CHARACTERIZATION OF MASS TRANSFER DURING MEMBRANE FILTRATION PROCESSES USING NOVEL TECHNIQUES

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For my family
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ABSTRACT

Membrane-based separation processes have broad applications in water and wastewater treatment, seawater desalination, food processing, ultrapure water production and energy harvest. However, the efficiency of both osmotically driven (e.g., forward osmosis, FO) and pressure-driven (e.g., reverse osmosis, RO) filtration processes are adversely affected by the coupled phenomena of concentration polarization (CP) and membrane fouling. The concentration build-up in the vicinity of the membrane surface is commonly known as the external CP (ECP) that is greatly affected by the fluid hydrodynamics. On the other hand, the solute accumulation in the porous support layer of the membrane is known as the internal CP (ICP) which is unique in the osmotically driven membrane processes such as FO. ICP is closely associated with the physical properties of the substrate and is usually characterized by the structural parameter, the $S$ value. To mitigate the negative influence of CPs and membrane fouling requires in-depth understanding of the mechanisms of mass transfers during filtration processes, which necessitates the development of novel techniques to visualize and quantify the dynamic physico-chemical processes associated with the membrane filtrations. In this study various novel techniques were exploited to characterize the mass transfers during membrane processes.

New experimental protocols were established based on the theoretical models to directly and independently characterize ICP and ECP. In particular, three methods were proposed in an RO mode to evaluate the $S$ value. The $J_r$-method (water flux), the $R_r$-method (solute rejection) and the $R_t$-method (trace contaminant rejection) were realized based on the measurements of the RO permeate flux, solute rejection (e.g., NaCl) and trace contaminant rejection (e.g., boron), respectively. $S$ values determined from the aforementioned methods were compared with that obtained by the conventional FO water flux fitting method. In particular, the $R_t$-method was recommended. By this approach it was able to determine the solute permeability graphically. It was also feasible to resolve the effect of ECP from that of ICP interpretively using the $R_r$-method.
ABSTRACT

To investigate the subtle interplay between various membrane substrate structures and ICP, an electrochemical impedance spectroscopy (EIS) system was modified to accommodate the FO processes. The effect of various support structures on CPs was systematically investigated. In particular, three commercial FO membranes with distinct substrate structures were characterized by an EIS incorporated FO system and the impedance spectra were analyzed based on their equivalent circuits. Both static (without osmosis) and dynamic (with osmosis) tests were implemented. In the static tests the limit behaviors of the impedance spectra were employed to resolve the FO membrane structural information from the electrolyte background which was further compared with the scanning electron microscopic micrographs. The dynamic tests under both membrane orientations were conducted to verify the feasibility of using the EIS technique to capture the variation of the developed concentration profiles within the FO substructures.

Furthermore, to visualize and quantify the dynamic processes during the membrane filtration (i.e., to study the CP by visualizing the fluid hydrodynamics in the proximity to the membrane surface and to investigate membrane fouling by direct observation of foulant deposition and formation), the optical coherence tomography (OCT) technique was exploited. The Doppler OCT facility incorporated with a cross-flow cell first was employed to characterize the hydrodynamics in a spacer-filled channel. The velocity profile normal to the membrane surface was successfully visualized which is difficult to characterize using conventional membrane characterization techniques. Various flow patterns were generated by varying the spacer orientations with respect to the bulk flow direction. A series of Doppler images was used to reveal the subtle interactions between the fluid and the spacer filaments. The characterization results obtained thereby were used to interpret the performance variation of an RO process with the same spacer configurations. The feasibility of using the Doppler OCT technique to characterize the hydrodynamics of the fluid in a spacer-filled channel was validated by the experimental results.

The OCT technique was further exploited to visualize and quantify the growth of a foulant layer during a filtration process. In particular, an OCT system
was incorporated with a lab-scale membrane filtration system, and the growth of a fouling layer was observed by using the structural OCT imaging. Taking advantage of the Doppler effects, the OCT-based characterization also provided the velocity profiles of the fluid fields, which is of great value in analyzing the fouling layer formation. The characterization results clearly reveal for the first time the evolution of the morphology of the cake layer under different micro-hydrodynamic environments. This study demonstrates that the OCT-based characterization is a powerful tool for investigating the dynamic processes during membrane fouling.
LIST OF PUBLICATIONS

Journal articles related to this study:


Other journal articles:


**Conference presentations:**


2. Li, W., **Gao, Y.** and Tang, C.Y. (2011). ”Network-based finite element analysis for studying the effect of support structure on internal concentration polarization during forward osmosis.” *AIChE Annual Meeting 2011, Minneapolis, MN, USA.*

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**Nomenclature**

- $a_p$: Particle diameter (m)
- $A$: Water permeability (m/s·Pa)
- $A_m$: Membrane area in the EIS system (m²)
- $B_s$: Salt permeability (m/s)
- $B_t$: Tracer permeability (m/s)
- $C_b$: Solute concentration of bulk feed solution (mol/L)
- $C_{b,f}$: Foulant concentration in the bulk feed solution (g/L)
- $C_m$: Solute concentration on membrane surface (mol/L)
- $C_p$: Solute concentration of permeate water (mol/L)
- $C_v$: Water concentration (mol/L)
- $C$: Global capacitive parameter defined by Equation (4.8) (F)
- $C_e$: Capacitance of electrolyte solution (F)
- $C_m$: Capacitance of membrane (F)
- $\bar{C}_m$: Average capacitance of membrane (F)
- $C_L$: Capacitance at low-end limit of the probing frequency (F)
- $d_h$: Hydraulic diameter (m)
- $D_s$: Diffusion coefficient of solute (m²/s)
- $D_t$: Diffusion coefficient of tracer (m²/s)
- $D_v$: Diffusion coefficient of water (m²/s)
LIST OF SYMBOLS

\( f \) \hspace{1cm} \text{Frequency (Hz)}

\( f_D \) \hspace{1cm} \text{Frequency shift (Hz)}

\( G \) \hspace{1cm} \text{Global conductive parameter defined by Equation (4.7) (S)}

