant accumulation onto a membrane depends not only on the rate that foulant is convected towards the membrane dM_f / dt , but also on the attachment coefficient α :

$$\frac{dm_f}{dt} = \alpha \frac{dM_f}{dt} \quad (3)$$

$$\text{i.e., } \alpha = \frac{dm_f}{dM_f} \quad (4)$$

In a way, the term dM_f / dt in Equation (3) can be viewed as the frequency that foulant molecules collide with the membrane while the attachment coefficient α represents the probability that a foulant molecule will attach onto a membrane resulting from a given collision event. The attachment coefficient decreases drastically at lower flux as a result of reduced hydrodynamic drag force (Tang and Leckie 2007). Equation (3) is useful to explain the observation that additional increase in throughput did not have further effect on flux reduction after the membrane flux was reduced to $\sim 100 \text{ L/m}^2\text{hr}$ (applied pressure 50 – 500 kPa, Figure 4.3(b)). The attachment coefficient had probably diminished to nearly zero such that the rate of foulant attachment was negligible even though M_f was still increasing. The same equation also explains why flux reduction was greater at higher applied pressure for any fixed throughput: the attachment coefficient was likely much higher at greater flux.

Figure 4.4: Effect of BSA adsorption on flux decline. A background electrolyte of 10mM NaCl at pH 5.8 was used.

Figure 4.3(c) shows a plot of stable flux against initial flux. It is interesting to note that the membrane samples tested at high initial fluxes (corresponding to applied pressure of 200, 350, and 500 kPa) all reached an identical stable flux $\sim 100 \text{ L/m}^2\text{hr}$. Further increase in applied pressure beyond 200 kPa did not translate into additional gain in stable flux although the initial was much higher at 500 kPa. There was an apparent limiting flux beyond which stable flux was not achievable. For membrane coupons with initial flux less than the limiting value, the flux reduction was much milder (15-30% of flux decline). Additional adsorption tests performed at zero applied pressure showed that a 15% of membrane resistance increase was due to BSA adsorption on to the membrane alone (Figure 4.4), which suggests that the strong form of critical flux did not exist in this particular case (Bacchin, Aimar et al. 2006). Similar limiting flux behavior has been reported by Tang and Leckie (Tang and Leckie 2007) for RO and NF membranes, which was explained by the interplay of positive hydrodynamic drag acting on a fouling molecule to promote deposition and the negative barrier force to resist fouling. They further suggested that fouling continues as long as the net driving force (drag force – barrier force resulting from foulant-membrane/foulant-deposited-foulant interactions) is greater than zero (Palecek and Zydney 1994; Tang and Leckie 2007). That is, $\alpha > 0$ as long as drag force $>$ barrier force. According to this model, elevated flux is not sustainable due to the excessive drag force, and the flux will be reduced to the limiting value at which the hydrodynamic drag force just balances with the barrier force (Tang and Leckie 2007). Tang and Leckie (Tang and Leckie 2007), however, observed a well defined limiting flux behavior for a large selection of non-porous membranes, i.e, almost no flux decline when initial flux $<$ limiting flux and flux approached the limiting value for initial flux $>$ limiting flux. In contrast, a wide transitional region corresponding to an initial flux range of $100 - 300 \text{ L/m}^2\text{hr}$ was observed in the current study (Figure 4.3(c)). Within this transitional region, the final stable flux was lower than the limiting value though the initial flux was much greater than the limiting flux. Such non-ideality was likely caused by the inherent non-homogeneity associated with porous UF and MF membranes (Bacchin 2004; Tang and Leckie 2007) – the local microscale flux over a pore can be significantly higher than the apparent macro scale average flux. Thus, it might be hypothesized that the local flux can

significantly exceed the limiting flux even if the apparent average flux had already reached the limiting value, which led to further flux reduction. Alternatively, the transitional region in the current study might be interpreted as a region where both pore plugging and cake layer formation took place (Figure 4.3(c)) (Kim, Fane et al. 1992; Palecek and Zydney 1994; Güell and Davis 1996; Ho and Zydney 2000; Huisman, Pradanos et al. 2000). At even higher initial flux beyond the transitional region, the stable flux was probably dominated by cake layer formation, as evident from the SEM micrographs (Figure 4.5).

(a)

(b)

Figure 4.5: SEM images of clean and fouled MW membranes. a) A clean membrane; b) membrane fouled at 200 kPa in 10 mM NaCl at pH 5.8.

Flux performance at three different cross-flow velocities (13.9, 27.8, and 41.7 cm/s) is shown in Figure 4.6. Identical initial flux and feedwater composition were used to make sure that any difference in fouling behavior was caused by cross flow velocity alone. Clearly, flux decline was significantly reduced at increasing cross-flow velocity. The membrane at the highest (41.7 cm/s) also achieved the highest flux ($137.4 \text{ L/m}^2\text{hr}$) at the end of the fouling tests, which was significantly greater than $51.0 \text{ L/m}^2\text{hr}$ at 13.9 cm/s and $74.7 \text{ L/m}^2\text{hr}$ at 27.8 cm/s. Similar effect of cross flow velocity on fouling has been reported by several groups (Seidel and Elimelech 2002; Tang, Kwon et al. 2007). Such beneficial effect of cross flow was likely due to the enhanced back transport and the reduced concentration polarization at greater cross flow velocity (Goosen, Sablani et al. 2004). Alternatively, the greater shear force along a membrane surface might also help to sweep foulant away from the membrane (Goosen, Sablani et al. 2004).

Figure 4.6: Effect of cross-flow velocity on BSA fouling. Other experimental conditions: applied pressure of 1 bar, 20 mg/L BSA, pH 5.8, 10 mM NaCl, and feed solution temperature at 25 °C.

4.3.2 Effect of solution composition on fouling

The role of solution composition (foulant concentration, pH, and ionic strength) on BSA fouling is presented in this section. Figure 4.7(a) shows the effect of foulant concentration (4 – 100 mg/L BSA). Clearly, more rapid flux decline was observed at higher foulant concentration during the initial stage of fouling. This was likely due to the greater amount of foulant mass convectively transported towards the membrane surface, i.e., the greater collision frequency between foulant molecules and the membrane surface, for any given duration of fouling (Tang and Leckie 2007). However, this phenomenon appeared to be transient. At longer filtration time, the stable flux was nearly identical regardless of the feed BSA concentration. In other words, foulant concentration had no effect on the stable flux, although the rate approaching to the stable flux increased with increasing foulant concentration. Our results agreed well with existing fouling studies on humic acid (Tang and Leckie 2007), BSA (Kelly and

Zydney 1995), and colloidal iron oxide (Cohen and Probstein 1986). Tang and Leckie (Tang and Leckie 2007) noted that the stable flux during humic acid filtration was only dependent on foulant-membrane/foulant-foulant interactions, which was unlikely affected by the foulant concentration for dilute solutions. That is, the collision coefficient α in Equation (3) was probably independent of the feed concentration. On the other hand, the rate at which foulant molecules were convected towards the membrane surface (the collision frequency) had a strong dependence on foulant concentration according to Equation (2). Consequently, stable flux was achieved at a faster rate for higher foulant concentration.

(a)

(b)

Figure 4.7. Effect of BSA concentration on BSA fouling. Other experimental conditions: applied pressure of 100 kPa, pH 5.8, 10 mM NaCl, and cross-flow velocity of 16.7 cm/s.

Figure 4.7(b) presents the flux performance normalized against the total convected foulant mass $V_p C_f / A_m$. Interestingly, the three flux decline curves appeared nearly identical. The same flux reduction was achieved for all three cases at any given amount of convected foulant mass, regardless of the foulant concentration in the feedwater. Similarly, the flux performance can also be normalized against Ct as shown in Fig 3.7(c). It is apparent that the rate of fouling increased by n fold when the concentration was increased by n times. The same analysis seems to fit well with other literature data (Kelly and Zydney 1995; Tang and Leckie 2007). This can be readily expected from Equation (3) by noting that α is independent of foulant concentration. By substituting Equation (2) into Equation (3), it is also clear that the rate of foulant attachment is directly proportional to the foulant concentration:

$$\frac{dm_f}{dt} = \alpha J C_f \quad (5)$$

Equation (5) is useful for understanding the different factors affecting membrane fouling. The rate of fouling depends on both the rate of throughput (J) and foulant concentration (C_f). Indeed, the term $J C_f$ represents the rate at which foulant is transported convectively towards the membrane surface (the collision frequency). In addition, the rate of fouling is also dependent on the attachment coefficient α which is a function of both flux and solution chemistry (Tang and Leckie 2007). Stable flux can be reached when α becomes zero at sufficiently low membrane flux.