\( G_e \) \hspace{1cm} \text{Conductance of electrolyte solution (S)}

\( G_{ef} \) \hspace{1cm} \text{Conductance of feed solution (S)}

\( G_{ed} \) \hspace{1cm} \text{Conductance of draw solution (S)}

\( G_m \) \hspace{1cm} \text{Conductance of membrane (S)}

\( \bar{G}_m \) \hspace{1cm} \text{Average conductance of membrane (S)}

\( G^H \) \hspace{1cm} \text{Conductance at high-end limit of the probing frequency (S)}

\( G^L \) \hspace{1cm} \text{Conductance at low-end limit of the probing frequency (S)}

\( I \) \hspace{1cm} \text{Alternating current (A)}

\( I_0 \) \hspace{1cm} \text{Amplitude of } I \hspace{1cm} (\text{A})

\( J_s \) \hspace{1cm} \text{Solute flux (g/m}^2\cdot\text{h)}

\( J_v \) \hspace{1cm} \text{Volume flux in forward osmosis (L/m}^2\cdot\text{h)}

\( k_B \) \hspace{1cm} \text{Boltzmann’s constant (1.38 \times 10^{-23} \text{J/K})}

\( k_{eff} \) \hspace{1cm} \text{Effective mass transfer coefficient (m/s)}

\( k_s \) \hspace{1cm} \text{Solute mass transfer coefficient outside support layer (m/s)}

\( K_{m,s} \) \hspace{1cm} \text{Solute mass transfer coefficient in support layer (m/s)}

\( K_{m,t} \) \hspace{1cm} \text{Trace compound mass transfer coefficient in support layer (m/s)}

\( l_m \) \hspace{1cm} \text{Length of the support layer (m)}

\( l_r \) \hspace{1cm} \text{Length of the rejection layer (M)}

\( L \) \hspace{1cm} \text{Distance between two electrodes (m)}

\( M_f \) \hspace{1cm} \text{Foulant mass deposition per unit membrane area (kg/m}^2\)
$n$ Refraction index (-)

$R_{app}$ Apparent rejection (-)

$R_f$ Hydraulic resistance of the foulant layer (s·Pa/m)

$R_{int}$ Intrinsic rejection (-)

$R_m$ Hydraulic resistance of the membrane (s·Pa/m)

$R_g$ Universal gas constant (8.31 J/mol·K)

$R_s$ Solute rejection (-)

$R_t$ Trace compound rejection (-)

$S$ Structure parameter of support layer (m)

$T$ Temperature (K)

$v$ Flow velocity (m/s)

$V$ Electrical potential (V)

$V_0$ Amplitude of $V$ (V)

$V_s$ Molar volume of water (L/mol)

$x$ Thickness of substructure (m)

$|Z|$ Impedance modulus (Ω)

$Z_{real}$ Real part of impedance (Ω)

$Z_{img}$ Imaginary part of impedance (Ω)

**Greek Letters**

$\alpha$ Inclination angle of the observation cell (deg)

$\alpha_f$ Specific cake resistance (-)

$\beta$ Attachment coefficient (-)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$</td>
<td>Doppler angle (deg)</td>
</tr>
<tr>
<td>$\delta_{ECP}$</td>
<td>Boundary layer thickness due to ECP (m)</td>
</tr>
<tr>
<td>$\delta_{_{eff}}$</td>
<td>Effective boundary layer thickness (m)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Dielectric permittivity (F/m)</td>
</tr>
<tr>
<td>$\varepsilon_{_{m}}$</td>
<td>Porosity of support layer (-)</td>
</tr>
<tr>
<td>$\pi_{_{m}}$</td>
<td>Osmotic pressure of membrane surface (Pa)</td>
</tr>
<tr>
<td>$\pi_{_{b}}$</td>
<td>Osmotic pressure of bulk feed solution (Pa)</td>
</tr>
<tr>
<td>$\pi_{_{p}}$</td>
<td>Osmotic pressure of permeate water (Pa)</td>
</tr>
<tr>
<td>$\pi_{_{draw}}$</td>
<td>Osmotic pressure of draw solution (Pa)</td>
</tr>
<tr>
<td>$\pi_{_{feed}}$</td>
<td>Osmotic pressure of feed solution (Pa)</td>
</tr>
<tr>
<td>$\tau_{_{m}}$</td>
<td>Tortuosity of support layer (-)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Centre wavelength (m)</td>
</tr>
<tr>
<td>$\lambda_{_{m}}$</td>
<td>Thickness of support layer (m)</td>
</tr>
<tr>
<td>$\gamma_{_{m}}$</td>
<td>Wall shear (Pa)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Electric conductivity (S/m)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Phase angle of impedance (rad)</td>
</tr>
<tr>
<td>$\phi_{_{b}}$</td>
<td>Particle fraction in the bulk solution (-)</td>
</tr>
<tr>
<td>$\phi_{_{w}}$</td>
<td>Particle fraction on the membrane wall (-)</td>
</tr>
<tr>
<td>$\phi_{_{I}}$</td>
<td>Phase angle of $I$ (rad)</td>
</tr>
<tr>
<td>$\phi_{_{V}}$</td>
<td>Phase angle of $V$ (rad)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Kinetic viscosity (m²/s)</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Dynamic viscosity (Pa·s)</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency (rad/s)</td>
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</table>
CHAPTER 1

INTRODUCTION

1.1 Problem statement and motivation

Limited amount of freshwater is available for farming, industrial and domestic usages. Additional stress directly impinged on water scarcity is the continuing increase of population worldwide. A United Nations report (Nations 2012) predicts that the number of people suffering from water stress is likely to hit two billion by the beginning of the 2030s. A great deal of efforts has been put on searching for alternative and sustainable sources to obtain freshwater. For example, much interest has been drawn in obtaining freshwater from saline water owing to its vast quantities in oceans. Membrane-based filtration processes, such as reverse osmosis (RO), have been the leading technology for seawater desalination for decades. In addition to the application in desalting seawater, RO also has wide applications in wastewater reclamation. For example, Singapore’s “NEWater” programme, high quality water reclaimed from the secondary effluent from activated sludge treatment processes has taken up a portion of industrial water usage. It has also been blended with reservoir water and then gone through conventional water treatment processes to produce potable water. Though RO is commonly considered as a state-of-the-art technology, there are still some concerning issues, e.g., inevitable membrane fouling, high electricity usage and brine discharge (not in a sustainable manner, location restricted). Due to such reasons, certain research focuses have been shifted to other alternatives, i.e., osmotically driven membrane processes.