Figure 4.8 presents the flux profiles under various feed solution pH. Apparently, the rate and extent of flux decline was greatest at isoelectric point of BSA (pH 4.7), and less fouling occurred as pH was away from pH 4.7. For $\text{pH} > 4.7$, both the rate and extent of fouling reduced at greater pH. Reasonably stable flux performance was also achieved at pH 3. The pH dependence of fouling might be well explained by the electrostatic interactions between foulant and already-deposited-foulant (Palecek and Zydney 1994; Hong and Elimelech 1997; Tang and Leckie 2007). The intermolecular electrostatic repulsion between BSA molecules becomes nearly zero at the IEP of BSA, which was likely responsible for the severe fouling at pH 4.7 (Palecek and Zydney 1994; Ang and Elimelech 2007; Mo, Tay et al. 2008). The net charge of BSA molecules increases at pHs away from the isoelectric point (Tanford, Swanson et al. 1955; Vilker, Colton et al. 1981). Consequently, the enhanced electrostatic repulsion resulted in the better flux performance under these pH values (pH 3, 7, and 9).

Figure 4.8: Effect of pH on the BSA fouling. Other experimental conditions: applied pressure of 1 bar, 20 mg/L BSA, 10 mM NaCl, cross-flow velocity of 16.7 cm/s, and feed solution temperature at 25 °C.

The effect of ionic strength was systematically studied with three different ionic concentrations (1, 10, and 100 mM NaCl) at various solution pHs (pH 3.0, 4.7, 5.8, and 7.0). Figure 4.9(a) shows that BSA fouling becomes more severe as the ionic strength of the feed solution increased at a fixed pH of 3.0. Rapid and severe fouling occurred in the presence of the 100 mM NaCl background electrolyte. Fouling was much milder at lower NaCl concentrations. At pH 3.0, the positively charged BSA molecules experienced intermolecular electrostatic repulsive force which can be significantly shielded at greater ionic strength, causing the rapid loss of membrane permeability. Similar effect of ionic strength has been well documented for proteins (Palecek and Zydney 1994; Ang and Elimelech 2007), natural organic matter (Hong and Elimelech 1997; Tang and Leckie 2007), and inorganic colloids (Zhu and Elimelech 1997), citing electric double layer (EDL) compression as the main cause for the severe fouling at high salt concentrations.

Figure 4.9: Effect of ionic strength (IS) on BSA fouling. Results are presented at various solution pHs: a) pH 3.0; b) pH 4.7; c) pH 5.8; and d) pH 7.0. Other experimental conditions: 20 mg/L BSA, applied pressure of 100 kPa, and cross-flow velocity of 27.8 cm/s.

Ionic strength did not seem to play an important role at pH 4.7. In Figure 4.9(b), the stable fluxes at all ionic strength were relatively low (~ 30 - 50 L/m²·hr) likely due to the lack of electrostatic repulsive force at pH_{IEP} . The insensitivity of the stable flux on the ionic strength is also consistent with the lack of electrostatic

repulsive force. As BSA molecules is neutral charged at pH 4.7, the EDL compression had nearly no effect on the interaction force between protein molecules. A closer look at Figure 4.9(b) also revealed that the stable flux increased slightly with increasing background salt concentration, which might be attributed to the greater BSA solubility at higher ionic strength (Chan and Chen 2001).

Interesting trend on the effect of ionic strength was observed at pH 5.8 (Figure 4.9(c)) and pH 7.0 (Figure 4.9(d)). At pH 5.8, the rate of fouling was significantly increased at lower ionic strength. The flux reduction at 1 mM NaCl was most severe. Drastic flux reduction of $\sim 80\%$ occurred within only 5 minutes. The flux was subsequently stabilized at $\sim 30 \text{ L/m}^2\text{hr}$. In contrast, membrane flux declined much more slowly at 100 mM NaCl. The flux was reduced to $\sim 180 \text{ L/m}^2\text{hr}$ for a fouling duration of 2 hours, which was significantly greater than the fluxes for 1 mM and 10 mM NaCl feed solutions. The results obtained at pH 5.8 seem to contradict with those obtained at pH 3.0. In addition, the trend shown in Figure 4.9(c) was also opposite to that observed by a number of researcher (Fane, Fell et al. 1983; Heinemann, Howell et al. 1988; Palecek and Zydney 1994; Ang and Elimelech 2007; Mo, Tay et al. 2008) who reported that BSA fouling was more severe at greater ionic strength due to EDL compression. On the other hand, our results at pH 5.8 were consistent with those reported by Chan (Chan and Chen 2001) and Salgin (Salgin 2007) who attributed the greater flux at higher ionic strength to greater BSA solubility in a more concentrated salt environment. Our observation at pH 5.8 suggests that factors other than the electrostatic repulsion were also important in determining the rate of fouling, which will be discussed in details in the later paragraphs.

It is also interesting to note that stable flux was attained within 30 minutes of fouling test for both 1 and 10 mM NaCl at pH 5.8 (Figure 4.9(c)). When the background electrolyte concentration was increased to 100 mM, however, the rate of flux reduction was still significant at a fouling duration of 2 hours. Fouling tests with longer durations demonstrated that membrane flux continues to decrease even beyond 10 hours (Figure 4.10). Similar behavior was also observed for 1-100 mM NaCl at pH 7.0 (Figure 4.9(d)). At pH 7.0, ionic

strength had little effect on flux behavior. The flux profile at pH 5.8 and 100 mM NaCl appeared very similar to those at pH 7.0 - the rate of flux reduction was almost constant within the first two hours (30-35 L/m²hr for every hour of fouling experiment). Corresponding to this peculiar fouling behavior, the BSA retention behavior was qualitatively similar under these conditions (Figure 4.11). The BSA retention was relatively low (0 - 20% rejection within the first two hours) for 100 mM NaCl at pH 5.8 and 10 mM NaCl at pH 7.0. Rejection slowly improved over a 10-hour period, which probably indicates the slow formation of a dynamic membrane or a foulant cake layer for additional sieving of BSA molecules. In contrast, a > 80% BSA retention was attained within 30 minutes for 10 mM NaCl at pH 5.8. This might suggest that a foulant cake layer was formed within ½ hour, consistent with the flux behavior shown in Figure 4.9(c). The lower retention at higher ionic strength (100 mM NaCl) or higher pH (pH 7.0) was consistent with the smaller molecular size of BSA under these conditions (Nossal, Glinka et al. 2004; Li, Lee et al. 2008). The ultrafiltration membrane used in the current study had a molecular weight cutoff of ~100 kDa, slightly greater than the molecular weight of BSA (67 kDa). Thus, any conformational change resulting in a small molecular size may significant reduce the membrane retention.

Figure 4.10: Effect of ionic strength on BSA fouling at 100 kPa.

Figure 4.11: Retention of BSA by the UF membrane as a function of filtration time. Other experimental conditions: 20 mg/L BSA, applied pressure of 100 kPa, cross-flow velocity of 27.8 cm/s.

The lower BSA retention was probably responsible for the slower rate of fouling at pH 5.8 with 100 mM NaCl, as compared to those at 1 and 10 mM at the same pH (Figure 4.9(c)). As shown in Equation (5), the rate of foulant attachment is proportional to the attachment coefficient α , where α can be a complex function of flux (drag force), foulant-membrane and foulant-foulant interactions (barrier force), and foulant retention. A lower retention suggests a lot of foulant molecules can escape through the membrane, which can be viewed as a loss term for foulant attachment. Consequently, a lower α value, i.e., slower fouling rate, might be expected.