Osmotically driven membrane processes such as forward osmosis (FO) have been attracting significant attention in the fields of seawater desalination, water/wastewater treatment, water recovery from high salinity feeds and osmotic power harvest owing to its potentially lower energy consumption and the possibility of lower fouling propensity (Loeb 1976; McCutcheon et al. 2006; Holloway et al.).
Instead of utilizing an externally-applied hydraulic pressure, FO processes occur spontaneously when there is a chemical potential difference across the membrane (Cath et al. 2006). Membrane performances such as the permeate water and the solute rejection are closely associated with mass transfers. In particular, different from an RO process in which only one mass transfer coefficient on the feed side is considered, three mass transfer coefficients are of interest during an FO process, which are on the feed side (lower salinity), on the draw side (higher salinity) and within the porous support layer of an FO membrane. Previous studies (Cath et al. 2006; McCutcheon and Elimelech 2008; Tang et al. 2010) revealed that significant flux reduction can be caused by the concentration polarization (CP). CP occurring near the membrane surface known as external CP (ECP) is common in both pressure-driven and osmotically driven membrane processes and may be attenuated via hydraulic means, such as increasing the cross-flow velocity (Cath et al. 2006; Tan and Ng 2008) and using spacers (Park and Kim 2013). In contrast, more significant flux reduction can be caused by the CP across the porous FO membrane substrate, i.e., the internal concentration polarization (ICP). Further studies (Li et al. 2011; Tiraferri et al. 2011; Wei et al. 2011) also highlighted the interplay between the ICP and the complex substrate structure. It is therefore critical to develop a better understanding of the FO membrane substrate to account for the effect of ICP during FO processes.

Despite the types of the filtration processes, either pressure-driven (e.g., RO) or osmotically driven (e.g., FO), the membrane performance in terms of permeate flux and solute rejection is undermined by the coupled phenomena of CP and membrane fouling. Along with numerous studies done on trying to understand the fundamental mechanisms of mass transfers involved during CP and membrane fouling, non-invasive and in situ characterization techniques have a significant role in quantifying the physico-chemical formations. There are many state-of-the-art techniques to characterize membrane fouling, for example, direct microscopic observation through membrane (DOTM) for particulate species deposition characterization (Wang et al. 2010; Wicaksana et al. 2012; Zou et al. 2013), confocal laser scanning microscopy (CLSM) for bio-fouling assessment (Peter-
Varbanets et al. 2010; Suwarno et al. 2012), electrical impedance spectroscopy (EIS) for characterization of foulant layers (Chilcott et al. 2002; Gaedt et al. 2002; Kavanagh et al. 2009) and etc.. Techniques for characterizing and/or visualizing the dynamic processes such as CP and the growth of a foulant layer on the other hand are inadequately addressed in the literature. In addition, numerous studies revealed that the fluid hydrodynamics have crucial influence on CP development and foulant deposition as well (In Seok and Ho Nam 1982; Neal et al. 2003; Subramani et al. 2006; Wardeh and Morvan 2008; Suwarno et al. 2012). This necessitates the need to develop and to adapt novel techniques to characterize and to visualize these dynamic processes.

1.2 Scope and objectives

The primary focus of this study was to explore fundamental understanding of mass transfer mechanisms during FO and RO processes, and thereby, to develop direct approaches and to incorporate novel techniques to characterize mass transfers (i.e., CP and membrane fouling) associated with these filtration processes. The specific objectives are listed below:

(i) To develop direct approaches and to establish new models to characterize the support structures of FO membranes;

(ii) To develop a novel EIS-based approach for investigating the effects of different FO membrane substructures on CP during FO processes;

(iii) To adapt the Doppler optical coherence tomography (OCT) technique to investigate the effect of the spacer configurations on the flow patterns during a filtration process;

(iv) To explore the feasibility of using the OCT technique to visualize and to quantify the growth of a foulant layer;

(v) To investigate the effect of fluid dynamics on membrane fouling via the OCT technique.
1.3 Significance of the research

This research has significant outcomes which include,

(i) Fundamental understanding of mass transfers during FO and RO processes;

(ii) Establishment of novel and facile approaches and models to predict both ICP and ECP during an FO process;

(iii) Application of the EIS technique to characterize CPs during an FO process;

(iv) Assessment of the velocity fields on the two dimensional plane perpendicular to the membrane surface via Doppler OCT technique;

(v) Visualization and quantification of the growth of a foulant layer and investigation of the effect of fluid dynamics on membrane fouling by the OCT technique.

1.4 Dissertation overview

This thesis contains seven chapters. A brief introduction on the membrane technology and problems obstructing further advancement of the membrane processes are given in Chapter 1. It also highlights the necessity to develop novel characterization techniques to study the dynamic processes associated with mass transfers during membrane filtrations. Chapter 2 critically reviews the fundamentals of mass transfers associated with membrane processes as well as the techniques employed in the literature to characterize the mass transfers associated processes, such as CPs and membrane fouling. The major findings of this study are summarized in Chapter 7 and recommendations for the future work are also provided therein. The main results and discussion are reported in Chapters 3 - 6. Chapters 3 and 4 have been published in Desalination and Chapter 5 has been published in Journal of Membrane Science. Part of the work reported in Chapter 6 has published in Environmental Science and Technology. The contents of Chapters 3 - 6 are briefly summarized as follows:
Chapter 3 presents new experimental protocols established to characterize the porous substrate structures of FO membranes. Three methods were proposed to determine the structural parameter. Among three approaches the one relying on measuring the salt rejection demonstrated superiority. The separation property of the selective layer was also determined from this method. This approach can also be employed as a handy tool to study ECP and ICP interpretively.

Chapter 4 demonstrates the feasibility of a new EIS application to characterize FO processes. The effect of FO membrane substructures on CP was systematically studied via the EIS measurements. Various substrate structures exhibited different degrees of ICP that were clearly reflected in the impedance spectra.

In Chapter 5 a new application of Doppler optical coherence tomography was explored which was to characterize the flow patterns in a spacer-filled channel. The effect of the spacer filament orientations on the fluid hydrodynamics was systematically examined. The fluid fields normal to the membrane surface were visualized via the Doppler OCT and they were analyzed and compared for different spacer orientations.

Chapter 6 further highlights the feasibility of using the OCT technique to study the dynamic process by visualizing the growth of a foulant layer. In particular, the dynamic process was analyzed and quantified by post-processing the images recorded by the OCT system. Furthermore, the effect of fluid fields on the foulant layer formation was systematically investigated using the OTC technique.
CHAPTER 2

LITERATURE REVIEW

This chapter reviews the fundamentals of mass transfers during membrane filtration processes, especially for the forward osmosis and reverse osmosis processes. Basic principles of concentration polarizations and membrane fouling are particularly addressed and the novel techniques relevant to characterization and/or visualization of CP phenomena and membrane fouling are critically reviewed here.

2.1 Overview of membrane technology and historical moments

Membranes existing in biological cells facilitate the uptake of the nutrients and the expulsion of the waste. In an engineering perspective artificial membranes fabricated from polymeric and inorganic materials are used as a semi-permeable barrier to separate the species of interest at a micro- and/or nano-scopic level. Development of membrane science and technology can be dated back to the mid 1700s that Nollet first discovered the osmosis phenomena from a pig’s bladder in 1748 (Strathmann 2000). Some historical moments of the development of membranes and membrane-based processes are listed chronically in Figure 2.1. In particular, the application of membrane technology in water related industry has been booming during the past 50 years since Loeb and Sourirajan developed the asymmetric cellulose acetate RO membranes in early 1960s. About 10 years later, thin film composite (TFC) membrane invented by Cadotte is recognized as a major advance in the membrane technology (Fane et al. 2011) owing to significant improvements of the water flux and the solute rejection achieved by the TFC membranes. On the other hand, in virtue of the great progress made in the development of RO membranes, growing interest has also been given to the development of FO membranes (Cath et al. 2006).
1748: **Nollet** discovered the relation between a semi-permeable membrane, osmotic pressure and volume flux.

1800s

1889: **Nernst** introduced flux equation for electrolytes under concentration gradients.

1884: **van’t Hoff** introduced van’t Hoff equation that relates the changes in the equilibrium constant $K$ of a chemical reaction to the change of temperature $T$.

1855: **Fick** introduced Fick’s Law of diffusion to interpret diffusion in liquids as a function of concentration gradients and provided a thermodynamic explanation for osmotic pressure of dilute solutions.

1890: **Plank** introduced flux equation for electrolytes under electrical potential gradients.

1899: **Nernst** introduced flux equation for electrolytes under concentration gradients.

1884: **van’t Hoff** introduced van’t Hoff equation that relates the changes in the equilibrium constant $K$ of a chemical reaction to the change of temperature $T$.

1855: **Fick** introduced Fick’s Law of diffusion to interpret diffusion in liquids as a function of concentration gradients and provided a thermodynamic explanation for osmotic pressure of dilute solutions.

1900s

1982: **Bray/Westmoreland** in 1962 developed the first RO membranes for desalination and other applications that were installed in spiral wound modules.

1976: **Loeb** discussed energy production from concentrated brines by pressure-retarded osmosis (PRO).

1975: **Riley** developed the first commercial interfacial composite membrane.

1972: **Cadotte** developed the first interfacial composite membrane.

1971: **Kesting** prepared asymmetric cellulose acetate membranes based on a phase inversion method.

1966: **Merten** proposed solution-diffusion model to described membrane processes. **Brian** derived the polarization equation for RO.

1962: **Loeb & Sourirajan** developed asymmetric cellulose acetate RO membranes.

1959: **Breton & Reid** demonstrated the desalination capacity of cellulose acetate reverse osmosis (RO) membranes.

1952: **Starverman** described membrane transport properties using a comprehensive theory based on the thermodynamics of the irreversible processes.

1911: **Donna** described the theory of membrane equilibria and membrane potentials in the electrolytes.

1966: **Merten** proposed solution-diffusion model to described membrane processes. **Brian** derived the polarization equation for RO.

1962: **Loeb & Sourirajan** developed asymmetric cellulose acetate RO membranes.

1959: **Breton & Reid** demonstrated the desalination capacity of cellulose acetate reverse osmosis (RO) membranes.

1952: **Starverman** described membrane transport properties using a comprehensive theory based on the thermodynamics of the irreversible processes.

1911: **Donna** described the theory of membrane equilibria and membrane potentials in the electrolytes.

Figure 2.1 Historical moments of the development of membrane science and technology (summarized from refs. (Strathmann 2000; Baker 2012)).
2.2 Membranes, membrane modules and membrane based separation processes