While increasing ionic strength appeared to reduce membrane fouling at pH 5.8 during the 2-hr fouling test (Figure 4.9(c)), it is important to bear in mind that such behavior was only transient and the flux at 100 mM was not yet stable. Fouling tests performed for longer duration (Figure 4.10) showed that the flux at 10 mM NaCl remained reasonably stable while that for 100 mM continued to decrease. Eventually, the fluxes crossed each other at ~ 10 hours, and the flux at 100 mM was lower than that at 10 mM beyond 10 hours. Thus, the trend for

ionic strength at longer fouling duration was directly opposite to the one observed for short fouling duration. The lower flux at 100 mM NaCl at beyond 10 hours was consistent with the EDL compression effect due to the high salt concentration. Many existing studies (Palecek and Zydney 1994; Hong and Elimelech 1997; Ang and Elimelech 2007; Tang and Leckie 2007; Mo, Tay et al. 2008) reported that fouling was more severe at greater ionic strength for charged foulants due to the reduction in foulant-foulant repulsive interaction. Tang (Tang and Leckie 2007) and Palecek (Palecek and Zydney 1994) further demonstrated that membrane stable flux is directly proportional to the electrostatic repulsive force between foulant molecules. However, strictly speaking, these models are only applicable to cases where relatively high foulant retention and complete cake layer formation have been achieved. These two conditions can be easily satisfied for non-porous RO and NF membranes, which might partially explain the more consistent trend observed for these membranes during macromolecular fouling. In the current study, however, the BSA retention at pH 5.8 and 100 mM NaCl was low ($< 20\%$) at short fouling duration (Figure 4.11). Thus, the slow fouling rate was likely a direct result of such low retention during the transient stage. The retention improved significantly to $\sim 90\%$ at > 10 hours, probably due to additional sieving by the eventual formation of a cake layer. Correspondingly, long term flux behavior was dominated by foulant-foulant electrostatic interaction. Our results seem to suggest that the long term flux behavior is likely dominated by foulant-foulant interaction, while transient behavior can be affected by many other factors such as the size of foulant relative to the membrane pore size.

The flux behavior for 1 – 100 mM NaCl at pH 5.8 with a constant pressure of 500 kPa was shown in Figure 4.12. The trend was qualitatively similar to that observed at lower applied pressure (100 kPa, Figure 4.9(c)): 1) during transient stage, increasing ionic strength decreased the rate of flux decline; 2) at long fouling duration, the trend was reversed, which was consistent with the EDL compression at greater ionic strength. Interestingly, the flux crossover occurred ~ 4 hours at 500 kPa, much earlier than 10 hours at 100 kPa. This is consistent with the observation that cake layer formation can be more easily promoted at greater applied pressures (Tang, Kwon et al. 2007).

Figure 4.12: Effect of ionic strength on BSA fouling at 500 kPa.

4.4 Conclusions

The effect of hydrodynamic conditions and solution chemistry on protein fouling during ultrafiltration was systematically investigated. Severe fouling occurred at high initial flux (above 100 L/m²hr) and/or low cross-flow velocity (below 41.7 cm/s). A limiting flux was observed at high applied pressure (above 200kPa), beyond which increase in pressure did not enhance the stable flux. The rate and extent of BSA fouling were strongly dependent on the feedwater composition, such as BSA concentration, pH, and ionic strength. Short-term BSA fouling was promoted at higher BSA concentration, while long-term BSA fouling was independent on the BSA concentration. BSA fouling was alleviated at the pH away from the isoelectric point. Increasing ionic strength at pH 3.0 promoted severe fouling likely due to electric double layer (EDL) compression. On the other hand, the flux behavior was insensitive to salt concentration at pH 4.7 due to the lack of electrostatic interaction. At a solution pH of 5.8, effect of ionic strength on long-term flux behavior was directly opposite to that on the transient behavior. While the long-term flux

behavior seemed to be governed by foulant-deposited-foulant electrostatic interaction, the transient behavior was also affected by the rate at which foulant was transported towards the membrane surface together with the retention of the foulant.

Chapter 5

Forward Osmosis Membrane Characterization and The Role of Hydrodynamic Conditions and Solution Composition on Forward Osmosis Membrane Fouling by Humic Acid

5.1 Introduction

Pressure-driven membrane processes, as the main streams among all the existed membrane technologies, have gained great development from laboratory research to the industrial application in past decades. However, hydraulic pressure is extensively required during the process of operation, which unavoidably increases the energy consumption. Unlike pressure-driven membrane processes, forward osmosis (FO) is an osmotically driven membrane process without using additional hydraulic pressure as driving force. In the FO process, water naturally transports from a dilute feed solution through a semi-permeable membrane to a concentrated draw solution based on the drive of osmotic pressure difference between these two solutions (Cath, Childress et al. 2006). With the potential advantages of low energy requirement and high recovery, FO process would be a potential alternative technology to pressure-driven membrane process and has attracted much attention from various researches recently.

It is reported that FO process has been applied in various fields (Cath, Childress et al. 2006), such as pharmaceutical industry, food processing, and water and wastewater treatment. In the recent publications, Cath et al. (Cath, Adams et al. 2005; Cath, Gormly et al. 2005) combined FO process with other membrane process to treat the metabolic wastewater for the airspace system, McCutcheon and Elimelech (McCutcheon, McGinnis et al. 2006) used the ammonian-carbon dioxide as the draw solution in the FO process to desalinate seawater, Cartinella et al. (Cartinella, Cath et al. 2006) tried the FO process to remove natural steroid hormones from wastewater, Holloway et al. (Holloway, Childress et al. 2007) used the FO for concentration of anaerobic digester centrate, and Tang and Ng (Tang and Ng 2008) concentrated the brine through FO process, all of which have substantially demonstrated the potential advantages of the FO process in the practical application even though the optimization of FO process is still required. In addition, pressure-retarded osmosis (PRO), still under the fundamentals of FO process but with the membrane active layer facing the concentrated draw stream, have been largely proposed for power generation

(Loeb 1974; Lee, Baker et al. 1981; Aaberg 2003; McGinnis, McCutcheon et al. 2007).

The widespread applications of FO also in turn promote the basic research to further understand the principle of FO process and improve the FO performance. Concentration polarization (CP), occurring on both sides of the asymmetric FO membrane, plays a prominent role in reducing the water flux and recovery. The effect of coupled external and internal concentration polarization (ECP and ICP) on the water transport in the FO process has been extensively investigated by groups of researchers (Gray, McCutcheon et al. 2006; McCutcheon and Elimelech 2007; Tan and Ng 2008). Additionally, as appropriate draw solution and FO membrane are the necessary elements in the FO process, many efforts have been spent to study the effect of draw solution, membrane structure/material, and membrane orientation on the performance of FO process (Cath, Childress et al. 2006; McCutcheon, McGinnis et al. 2006; Ng, Tang et al. 2006; Wang, Chung et al. 2007; Cornelissen, Harmsen et al. 2008; McCutcheon and Elimelech 2008).

Membrane fouling always unavoidably limits the efficiency of membrane technology in the application, the mechanism of which has been extensively investigated in the pressure-driven membrane process, however, only a few publications reported the membrane fouling in the FO process. Cornelissen et al. (Cornelissen, Harmsen et al. 2008) investigated the active sludge on the FO membrane fouling in the osmotic membrane bioreactor, nevertheless, neither reversible nor irreversible membrane fouling was found. They ascribed this to their operation of low flux conditions, probably below the critical flux for membrane fouling. Mi and Elimelech (Mi and Elimelech 2008) systematically investigated the FO membrane fouling by protein, humic acid and alginate. They revealed that the FO fouling is governed by the coupled influence of chemical and hydrodynamic interactions. However, their studies on membrane fouling were based on the membrane active layer facing the feed solution. The fouling behavior on the other side of membrane surface was less investigated, which also proposed an interesting topic for the research.

This study aims to systematically investigate the hydrodynamic conditions (initial flux and cross-flow velocity) and solution composition (foulant concentration, pH, ionic strength, and divalent ions) on the humic acid fouling in the FO process with the FO membrane support layer facing the feed solution. FO membrane was characterized by the scanning electron microscopy (SEM), atomic force microscopy (AFM), the hydraulic resistance and salt rejection. Both water and salt fluxes prior to adding foulant were employed to evaluate the FO membrane performance. Effect of salt transportation on flux decline is also investigated in this work.

5.2 Materials and methods

5.2.1. Chemicals and materials

5.2.1.1. Chemicals

Sodium chloride (VWR, BDH PROLABO) was used in this study to prepare for the corresponding draw solutions. Ultrapure water with resistivity of 18.2 Mohm.cm was supplied by an ELGA water purification system (UK) to prepare for all reagents and working solutions. Analytical of grade sodium hydroxide and hydrochloric acid (Sigma-Aldrich, St. Louis, MO) were added by drop to adjust the solution pH. The ionic strength of the feed solution was adjusted by dissolving desired solid sodium chloride. The salt concentration in the solution is determined by the conductivity using a calibration curve for each type of (single) salt solution.

5.2.1.2. Purified Aldrich® humic acid (PAHA)

Aldrich® humic acid (AHA) (H16752, technical grade, St. Louis, MO) was used as a model foulant in this study. It is a terrestrial peat-derived humic material with larger weight-averaged molecular weight (M_w) compared to typical aquatic humic (Chin, Aiken et al. 1994; Hur and Schlautman 2003). M_w was reported ranging from 4000 to 23,000 Da (Chin, Aiken et al. 1994; Vermeer, Van Riemsdijk et al. 1998; Hur and Schlautman 2003). The total

acidity is about 5 mmol/g (5 meq/g), with an estimated carboxylic acidity of 3.4 mmol/g (3.4 meq/g) (Hong and Elimelech 1997).

Prior to use, AHA was pretreated extensively to remove fulvic, metal, and ash content based on a slightly modified method from the International Humic Substances Society (Swift 1996). The detailed procedures of pretreatment of AHA were described in Tang and Leckie's work (Tang, Kwon et al. 2007). The purified Aldrich® humic acid was freeze dried and stored in the dark at 4 °C. Stock solutions of 1 g/L at pH ~7.5 were prepared from freeze dried PAHA and stored at 4 °C in dark. PAHA working solutions were prepared from the stock solution and stirred about 12 h before use.

5.2.1.3. Forward osmosis membrane

Forward osmosis membrane used in this study was gained from Hydrowell Filter System Filter, which is a commercial FO product purchased from Hydration Technologies, Inc. The Hydrowell Filter System Filter was first flushed with ultrapure water several times to dissolve and dilute the syrup sticking to the FO membrane. Then, FO membrane housed in the system was cut into small pieces and soaked in the ultrapure water. The soaked membrane was stored in the dark at 4 °C. Prior to use, FO membrane was taken out and cut to the desired dimensions. It is reported that the active layer of the FO membrane is made of cellulose triacetate (CTA) (Cath, Childress et al. 2006). Contact angles of the active layer and support layer were measured to be 76° and 87° by the Contact Angle Analyzer (OCA, LMS Technologies PTE LTD), respectively. Other characters are described in section 5.3.1.

5.2.2. FO cross-flow setup and FO membrane fouling experiments

The schematic diagram of the bench-scale FO system is shown in Figure 5.1. The FO cross-flow setup was modified from previous UF cross-flow setup. The pressurized pump was replaced by the variable speed peristaltic pump. Two peristaltic pumps were connected to the feed solution side and draw solution

side respectively to recirculate the feed and draw solutions and generate the cross-flows. The FO membrane was installed in the modified membrane cell (Mode C10-T, Nitto Denko, Japan) that has symmetric channels on both sides of the membrane. The effective membrane surface area was 60 cm². Mesh spacers were placed in each of the feed and draw channel to support the membrane and enhance mixing. The feed solution and draw solution were mixed by the flow of the recirculated solution. The feed solution was placed on a digital mass balance and its weight changes of predetermined time intervals were logged into a computer to record the permeate flux. Prior to each experiment, all the required solutions and membrane were placed in the airconditioned room with a temperature of 22 – 24 °C for overnight to maintain the consistent temperature for the whole system.

Figure 5.1: Schematic diagram of bench-scale forward osmosis (FO) system.

Pure water experiments and PAHA fouling experiments were performed in this study. The conductivity in the feed water was measured at the predetermined time intervals to indicate the salt flux in each experiment. For PAHA fouling experiments, membrane were precompacted and equilibrated for 0.5h under the desired ionic strength and pH to eliminate the effect of membrane swelling and compaction on the flux decline. Then, the desired PAHA with the identical

ionic strength and pH was added into the feed solution to perform the membrane fouling test. The water flux was determined by the weight changes in the feed solution which was measured by a digital mass balance connected to a personal computer. The typical fouling test was continued for 8 hours. Unless otherwise specified, the following reference conditions were applied in the whole study: draw solution concentration of 2 M NaCl, 10 mg/L PAHA, 10 mM NaCl, and pH 6.0 in the feed solution composition, cross-flow velocity of 23.2 cm/s on both draw and feed side, and the temperature of 22 – 24 °C.

Baseline tests of the feed solution with the same ionic strength and pH were also conducted to indicate the flux decline due to the decrease of osmotic driving force during the fouling experiments resulting from the continuous dilution of the draw solution by the permeate water.

5.2.3. FO membrane characterization

The fresh FO membranes were characterized by the scanning electron microscopy (SEM), atomic force microscopy (AFM), salt rejection, hydraulic resistance, and membrane permeability.

5.2.3.1 Scanning electron microscopy (SEM)

Both virgin and fouled FO membranes were imaged by the scanning electron microscopy (SEM, Zeiss Evo®). Membrane samples were dried in the freeze drier prior to the SEM imaging. Detailed procedures were similar to SEM imaging of UF membranes in our previous work.

5.2.3.2 Atomic force microscopy (AFM)

Membrane samples used for the AFM microscopy were dried in the freeze drier (CHRIST ALPHR 1-4 LD, Germany) overnight. Tapping Mode® AFM micrographs of virgin membrane coupons were obtained with a MultiMode® SPM equipped with a J type piezoelectric scanner and a NanoScope® III

controller (Santa Barbara, California) on a scan size of 3 x 3 microns. The Version 5.12 of the Nanoscope control software was used for image acquisition. Single crystal etched silicon probes (Santa Barbara, California) were oscillated at 98% of its resonant frequency to yield a 2 V rms amplitude before engagement. Once engaged, the rms signal was adjusted to 0.9 – 1.4 V for optimal imaging quality. The manufacturer specified resonance frequency and spring constant for the probes were 265-309 kHz and 20-80 N/m, respectively. The actual resonance frequency determined using the auto-tune function of the control software was very close to 300 kHz. Typical scan rate used was 0.3-1.0 Hz.

5.2.3.3 Hydraulic resistance and salt rejection

Pressure-driven cross-flow membrane filtration system was employed to determine the hydraulic resistance of the clean FO membrane. In this case, the fluxes of the 10 mM NaCl electrolyte at different applied pressure were measured.

Based on the Darcy's Law, the flux in this case is described as the following equation (Yuan and Zydney 2000)

$$J = \frac{1}{A} \frac{dV}{dt} = \frac{\Delta p}{\eta(R_m + R_c)} \dots\dots\dots(1)$$

Where J is the permeate flux, V is the total volume of permeate, A is the effective membrane area, Δp is the transmembrane pressure, η is the viscosity of permeate, R_m is the hydraulic resistance of clean membrane, and R_c is the resistance of concentration polarization. R_m can be evaluated from Eq. (1).

The salt rejection of FO membrane was described as the ratio of the concentration of salt retained in the feed solution to the initial salt concentration in the feed solution, which can be calculated by measuring the conductivity of salt in the permeate solution

$$R = \left(1 - \frac{C_{permeate}}{C_{feed}}\right) \times 100\% \dots\dots\dots (2)$$

Where R is the salt rejection, $C_{permeate}$ is the salt concentration in the permeate solution, and C_{feed} is the salt concentration in the feed water.

5.2.3.4 FO membrane permeability

During the FO process, both water and salt can simultaneously transport through the permeable FO membrane with the opposite direction of flux due to the osmotic pressure difference and salt concentration gradient across the FO membrane. The FO membrane permeability can be characterized by the water flux and salt flux.

The water flux was directly evaluated from measuring the weight changes of feed solution in the predetermined time interval, while the evaluation of salt flux was relatively complicated. With reference to the salt flux measurement, concentration of salt (denoting C_{NaCl}) in the feed solution was first determined from the measured conductivity in the predetermined time interval, then the corresponding volume of feed solution (denoting V_f) was calculated by the difference of the initial total volume of feed solution and accumulated volume of water transporting to the draw solution. Thus, $C_{NaCl} \times V_f$ indicated the total mass of salt in the feed solution at the exact time (t). The cumulative mass of salt in the feed side transported per unit area of FO membrane from the draw side was determined by the difference of the total mass of salt (referring to $C_{NaCl} \times V_f$) and the initial mass of salt in the feed solution divided by the FO membrane area. Plot the figure of cumulative salt transport against t , then gain the slop (S) from the figure. Finally, S could be regarded as the salt flux.

Detailed deduction for the simulation of the water and salt flux was described in the appendix, where all the parameters in the equations for simulation were based on our experimental results.