Membrane is the core of filtration processes and in general it is a semi-permeable thin film allowing the passage of water yet retaining solutes or particles (Mulder 1996). As mentioned previously a major advance during the development of membrane technology is the invention of the TFC membranes which allows more water passing through while rejecting more solutes. Figure 2.2(a) presents a typical structure of a TFC RO membrane wherein a porous and non-selective polysulfone (PS) substrate is casted on top of a non-woven fabric support. The non-woven support enhances the mechanical strength of the membrane during high pressure operation (Tang et al. 2007). A very thin selective layer (hundreds of nanometers) then is formed on top of the PS substrate via interfacial polymerization (IP) (Mulder 1996). On the other hand, it is commonly known that most of the pressure driven membranes will fail during osmotically driven membrane processes owing to the fact that FO processes suffer severely from the CP phenomena, especially the CP occurring inside the porous support of the FO membrane, known as internal CP (ICP) (McCutcheon and Elimelech 2006). As a result, more and more attention has been given to fabricating FO membranes with tailored support structures for various applications though commercially available FO membranes are still limited (Wang et al. 2010; Yip et al. 2010; Wei et al. 2011; Ma et al. 2013; Wei et al. 2013). Figure 2.2(b) shows one of the most commonly used commercial FO membranes from Hydration Technologies Inc. (HTI, Albany, OR) (Wang et al. 2012). This membrane has an asymmetric structure and is made of cellulose triacetate which is embedded with polyester meshes (Jin et al. 2011). One recent study reported the first generation of TFC FO membranes newly launched from HTI (refer to Figure 2.2(c)) (Ren and McCutcheon 2014). It is evident that FO membranes have much thinner and more porous substrates comparing to RO membranes and FO membranes are mostly reinforced by the embedded polyester fabric rather than the thick non-woven fabric support for RO membranes. Consequently, the severity of CP during FO processes can be alleviated to some extent due to the characteristics of FO substrate structures.
Figure 2.2 Micrographs of (a) BW30 RO membrane, (b) commercial CTA FO membrane, and (c) commercial TFC FO membrane (reproduced from refs. (Ren and McCutcheon. 2014; Tang et al. 2007; Wei et al. 2011; Wang et al. 2012) with copyright permission).
Though numerous membranes with improved performances have been designed the challenge is how to apply these membranes in a large-scale process. It is therefore essential to incorporate membranes into modules. It is critical for membrane modules to support the membrane elements and to provide efficient flow management (Fane et al. 2011). There are four types of modules that are popular in the water industry, namely spiral wound module (SWM), plate-and-frame module, tubular module and hollow fiber module (Baker 2004) among which the SWM modules are predominant in large-scale RO and FO applications such as seawater desalination and wastewater reclamation due to the large surface to volume ratio (Xu et al. 2010; Fane et al. 2011). A schematic of a typical SWM is illustrated in Figure 2.3. Spacers present in the feed channel are essential to the SWM modules that they can be optimized in order to improve the hydrodynamic conditions and minimize the pressure drops. As a result, CPs and membrane fouling are alleviated that leads to improved membrane performances (Geraldes et al. 2004; Schwinge et al. 2004).

Figure 2.3 Schematic of a typical spiral wound membrane module (adapted from http://www.kochmembrane.com).

Pressure-driven membrane processes are well known as the state-of-the-art technologies with wide applications and they are mainly classified based on the membrane pore size and the rejection properties of certain solutes as microfiltration
(MF), ultrafiltration (UF), nanofiltration (NF) and RO. The use of RO as a viable separation process can be dated back to 1950s though the studies of osmosis or forward osmosis have a history of more than two hundred years (Strathmann 2000; Greenlee et al. 2009). FO is a membrane process that utilizes natural osmotic pressure of a concentrated draw solution to extract pure water from a less concentrated feed stream. This is because water will naturally diffuse from a region of high water chemical potential to a region of low water chemical potential. Another interesting topic that is considered as the intermediate process between FO and RO, known as pressure-retarded osmosis (PRO), has also drawn much attention during the past few decades. A number of work done in 1960s investigated FO and PRO which were considered to have a promising future in the field of water treatment and energy harness from a mixture of dilute and concentrated brine (Loeb 1976; Cath et al. 2006; Holloway et al. 2007; Xu et al. 2010; Garcia-Castello and McCutcheon 2011; She et al. 2012). Figure 2.4 elucidates patterns of the water flow in three aforementioned membrane processes. First, for FO the applied pressure $\Delta P$ is approximately zero as the driving force in this scenario is the chemical potential difference across the membrane. For a PRO process, the direction of the water transport is the same as in an FO process but this process is subjected to a positive pressure ($\Delta \pi > \Delta P$, where $\Delta \pi$ is the osmotic pressure difference across the membrane). As for RO, water diffuses to the side with less saline under an additional hydraulic pressure ($\Delta \pi < \Delta P$).
2.2 Mass transfer during membrane processes

Membrane performances in terms of permeate flux and solute rejection are determined by the synergetic effect of the mass transfer across the membrane (Section 2.2.1) as well as that toward a membrane surface (Section 2.2.2).
2.2.1 Transport models for non-porous membranes

The mathematical description of the permeation in all membranes is based on thermodynamics. The driving forces of pressure, temperature, concentration and electromotive force are all interrelated. The net driving force of the permeate movement is the gradient following its chemical potential. The most general form of mass transport, the flux $J_i$ of a component $i$ through a membrane can be expressed as (Strathmann 2000; Baker 2004)

$$J_i = -L_i \frac{d\mu_i}{dz}$$  \hspace{1cm} (2.1)

where $J$ is the flux, $L$ is the general permeability coefficient, the term $\frac{d\mu}{dz}$ denotes the general expression of the driving force and the subscript $i$ represents a certain component.

This general form of mass transfer can be further expressed by different laws owing to the difference in the transport mechanisms of a certain component through a membrane, noted as convection, diffusion and migration (Strathmann 2000). Convection is a movement of mass due to a mechanical force generally a hydrostatic pressure difference and is described by the Hagen-Poiseuille law (a.k.a., the pore-flow model). Diffusion is a flux of molecular component due to a local gradient in the chemical potential and is described by the Fick’s law. Migration is a movement of ions due to an electrical potential gradient and is given by the Ohm’s law. A brief summary of the mass transfer models based on different driving forces is provided in Figure 2.5. The phenomenological Darcy’s law is applicable to both porous and nonporous membranes, in particular, for RO membranes it is often expressed as (Fane et al. 2011)

$$J_v = \frac{\Delta P - \Delta \pi}{\eta R_m}$$  \hspace{1cm} (2.2)