5.3. Results and discussion

5.3.1 FO membrane characterization

5.3.1.1 SEM micrographs

SEM images of FO membrane are presented in Figure 5.2. Figure 5.2a is the cross-sectional structure of virgin FO membrane, which shows that the total thickness of the FO membrane is approximately 50 μm and the active layer in the top side is extremely thin. Both the external and internal surfaces of active layer of the virgin FO membrane are quite smooth from the SEM images in Figure 5.2b and c. The thin active layer is supported by cross-linked mesh and it is even transparent (Figure 5.2d). The FO membrane is lack of any thick fabric layer compared to most of the pressure-drive membranes. The internal surface of fouled FO membrane in Figure 5.2e clearly shows that a cake layer of foulant was formed on that surface, which would result in the flux decline.

(b)

(c)

(d)

(e)

Figure 5.2: SEM images of FO membranes. (a) cross-section of virgin FO membrane; (b) external surface of active layer of virgin FO membrane; (c) internal back surface of support layer of virgin FO membrane; (d) surface of virgin FO membrane (in larger scale); (e) back surface of fouled FO membrane. Fouling experimental conditions: membrane active layer towards draw solution (2 M NaCl), feed solution (10 mg/L PAHA, pH 6.0, 10 mM NaCl), and cross-flow velocity 23.2 cm/s on both side of the FO membrane.

5.3.1.2 AFM micrographs

For the AFM images of the FO membrane surface, multiple locations were measured. Figure 5.3 presents the AFM images of active layer surface of virgin membrane. The scan size was $3 \times 3 \mu\text{m}$ and the data scale was 20 nm. The mean roughness of the FO membrane surface analyzed from the AFM images was 35.708 nm, which is much smoother compared to most of reverse osmosis membranes (Tang 2007), suggesting the likely high performance of this FO membrane and less likely fouling on this FO membrane.

Figure 5.3: AFM image of FO membrane active layer.

5.3.1.3 Hydraulic resistance and salt rejection of the FO membrane

Due to the low permeate flux within the range of applied hydraulic pressure (Figure 5.4) as well as the low salt concentration in the feed water during the cross-flow membrane filtration tests, salt boundary layer would not be easy to form, suggesting that effect of concentration polarization could be neglected. Furthermore, identical flux was gained with the cross-flow velocity of 9.5 cm/s and cross-flow velocity of 19 cm/s in the membrane filtration test, further

demonstrating the neglectable effect of concentration polarization. Thus, Eq. (1) can be modified into Eq. (3) to calculate the FO membrane resistance.

$$R_m = \frac{\Delta p}{\eta J} \dots \dots \dots (3)$$

Figure 5.4 shows the water flux of the FO membrane as a function of applied hydraulic pressure. It is apparent that the flux increased linearly with the applied pressure from 3.45 to 15.50 atm and the R^2 value is more than 0.99. The resistance of FO membrane was determined through the ratio of the slope of Figure 5.4 to the viscosity (η). Furthermore, the water permeability constant, A , at 24 °C could also be determined through Figure 5.4. According to the literature (Cath, Childress et al. 2006; Tan and Ng 2008), the water permeability (A) can be found using RO experiments with pure water. In this case, the water flux is determined by $J_w = A\Delta P$. Thus, the water permeability A is calculated through $A = \frac{J_w}{\Delta P}$, that is $2.2 \times 10^{-7} \text{ m}/(\text{s} \cdot \text{atm})$. The water flux generated by the effective osmotic driven force across the dense selective layer of the membrane for FO process should be consistent with the water flux corresponding to the data shown in Figure 5.4.

Figure 5.4: Water flux as a function of applied hydraulic pressure at 24 °C.

Figure 5.5: Relationship between NaCl concentration and conductivity.

In this study, the salt concentration in the permeate solution was determined based on the conductivity measurement. The relationship between salt concentration and conductivity is illustrated in Figure 5.5. According to the FO membrane filtration test in section 5.3.1.3, the salt rejection of the FO membrane is evaluated to be more than 90%. Also, using the method described in the literature (Loeb, Titelman et al. 1997; Cath, Childress et al. 2006), the salt permeability constant (B) can be obtained from the measurements of salt rejection (R) in RO experiments. It can be shown that $B = \frac{(1-R)A(\Delta P - \Delta \pi)}{R}$, thus B was found to be 1.8×10^{-7} m/s.

5.3.1.4 Water and salt flux in the FO process

In terms of the method described in section 5.2.3.4, salt flux under various concentrations of draw solution can be evaluated from slope of each line in Figure 5.6.

Figure 5.6: Cumulative salt transport in the feed solution versus time under various concentrations of draw solution.

Figure 5.7 shows both the experimental and simulation results for water and salt flux at different concentration of draw solution. The feed solution was 10 mM NaCl, and the membrane active layer faced the draw solution. Clearly, water flux and salt flux increased with increasing the concentration of draw solution. However, the increase of water flux and salt flux was not linear with the concentration of draw solution, especially at higher concentration of draw solution.

On one hand, an increase in the draw solution concentration elevated the osmotic driving force and salt concentration difference across the membrane, thus the amount of both water and salt transporting through membrane increased. On the other hand, high driving force and correspondingly high water fluxes due to high draw solution concentration can cause severe effect of concentration polarization, which occurs on both the feed side and permeate side of the FO membrane. Since the membrane active layer faced the draw

solution in this study, the dilutive ECP occurred in the permeate side (in this case, the active layer side), whereas the concentrative ICP occurred at the feed side (in this case, the support layer side). Even though the ECP can be alleviated through cross flow in the membrane surface, the higher draw solution concentration and thus higher corresponding flux can still induce the form of the diluted boundary layer close to the active layer. In the feed side, more salt convected towards the support layer at higher water flux, thus a concentrated polarized layer was established along the inside of porous support layer and the concentrative ICP was enhanced. The higher water and salt fluxes, the higher effects of ECP and ICP, which in turn decrease the effective osmotic driving force and salt concentration difference across the membrane, inhibiting the linear increase of the water and salt fluxes with draw solution concentration. Similar results have been reported by previous researchers (McCutcheon and Elimelech 2007; Cornelissen, Harmsen et al. 2008).

Figure 5.7: Experimental and simulation results of water flux and salt flux in the forward osmosis process with membrane active layer (AL) facing draw solution (DS).

(note: water flux and salt flux were the initial flux.)

Water flux with the membrane active layer facing the feed solution was comparatively lower than that with membrane active layer facing the draw solution, as illustrated in Figure 5.8. This is attributed to more pronounced ICP in the membrane orientation of active layer facing the feed solution, which significantly decreases the effective osmotic pressure difference (Gray, McCutcheon et al. 2006; Tan and Ng 2008).

Furthermore, simulation results for the water and salt flux described in Figure 5.7 and Figure 5.8 were in excellent agreement with the experimental results. Therefore, the water and salt flux can be predicted through the simulation.

Figure 5.8: Experimental and simulation results of water flux in the forward osmosis process with membrane active layer (AL) facing feed solution (FS).

(note: water flux was the initial flux.)

5.3.2 Baseline test

Due to the water transportation through the FO membrane from the feed solution side to the draw solution side in bench-scale experimental system for the FO experiments, the draw solution was diluted, while the feed solution was concentrated. Thus the effective driving force for the FO process was decreased with the FO membrane filtration progressing and the flux decline was not only due to the membrane fouling when the foulant existed in the feed solution but also due to the effect of dilution. Therefore, it is necessary to perform the baseline tests to make effectively comparison for the fouling behavior.

Baseline experimental results at various draw solution concentrations are illustrated in Figure 5.9. Figure 5.9a shows the water fluxes as a function of filtration time at various draw solution concentration, while Figure 5.9b

presents the original water flux from Figure 5.7 and water fluxes as a function of draw concentration calculated from Figure 5.9a based on the dilution effect. As shown in Figure 5.9a, flux decline was much more severe at higher draw solution concentration. Higher draw solution concentration leads to higher water flux, in turn, more amount of water transports into the draw solution from the feed side, enhancing the effect of dilution in the draw solution with time progressing. However, from Figure 5.9b, the lines of water fluxes versus draw solution concentration were not continuous. The initial flux at lower draw solution concentration was higher than that calculated from dilution of higher draw solution concentration, which was attributed to the effect of concentration polarization. The increase of salt concentration in the feed solution was not only due to the concentration but also caused by the salt leakage from the draw solution. As a result, the ICP was enhanced with FO membrane filtration progressing. In a way, the decline of the baseline fluxes was caused by the coupling effects of concentration polarization and solution dilution.

Figure 5.9: Water flux with various concentrations of draw solution. (a) Baseline water flux versus time at different concentration of draw solution; (b) Original water flux and water flux with dilution based on baseline water flux. Membrane active layer faced draw solution in (a) and (b).