where the term $(\Delta P - \Delta \pi)$ represents the net driving force, $\eta$ is the dynamic viscosity of water and $R_m$ is the hydraulic resistance experienced by the membrane.
Factors such as membrane structures and properties are not reflected in the Darcy’s law owing to the fact that it treats the membrane as a ‘black box’. On the other hand, solution-diffusion model is usually employed to rationalize RO processes. This model is closely linked to the membrane properties and it is developed based on the assumptions that both the solvent (e.g., water) and the solute (e.g., salt) are first absorbed into the selective layer through which they diffuse independently under their respective chemical potential gradients. The permeate flux and solute flux are proportional to the net driving force ($\Delta P - \Delta \pi$) and the concentration difference across the active layer of the membrane ($C_m - C_r$), respectively, and they are expressed as (Baker 2004).
\[ J_v = A(\Delta P - \Delta \tau) \]  
\[ J_s = B_s \left( C_m - C_p \right) \]

where \( A \) and \( B_s \) are the water and solute permeability coefficients, respectively. \( C_m \) and \( C_p \) are the solute concentrations near the membrane surface and that of the permeate stream, respectively, and to be noted that \( C_m \) is usually an unknown parameter and \( C_p \) is determined by the ratio of the solute flux to the water flux \( \left( C_p = \frac{J_s}{J_v} \right) \). More specifically, the two permeability coefficients can be presented in terms of membrane properties, that \( A = \frac{D_v C_v V_v}{R_g T l_a} \) and \( B_s = \frac{D_s k_t}{l_a} \), respectively (Fane et al. 2011), where \( D_v \) and \( D_s \) are the diffusion coefficients of the water and the solute, respectively, \( C_v \) is the water concentration in the active layer, \( V_v \) is the water molar volume, \( R_g \) is the universal gas constant, \( T \) is the temperature, \( l_a \) is the thickness of the active layer and \( k_t \) is the solute mass transfer coefficient.

Different from porous membranes such as MF and UF, of which the rejection is mainly based on a sieving mechanism, the selectivity of an RO membrane is based on the solution-diffusion mechanism and is evaluated using the membrane rejection (Mulder 1996). The intrinsic rejection \( R_{int} \) is defined as

\[ R_{int} = 1 - \frac{C_p}{C_m} \]  

As discussed previously that most of the time \( C_m \) is not known, therefore, in practice apparent rejection \( R_{app} \) is more commonly used to evaluate the selectivity of an RO membrane that

\[ R_{app} = 1 - \frac{C_p}{C_b} \]
where $C_b$ is the concentration of the bulk feed solution.

Similar to the pressure-driven processes, the water and solute transports during an FO process are modeled based on the solution-diffusion model coupled with the diffusion-convection transport within the substrate of the FO membrane (Tang et al. 2010). Due to the characteristics of the FO processes such as the inherent presence of ICP, more details on the mass transfers during FO will be addressed in Section 2.2.2.

### 2.2.2 Concentration polarization

#### 2.2.2.1 CP during an RO process

During an RO filtration process, the solute concentration near the membrane surface ($C_m$) is usually higher than that of the bulk solution ($C_b$). This is because when water is permeating through the membrane while the solute is retained by the selective layer leading to a concentration build-up adjacent to the membrane surface (Mulder 1996; Sablani et al. 2001). This is considered as external concentration polarization that is undesirable owing to the reduced effective driving force (refer to Equation (2.3), osmotic pressure difference $\Delta\pi$ increases). When a steady state is reached, the rate of the transport of the solute by the water flux (difference in the solute flux brought towards the membrane, $J,C$ due to convection and the solute flux through membrane, $J,C_p$) shall be balanced with the solute diffused back to the feed solution $D \frac{dC}{dx}$. A schematic of CP during an RO process is described in Figure 2.6.
Figure 2.6 Schematic of concentration polarization during an RO process (adapted from ref. (Sablani et al. 2001) with copyright permission).

The mass balance of this process described in a mathematical way is

\[ J_v C - J_v C_p = D \frac{dC}{dx} \]  \hspace{1cm} (2.7)

with two boundary conditions that at the bulk solution and boundary layer interface \((x = 0)\), \(C = C_b\) and at the boundary layer and membrane surface interface \((x = \delta)\), \(C = C_m\), Equation (2.7) can be solved that

\[ \frac{C_m - C_p}{C_b - C_p} = \exp \left( \frac{J_v}{D_s \frac{\delta}{\gamma}} \right) \]  \hspace{1cm} (2.8)

Recognizing that the ratio of \(\frac{J_v}{D_s \frac{\delta}{\gamma}}\) defines the Péclet number. It is also worth noting that \(D_s \frac{\delta}{\gamma}\) is commonly known as the mass transfer coefficient \(k_s\) and can be
determined by relating the Sherwood number \((Sh)\) to the Reynolds number \((Re)\) and the Schmidt number \((Sc)\) (Gekas and Hallström 1987; Schock and Miquel 1987)

\[
Sh = \frac{k_s d_h}{D} = const \cdot Re^a Sc^b \tag{2.9}
\]

where \(d_h\) is the hydraulic diameter, Reynolds number and Schmidt number can be determined from \(Re = \frac{d_h \nu}{\nu}\) and \(Sc = \frac{\nu}{D}\), and \(\nu\) is the flow velocity while \(\nu\) is kinetic viscosity of the solution.

Equation (2.8) is the classical film model derived by Brian and it describes the boundary layer. The left hand side of the equation is commonly termed as the CP modulus. It is obvious that the degree of CP is enhanced with an increase in the permeate flux \((J_v)\) and/or and a decrease in the mass transfer coefficient \((k_v)\). A series of Sherwood numbers is reported in the literature that describes the mass transfer correlations based on various conditions, such as the flow region (laminar or turbulent), the channel geometry (with or without spacer) and even the spacer geometry (diamond or ladder) (van den Berg et al. 1989; Da Costa et al. 1991; Tang et al. 2011). It is therefore difficult to precisely select a relationship that can accurately describe a particular system.

### 2.2.2.2 CP during an FO process

In contrast to RO that only one mass transfer coefficient is considered, there are three mass transfer coefficients of particular interest for an FO process (Tan and Ng 2008; Xiao et al. 2012; Field and Wu 2013). First, both sides of the FO membrane experience ECP regardless of membrane orientations. This is known as concentrative ECP and dilutive ECP (Cath et al. 2006; McCutcheon and Elimelech 2006; Tan and Ng 2008). Taking the membrane orientation of the active-layer-facing-feed-solution (AL-FS, a.k.a., the FO mode) for example, concentrative ECP is analogous to the CP occurring during an RO process and it takes place as a result of water permeating through the membrane while leaving solutes behind.
Meanwhile, the draw solution at the permeate side of the membrane is being diluted by the permeate water. This is often known as the dilutive ECP (Cath et al. 2006). Numerous studies suggest that the decreased effective osmotic driving force due to ECP can be minimized by increasing the cross-flow velocity and/or providing turbulent promoters such as spacers at the membrane surface (Gekas and Hallström 1987; Tan and Ng 2008; Tang et al. 2010; Jin et al. 2011; Xiao et al. 2012; Zhao et al. 2012). On the other hand, CP occurring within the support layer of an FO membrane is commonly known as internal CP (ICP) which is more detrimental to the FO processes. There are two phenomena of ICP depending on which membrane orientation is used. In Figure 2.7(a) if the active layer faces the feed solution (AL-FS, a.k.a., the FO mode), as the water permeates through the active layer, the draw solution in the porous substrate is diluted and this is known as the diluted ICP. Figure 2.7(b) shows the opposite orientation in which the selective layer of the membrane is facing the draw solution (AL-DS, a.k.a., the PRO mode). As the feed solution (both water and solutes) transporting through the porous layer, a polarized layer is established along the interior of the dense active layer and such phenomenon is known as concentrative ICP.

![Diagram of concentrative ICP and dilutive ICP during FO processes](image)
The permeate flux during an FO process accounting for both ECP and ICP is given by (Xiao et al. 2012; Field and Wu 2013)

\[
J_v = \left( \frac{1}{k_{\text{feed}}} + \frac{1}{K_{m,s}} + \frac{1}{k_{\text{draw}}} \right)^{-1} \ln \left( \frac{A\pi_{\text{draw}} + B_v}{A\pi_{\text{feed}} + B_v + J_v \exp \left( -\frac{J_v}{k_{\text{feed}}} \right)} \right) \quad \text{(AL-FS) (2.10)}
\]

\[
J_v = \left( \frac{1}{k_{\text{feed}}} + \frac{1}{K_{m,s}} + \frac{1}{k_{\text{draw}}} \right)^{-1} \ln \left( \frac{A\pi_{\text{draw}} + B_v - J_v \exp \left( J_v/k_{\text{draw}} \right)}{A\pi_{\text{feed}} + B_v} \right) \quad \text{(AL-DS) (2.11)}
\]

where \( k_{\text{feed}} \) and \( k_{\text{draw}} \) are the mass transfer coefficients on the feed and draw sides, respectively. \( \pi_{\text{feed}} \) and \( \pi_{\text{feed}} \) are the osmotic pressures of the feed and draw solutions, respectively. \( K_{m,s} \) represents the mass transfer coefficient of the porous support layer which is given by (Tang et al. 2010; Li et al. 2011)

\[
K_{m,s} = \frac{D_s}{S} \quad \text{(2.12)}
\]

where \( D_s \) is the diffusion coefficient inside the porous support and \( S \) is termed as the structural parameter correlating to the intrinsic properties of the support structure of an FO membrane, i.e., thickness \( l_m \), porosity \( \varepsilon_m \) and tortuosity \( \tau_m \) (Tang et al. 2010; Yip et al. 2011)

\[
S = \frac{l_m \tau_m}{\varepsilon_m} \quad \text{(2.13)}
\]

Equations (2.12) and (2.13) suggest that the \( S \) value reflects the severity of the ICP. A smaller \( S \) is desired as a higher \( K_{m,s} \) value can be obtained. Therefore, the \( S \) value has been commonly employed by researchers as it sets the standards for FO membrane fabrications that thinner and more porous support structures with less tortuous pores are favored (Tang et al. 2010; Wei et al. 2011). In addition to a
smaller $S$ value, a very thin skin layer with high water permeability while low solute permeability is also a key to achieve good performances of FO membranes (Wang et al. 2010). Most commonly adopted approach to obtain the $S$ value is to fit the FO permeate flux using the classical ICP models (modified versions of Equations (2.10) and (2.11) that neglects the effect of ECP).

$$J_v = \frac{D_s}{S} \ln \left[ \frac{A\pi_{\text{draw}} + B_s}{A\pi_{\text{feed}} + B_s + J_v} \right] \quad (\text{AL-FS}) \quad (2.14)$$

$$J_v = \frac{D_s}{S} \ln \left[ \frac{A\pi_{\text{draw}} + B_s - J_v}{A\pi_{\text{feed}} + B_s} \right] \quad (\text{AL-DS}) \quad (2.15)$$

where the water permeability coefficient $A$ and the solute permeability coefficient $B_s$ are obtained beforehand in an RO testing mode.

As discussed previously in an FO process the hydraulic pressure is nearly zero or in most cases rather low pressure is required thus the fouling induced by ECP has less significant effect on water flux in contrast to the pressure-driving membrane processes (McCutcheon et al. 2006). The presence of ICP leads to severe reduction in the osmotic pressure gradient across the active layer of the membrane. Thus the permeate water flux declines (Tang et al. 2010). As ICP occurs within the membrane porous support layer, water flux decline cannot be mitigated by optimizing the hydrodynamic conditions. Consequently, a lot of effort has been devoted to FO membrane fabrications with tailored support structures that minimize the adverse effects of ICP (Wei et al. 2011; Yip et al. 2011; Ma et al. 2013).