5.3.3 Effect of hydrodynamic conditions on fouling

5.3.3.1 Effect of initial flux

As discussed in section 5.3.2, initial water flux increased with increasing the concentration of draw solution. With respect to the initial flux on FO membrane fouling, fouling experiments were performed under different draw solution concentration ranging from 0.5 M to 4 M. Figure 5.10a illustrates the flux behavior at various draw solution concentrations. While comparing flux behavior between fouling test and baseline, it is interesting to note that nearly

no additional flux decline was observed in the fouling test when the draw solution concentrations are 0.5 M and 1 M, suggesting that no fouling occurred with the initial flux of 16.0 and 27.1 L/m²hr. However, rate and extent of flux decline became significant in the 8h fouling test while the draw solution concentrations were elevated to 2 M and 4 M. In addition, extent of flux decline with 4 M draw solution was greater than that with 2 M draw solution because of higher initial flux with higher draw solution concentration.

Figure 5.10: Effect of initial flux on FO membrane fouling. (a) flux behavior at various draw solution concentrations; (b) normalized flux at various draw solution concentrations. Other fouling experimental conditions: active layer towards draw solution, feed solution (10 mg/L PAHA, 10 mM NaCl, and pH 6.0), cross-flow velocity 23.2 cm/s on both side of the FO membrane, and temperature 22-24 °C.

Initial flux mainly affects the hydraulic drag force on the humic acid molecules towards on the membrane surface. Higher initial flux, higher hydraulic drag force due to the convective flow towards the membrane (Tang and Leckie 2007). As a result, humic acid molecules with higher initial flux tend to more readily overcome the barrier force resulting from the membrane surface and the deposited humic acid molecules on the membrane surface (Tang and Leckie 2007), and cake layer formed on the membrane surface would become much more compact (Tang, Kwon et al. 2007). In addition, as discussed in the UF membrane fouling by protein in chapter 4, the total amount of foulant convected towards the membrane is proportional to the membrane throughput at a constant foulant concentration. Therefore, greater initial flux, greater amount of humic

acid convected towards the membrane, which increases the possibility of humic acid deposition on the membrane. Furthermore, concentrative internal concentration polarization was enhanced at higher initial flux due to the increase of the concentration of humic acid and salt in the porous structure of the back support layer. Consequently, flux decline was much more pronounced at higher initial flux.

However, since the dilution of draw solution and effect of concentration polarization also contribute largely to the flux decline both in the baseline test and membrane fouling test, it is essential to employ another conceptually normalized flux (Eq. (4)) to analyze the flux behavior through eliminating the effect of dilution and concentration polarization.

$$J_n = J_0 \times \frac{J_f}{J_b} \dots\dots\dots(4)$$

Where J_n denotes the normalized flux based on Eq. (4), J_0 represents the initial flux, J_f is the flux in the membrane fouling test, and J_b is the flux in the baseline test. Since both J_f and J_b are the function of effect of dilution and concentration polarization, $\frac{J_f}{J_b}$ could be employed to roughly describe the normalized factor which solely depends on the fouling effect but eliminates the effect of dilution and concentration polarization. Then, $J_0 \times \frac{J_f}{J_b}$ could roughly represents the flux solely affected by membrane fouling.

Figure 5.10(b) illustrates the normalized flux based on Eq. (4). Clearly, little flux decline was observed with the draw solution concentration below 2 M, while flux decline increased with increasing the draw solution concentration from 2 M to 4 M. This is quite consistent with our previous discussion.

5.3.3.2 Effect of cross-flow velocity

Effect of cross-flow velocity on FO membrane fouling is illustrated in Figure 5.11. It is interesting to note that little difference of flux decline was observed

between the cross-flow velocity of 23.2 cm/s and 11.6 cm/s, suggesting that cross-flow velocity has no significant effect on FO membrane fouling when the porous support layer faces the feed solution.

Figure 5.11: Effect of cross-flow velocity (CFV) on FO membrane fouling. Other fouling experimental conditions: active layer towards draw solution (2 M NaCl), feed solution (10 mg/L PAHA, 10 mM NaCl, and pH 6.0), and temperature 22-24 °C.

It is generally recognized that increasing the cross-flow velocity can mitigate membrane fouling in most of the pressure-driven membrane separation process due to the reduction of concentration polarization and foulant accumulation on the membrane surface. Nevertheless, the osmotically-driven membrane process (i.e., FO process), unlike pressure-driven membrane process, allows the membrane to orientate in two directions, referring to the active layer towards the feed solution and porous support layer towards the feed solution. When the membrane active layer faces the feed solution, fouling is not significant (discussed in section 5.3.5). In our study, effect of cross-flow velocity on

fouling was investigated with the membrane support layer facing the feed solution. From the large scale SEM images of the support layer, it is typically composed of embedded polyester mesh, which forms the porous structure (Figure 5.2d). Therefore, the role of shear force parallel to the membrane surface caused by cross flow is mainly played at the outside of the porous support layer but can not sweep away the foulant and salt within the particular porous structure. To some extent, the mode of membrane filtration system inside the porous structure can be regarded as dead-end filtration rather than cross-flow filtration. In other words, increasing the cross-flow velocity can significantly reduce the external concentration polarization but can not effectively reduce the internal concentration polarization. As a result, flux decline exhibited identical trend with different cross-flow velocity.

5.3.4 Effect of solution composition on fouling

5.3.4.1 Effect of concentration

Figure 5.12 shows the flux profiles at various PAHA concentrations (10 mg/L and 100 mg/L). Clearly, flux decline was much more severe at higher PAHA concentration during the 8h FO membrane fouling experiment. Similar result was observed in the RO/NF membrane fouling by humic acid in Tang and coworkers' research (Tang, Kwon et al. 2007). This is probably attributed to larger amount of humic acid convection towards the back support layer of FO membrane at higher feed concentration. For one thing, more humic acid accumulated inside the porous support layer but could not be swept off by cross flow, and consequently the concentrative internal concentration polarization caused by humic acid (ICP_{HA}) was enhanced. For another, increasing the feed concentration also increase the collision efficiency between humic acid molecules and the back internal surface of the FO membrane (Tang, Kwon et al. 2007). Thus greater amount of humic acid deposited onto the back surface of the FO membrane as a result of higher possibility to collide with the membrane at higher feed concentration. A thick and rough cake layer with the PAHA concentration of 100 mg/L was formed detected through SEM image (Figure 5.2e). As shown in table 1, the density of humic acid deposition onto the

membrane surface at the feed concentration of 100 mg/L was much greater compared to that at the feed concentration of 10 mg/L. Greater PAHA deposition and correspondingly greater specific cake layer resistance, thus greater flux decline (Tang, Kwon et al. 2007). In a word, both the effects of ICP_{HA} and foulant deposition are essential to the flux decline.

Figure 5.12: Effect of PAHA concentration on FO membrane fouling. Other fouling experimental conditions: active layer towards draw solution (2 M NaCl), feed solution (10 mM NaCl, pH 6.0), cross-flow velocity 23.2 cm/s on both side of the FO membrane, and temperature 22-24 °C.

Table 5.1 Density of PAHA accumulation on the membrane surface under various experimental conditions.

DS (M)	PAHA (mg/L)	pH	IS (mM)	Accm ($\mu\text{g}/\text{cm}^2$)
2	10	6	10	25.59249
2	100	6	10	133.3024
2	10	8	10	19.42372
4	10	6	10	27.65507
2	10	4	10	30.71732

Note: DS represents draw solution concentration; IS represents ionic strength; Accm represents density of PAHA accumulation.

Figure 5.13: Effect of pH on FO membrane fouling. Other fouling experimental conditions: active layer towards draw solution (2 M NaCl), feed solution (10 mM NaCl, 10 mg/L PAHA), cross-flow velocity 23.2 cm/s on both side of the FO membrane, and temperature 22-24 °C.

5.3.4.2 Effect of pH

Figure 5.13 presents the effect of solution pH on the FO membrane fouling. Flux decreased more rapidly at lower solution pH, consistent with previous results in pressure-driven membrane fouling by humic acid (Hong and Elimelech 1997; Yuan and Zydney 1999; Yuan and Zydney 2000; Schafer, Pihlajamaki et al. 2004; Tang, Kwon et al. 2007). From the result of acid-base titration of PAHA (Tang, Kwon et al. 2007), PAHA is negatively charged within the normal pH range (pH 4 - 10) and the charge density decreases greatly with decreasing pH. Therefore, the electrostatic repulsion among humic acid molecules was weakened at lower pH, resulting in larger size of aggregate of humic acid and greater amount of humic acid attaching onto back surface of the FO membrane. Previous zeta potential measurement of the cellulose triacetate (CTA) and cellulose acetate (CA) RO membrane showed that the surface of the CA membrane was much more negatively charged with increasing pH while pH above 4 (Elimelech, Zhu et al. 1997; Xu, Drewes et al.

2006), suggesting that the FO membrane made from the same material probably possesses the same characteristics of zeta potential as the CA/CTA RO membrane. Thus, lowering pH also weakened the electrostatic repulsion between humic acid molecules and membrane surface, which can also promote the deposition of humic acid. In addition, previous studies have demonstrated that the solubility of humic acid increases with its charge (Tipping, Backes et al. 1988; Schafer, Fane et al. 1998). As a result, pH reduction decreased the solubility of humic acid, which also promoted the amount of humic acid deposition. The deposition measurement of humic acid in Table 5.1 also shows that the amount of humic acid deposition increased with decreasing pH.

5.3.4.3 Effect of ionic strength

Effect of ionic strength on FO membrane fouling was illustrated in Figure 5.14. Increasing the salt concentration in feed solution enhanced the effect of ICP and decreased the effective osmotic pressure difference across FO membrane. Therefore, it is interesting to note that the baseline fluxes under the condition of 2 M NaCl in draw solution and 100 mM NaCl in feed solution exhibit identical trend with fluxes under the condition of 1 M NaCl in draw solution and 10 mM NaCl in the feed solution. Flux decreased slightly faster at higher ionic strength upon adding humic acid. At higher ionic strength, the electric double layer of humic acid molecules is compressed and negative charge is shielded, leading to reduction of the electrostatic repulsion between humic acid molecules. Consequently, humic acid are more easily aggregating together and attaching onto the membrane. The hydraulic resistance of the fouling layer is increased as a result of formation of much more compact and thicker humic acid depositing layer at higher ionic strength (Hong and Elimelech 1997; Yuan and Zydney 1999). Therefore, greater flux decline was observed at higher ionic strength. Through close investigation of the data, it is essential to point out that the flux decline was much milder during 8 hr fouling test compared to previous results in pressure-driven membrane (Hong and Elimelech 1997; Yuan and Zydney 1999). This may be attributed to the lower initial flux (around 28 L/m²hr) in our FO membrane fouling tests. Lower initial flux reduced the

hydrodynamic drag force on the humic acid molecules, thus less humic acid deposited on the membrane surface and less flux decline was observed.

Figure 5.14: Effect of ionic strength on FO membrane fouling. Other fouling experimental conditions: active layer towards draw solution (2 M NaCl while feed solution containing 100 mM NaCl, and 1 M NaCl while feed solution containing 10 mM NaCl), feed solution (10 mg/L PAHA, pH 6.0), cross-flow velocity 23.2 cm/s on both sides of the FO membrane, and temperature 22-24 °C.

5.3.4.4 Effect of divalent ions on fouling

Figure 5.15 illustrates the divalent ions on the FO membrane fouling. Fouling tests were performed under the Ca^{2+} concentration of 0 mM, 0.1 mM and 1mM as well as the Mg^{2+} concentration of 1mM. The total ionic strength of the feed solution was fixed at 10 mM by varying the NaCl concentration. As shown in Figure 5.15, significant flux decline was observed while divalent ions (Ca^{2+} , Mg^{2+}) existed in the feed solution. Furthermore, the more divalent ions in the feed solution, the greater flux decline and correspondingly severer membrane fouling. Divalent ions, such as Ca^{2+} , Mg^{2+} , can bind with the carboxylic groups in the humic acid molecules through complex formation, leading to partial

charge neutralization of the humic acid (Yuan and Zydney 1999; Tang, Kwon et al. 2007). Thus, the presence of Ca^{2+} , Mg^{2+} reduced the intermolecular electrostatic repulsion and promoted more humic acid depositing onto the membrane surface. In addition, calcium and magnesium can act as a medium binding two humic acid molecules through the bridging effect. As a result, the thickness and compactness of foulant layer was enhanced and membrane fouling was accelerated by the Ca^{2+} , Mg^{2+} .

It also should be noted that flux decline with 1 mM Mg^{2+} were slightly lower than those with 1 mM Ca^{2+} . This is likely due to the different ability of these divalent ions complex with the carboxylic groups. It was reported that Ca^{2+} complexes were more stable than the Mg^{2+} complexes through the evaluation of the stability constant ($\log K$) (Schnitzer and Hansen 1970).

Figure 5.15: Effect of divalent ions on FO membrane fouling. Other fouling experimental conditions: active layer towards draw solution (2 M NaCl), feed solution (10 mM of total ionic strength, pH 6.0, and 10 mg/L PAHA), cross-flow velocity 23.2 cm/s on both side of the FO membrane, and temperature 22-24 °C.

5.3.5 Effect of membrane orientation on fouling

Due to the asymmetric structure of the FO membrane, two types of membrane orientation are allowed in the forward osmosis operation without adding additional hydraulic pressure. Previous studies have demonstrated that internal concentration polarization is more severe with the membrane active layer facing the feed solution than that with membrane active layer facing draw solution (Gray, McCutcheon et al. 2006; McCutcheon and Elimelech 2006; McCutcheon and Elimelech 2007; Tan and Ng 2008). This is in agreement with our results of baseline test, i.e., initial flux with active layer facing lower concentration of draw solution (1 M NaCl) was consistent with the initial flux while support layer facing higher concentration of draw solution (5.5 M NaCl). With time progressing, salt in the draw solution passes through the membrane to the feed solution. Consequently, the concentrative ICP will be enhanced due to increasing amount of salt accumulating in the porous support layer when the active layer faces the draw solution, whereas the enhancement of concentrative ECP in the feed side could be mitigated through cross flow and dilutive ICP would become less severe with the flux decline when the active layer faces the feed solution. As a result, greater flux decline in the baseline was observed when active layer faces the draw solution in the later filtration.

(a)

Figure 5.16: Effect of membrane orientation on FO membrane fouling. Other experimental conditions: (a) draw solution (1 M NaCl with AL facing DS, 5.5 M NaCl with AL facing FS), feed solution (10 mg/L PAHA, pH 6.0, 1 mM CaCl_2 , and 10 mM of total ionic strength), cross-flow velocity 23.2 cm/s on both side of the FO membrane, and temperature 22-24 °C; (b) draw solution (0.75 M NaCl with AL facing DS, 2 M NaCl with AL facing FS), feed solution (10 mg/L PAHA, pH 6.0, 0 mM CaCl_2 , and 10 mM of total ionic strength), cross-flow velocity 23.2 cm/s on both side of the FO membrane, and temperature 22-24 °C.

As illustrated in Figure 5.16a, upon adding PAHA to the feed solution, flux decline was more rapid when active layer faced the draw solution, while little flux decline was observed when support layer faced the draw solution. Similar phenomenon was observed by previous publication (Mi and Elimelech 2008). This is ascribed to the coupled effect of chemical and hydrodynamic interactions (Seidel and Elimelech 2002; Mi and Elimelech 2008). As discussed in section 5.3.4.4, fouling was accelerated in the presence of calcium through complex formation and bridging effect. However, membrane

orientation can strongly affect the hydrodynamic effect, such as the hydraulic drag force perpendicular to the membrane surface and shear force parallel to the membrane surface, which will affect the foulant deposition and accumulation on the membrane surface. When the membrane porous support layer faces the feed solution, foulant can easily deposit into the porous structure of the membrane with little influence of the shear force caused by the cross flow (detailedly discussed in section 5.3.3.2). Instead, with the membrane active layer towards the feed solution, foulant is less prone to depositing on the highly smooth and hydrophilic FO membrane surface. Furthermore, effect of cross flow becomes more significant, which prevents the deposition of foulant on the membrane surface through the shear force sweeping the foulant away. In the absence of calcium and at lower initial flux, nearly no fouling occurred in the two types of membrane orientation (Figure 5.16b), further demonstrating the coupled effect of chemical and hydrodynamic interactions on fouling.

5.4 Conclusions

The FO membrane used in the study was thoroughly characterized by the AFM, SEM, rejection, and flux behavior. This FO membrane is comprised of a porous support layer and a quite smooth active layer. The water and salt flux was found to exhibit non-linear increase with increasing draw solution concentration in the forward osmosis process due to internal concentration polarization. Fouling of FO membrane by humic acid was observed to be affected by the hydrodynamic conditions and feedwater composition as well as the membrane orientation. While the membrane active layer faced the draw solution, severe membrane fouling occurred at higher draw solution concentration (above 2 M NaCl) together with the higher concentration of humic acid, proton, salt and divalent ions in feed solution, however, cross-flow velocity has no significant effect on the membrane fouling likely due to the particular structure of the porous back support layer. FO membrane active layer orientated the feed solution was found to be able to mitigate fouling but need higher concentration of draw solution to achieve the same water flux as that membrane active layer towards the draw solution.

Chapter 6

Summary and conclusions

This study systematically investigated the membrane fouling during pressure-driven ultrafiltration (UF) and osmotically-driven forward osmosis (FO) by macromolecular organic compounds – protein and humic acid. The overall objective of this study was to investigate the effect of the feedwater composition (foulant concentration, pH, ionic strength, and calcium concentration) and hydrodynamic conditions (initial flux and cross-flow velocity) on organic compounds fouling of UF and FO membranes.

Bovine serum albumin (BSA) and purified Aldrich humic acid (PAHA) were chosen as the model organic foulant. UF membrane fouling tests were performed in a lab-scale crossflow filtration unit under constant applied pressure, while flux behavior of FO membranes were determined in a modified crossflow filtration unit under the osmotic pressure produced by the salt solution. The major findings and conclusions are:

- (1) The flux performances of both UF and FO membranes were dependant on both hydrodynamic conditions (initial flux and cross-flow velocity) and solution composition (foulant concentration, pH, ionic strength, and calcium concentration). During protein ultrafiltration, lowering the cross-flow velocity and increasing the initial flux and BSA concentration apparently accelerated fouling, however, pH and ionic strength affected the fouling behavior much more complicatedly. BSA fouling was most severe at its isoelectric point, while the effect of ionic strength on fouling varied with the pH changes. In the FO process, membrane fouling was enhanced at lower pH and higher initial flux, humic acid concentration, ionic strength and divalent ion concentration, whereas effect of cross-flow velocity was insignificant. High initial flux and foulant concentration accelerating fouling in both UF and FO process was probably due to the increased amount of foulant convected towards the membrane surface in a given duration and correspondingly

the collision efficiency between the foulant and membrane or foulant and deposited-foulant. Apart from that, hydrodynamic drag force and concentration polarization could also be increased at high initial flux. On the other hand, effect of ionic composition of the solution on fouling was probably through altering the electrostatic interaction between the charged organic molecules.

- (2) Electrostatic interaction between foulant and foulant or foulant and deposited-foulant plays an important role on organic fouling both on UF and FO membranes. Varying the pH, ionic strength and calcium concentration in the ionic solution can change the charge density of the protein and humic acid and corresponding electrostatic repulsion, which would affect the foulant deposition on the membrane surface.
- (3) Long-term fouling behavior and short-term fouling behavior are governed by different fouling mechanisms in the porous UF membrane filtration process. In the protein ultrafiltration process, greater flux decline was observed in the short fouling stage due to the dominant foulant-membrane interaction, while flux decline became much milder in the longer filtration duration as a result of the foulant-foulant interaction.
- (4) Both UF and FO membranes with severe flux decline were completely covered by a layer of foulant through SEM images. Greater amount of foulant deposited on the FO membrane surface was measured while fouling was more severe.
- (5) Limiting flux existed at high applied flux in the protein ultrafiltration process, defined as beyond which increase in pressure did not enhance the stable flux. Membranes with initial flux greater than the limiting flux experienced severe fouling and their stable flux approached the limiting flux.
- (6) A transitional region corresponding to the initial flux higher than the limiting flux was observed in the porous UF membrane. Within the

transitional region, the final stable flux was lower than the limiting flux value even though the initial flux was much greater.

- (7) The limiting flux was dependent on the ionic composition of the feedwater. pH and ionic strength showed influence on the limiting flux probably due to the influence on the electrostatic interaction. However, foulant concentration seemed to solely affect the rate of flux approaching the limiting flux value but not influence limiting value. This was likely attributed to the influence of the collision efficiency not the attachment coefficient by the foulant concentration.
- (8) Concentration polarization was much more complicated in the osmotically-driven membrane separation process compared to the pressure-driven membrane separation process. In the FO process, internal concentration polarization was much more pronounced than the external concentration polarization.
- (9) FO membrane orientation had significant influence on the performance of water flux as well as the humic acid fouling. Greater water flux was observed when the membrane active layer faced the draw solution, while fouling was alleviated with the membrane active layer faced the feed solution.

The current work investigated the organic macromolecules fouling on both pressure-driven and osmotically-driven membranes. The limiting flux concept from Tang and Leckie (Tang and Leckie 2007) was employed to better understand the BSA fouling on UF membrane. However, this limiting flux conceptual model might be applicable to other types of foulants (such as humic acid, polysaccharides, and inorganic foulants) and other types of porous UF and MF membranes. In addition, limiting flux underlying the mixture of multiple foulants fouling on the membrane might be much more interesting. It is recommended that these types of membranes and foulants be included in the future research. Furthermore, limiting flux was not observed in the short duration of FO membrane fouling. Further researches could be devoted to the limiting flux in the membrane fouling of FO process, especially the cases with different membrane orientations. In the FO process, influence of different types

of draw solutions and membranes on the FO performance was less investigated in this work. Further improvement could focus on the draw solutions and membranes used in the FO process.

Appendix

Simulation of water and salt flux in the forward osmosis (FO) process

Due to the osmotic pressure gradient across the membrane, water diffuses through the semipermeable FO membrane from the feed solution to the draw solution, which implies the principle of forward osmosis (FO) membrane processes. Meanwhile, the solute can also transport through the membrane from the draw solution to feed solution as a result of the solute concentration gradient between the two solutions. In figure 1, the nonporous rejection layer (active layer) of the FO membrane is facing the draw solution and the porous backing layer is facing the feed solution.

Figure A.1. Solute and water transport in a FO process (Cath, Childress et al. 2006).

Based on the solution-diffusion model to the nonporous layer, the water flux and salt flux in the forward osmosis process are given by

$$J_w = A(\pi_4 - \pi_3) \dots \dots \dots (1)$$

$$J_s = B(C_4 - C_3) \dots \dots \dots (2)$$

Where A and B are the transport coefficients for water and solute, respectively, J_w is the water flux, J_s is the salt flux, π_4 and C_4 are the osmotic pressure and solution concentration in the draw solution, π_3 and C_3 are the osmotic pressure and solution concentration in the feed solution.

For the solute transport in the backing layer

$$J_w C + J_s = D_{eff} \frac{dC}{dx} \dots \dots \dots (3)$$

Where D_{eff} is the effective diffusion coefficient of solute in the porous back layer; C is the solute concentration in the porous backing layer at a distance x away from the interface between the active layer and the backing.

The boundary conditions for Equation (3) are:

$$C = C_2 \text{ at } x = 0 \dots \dots \dots (4)$$

$$\text{and } C = C_3 \text{ at } x = t_{eff} \dots \dots \dots (5)$$

Based on Equations (1 – 5), the water flux can be solved as

$$\ln \left[\frac{(A\pi_4 + J_w) + B}{A\pi_2 + B} \right] = \frac{J_w}{K} \dots \dots \dots (6)$$

and the salt flux can be solved as

$$J_s = \frac{C_4 - C_2 \exp\left(\frac{J_w}{K}\right)}{\frac{1}{B} + \frac{1}{J_w} \left[\exp\left(\frac{J_w}{K}\right) - 1 \right]} \dots \dots \dots (7)$$

where K is the mass transfer coefficient, given by

$$K = \frac{D_{eff}}{t_{eff}} = \frac{\varepsilon \cdot D}{\tau \cdot t} = \frac{D}{S} \dots \dots \dots (8)$$

In Equation (8), D is the solute diffusivity ($D = 1.61 \times 10^{-9}$ m²/s for NaCl), t is the actual thickness of the backing layer, ε is the porosity of the backing layer, and τ is the tortuosity of the backing layer. The structure parameter S , defined as $\tau t / \varepsilon$, is analogous to the boundary layer thickness for external concentration polarization in a typical reverse osmosis process.

In the same way, water flux with membrane active layer towards feed solution can be solved as:

$$\ln \left[\frac{A\pi_4 + B}{A\pi_2 + J_w + B} \right] = \frac{J_w}{K} \dots\dots\dots (9)$$

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