### 2.2.3 Membrane fouling

Membrane fouling is defined as the deposition of undesired materials (contaminants) on the membrane surface and/or inside the membrane pores (Greenlee et al. 2009; Fane et al. 2011). It is commonly categorized as (i) scaling of insoluble salts, (ii) inorganic colloids/particulates, (iii) organic compounds and
(vi) microorganisms and/or bio-film (Baker 2004). CPs and membrane fouling are closely tied with each other that severe CPs may accelerate membrane fouling because the region in the proximity to the membrane surface experiences a higher foulant concentration. Nonetheless, the porous cake layer formed on the membrane surface will trap solutes which are rejected by the active layer. Consequently, this leads to a severe CP in the unstirred cake layer. This phenomenon is known as the cake enhanced concentration polarization (CECP) effect which is common in RO membrane fouling (Hoek and Elimelech 2003; Chong et al. 2007; Chong et al. 2008).

With regards to fouling mechanisms, it is sometimes classified as the accumulation of solutes and particles on the membrane surface and plugging the membrane pores. Here attention will be given to the particle deposition and/or the cake formation which are more commonly seen in the so-called non-porous membrane processes (e.g., RO) (Schwinge et al. 2002; Greenlee et al. 2009). In the presence of membrane fouling additional resistance occurs, leading to reduced water flux. The Darcy’s law is thereby expressed as

\[ J_v = \frac{\Delta P - \Delta \pi}{\eta (R_m + R_f)} \]  

(2.16)

where \( R_f \) is the additional hydraulic resistance introduced by the foulant.

The resistance of the cake layer is proportional to the foulant mass deposited on the membrane surface per unit membrane area \( (M_f) \) that is \( R_f = \alpha_f M_f \), where \( \alpha_f \) is the specific cake resistance and it is a strong function of properties of the foulant particles (i.e., particle size and density) and the foulant layer as well (i.e., porosity). It is worth noting that in a cross-flow filtration system, only a portion of the total mass load deposits on the membrane surface. Therefore, an attachment coefficient (\( \beta \)) is used to better describe the particle deposition that

\[ M_f = \beta C_{b,f} \int_0^t J_v dt \] where \( C_{b,f} \) denotes the foulant concentration in the bulk
solution (Hong and Elimelech 1997; She et al. 2009). Therefore, the rate of fouling can be related to the rate of the foulant mass deposits per unit membrane area,

\[
\frac{dm_f}{dt} = \beta J v_b f d\mu JC dt \beta
\]  

(2.17)

Tang et al. presented a comprehensive review on colloidal fouling of NF and RO membranes (Tang et al. 2011). It suggests that colloidal fouling is closely associated with three aspects, (i) composition of the feed solution, (ii) membrane properties, and (iii) hydrodynamic conditions. There are two stages of interest regarding the dynamic fouling process that the foulant particles first transport from the bulk solution toward the membrane surface and then start to attach to that surface. As illustrated in Figure 2.8 particles are brought toward the membrane surface due to the permeate flux, at the same time they are dragged away in the axial direction due to the cross flow. A portion of the particles also transports back to the bulk solution.

Figure 2.8 Forces and torques acting on a charged spherical particle suspended in a viscous fluid undergoing laminar flow in the proximity of a flat porous surface. This figure is adapted from ref. (Yoon et al. 1999) with copyright permission.
The particle transport mechanisms have been well studied and summarized in the literature (Belfort et al. 1994; Bowen and Jenner 1995; Altmann and Ripperger 1997; Sablani et al. 2001; Tang et al. 2011). Briefly, four mechanisms are of significant importance and they are dominant at various particle sizes (Tang et al. 2011).

- Brownian diffusion has strong influence on smaller particles with a diameter \( (a_p) \) typically less than 0.1 μm. The flux is described by (Trettin and Doshi 1980),

\[
J = 1.31 \left( \frac{\gamma_w D_{Br}^2}{L} \cdot \frac{\phi_w}{\phi_b} \right)^{1/3}
\]

where \( D_{Br} \) is the Brownian diffusion coefficient and is described as \( D_{Br} = \frac{k_B T}{6 \pi \mu a_p} \), \( k_B \) is the Boltzmann’s constant, \( T \) is the temperature, \( \gamma_w \) is the wall shear rate and \( L \) denotes the length of the channel. \( \phi_w \) and \( \phi_b \) are particle fractions at the membrane wall and in the bulk, respectively.

- Shear-induced diffusion based mechanism describes the particles \( (a_p > \sim 0.2 \, \mu m) \) move randomly along the streamlines in a shear flow as there is an interaction between the particles. The modeled flux is (Zydney and Colton 1986)

\[
J = 0.078 \gamma_w \left( \frac{a_p^4}{L} \right)^{1/3} \ln \left( \frac{\phi_w}{\phi_b} \right)
\]

- Inertial lift leads to the lateral migration of the particles with a relatively large size \( (a_p > \sim 10 \, \mu m) \) and the flux based on this model is expressed as (Drew et al. 1991)

\[
J = 0.036 \frac{\rho a_p^3 \gamma_w^2 \gamma_w}{\mu}
\]
In addition to the mechanisms listed above, another concept closely associated with membrane fouling is the critical flux. It was brought up in 1995 that three studies were published on this topic (Bacchin et al. 1995; Field et al. 1995; Howell 1995). It basically defines the critical flux as the flux level below which no decline in flux is observed whereas above which fouling occurs. A critical review on this topic is given by Bacchin et al. (Bacchin et al. 2006). This concept has been successfully applied in membrane processes for fouling control and process optimization. On one hand, by operating the filtration process below the critical flux, severe fouling can be potentially avoided (Schwinge et al. 2002; Tang et al. 2011). On the other hand, by enhancing the mass transfers such as increasing the cross-flow velocity and employing a feed spacer, the critical flux can be increased thereby and as a result, the productivity of the permeate is increased (Chong et al. 2007).

2.3 Characterization techniques to study CPs and membrane fouling

As discussed in the previous sections that CPs and/or membrane fouling are inevitable in both pressure-driven (e.g., RO) and osmotically driven membrane processes (e.g., FO). As a result, characterization techniques play a crucial role in assisting researchers to better understand the mechanisms of fouling and CP phenomena. Specifically, the major targets of the characterization include (i) membrane structures, (ii) fluid dynamics in a channel during a filtration process and (iii) other dynamic processes such as membrane fouling. Along with the development and advancement of membrane science and technology, characterization techniques focusing on visualizing membrane structures are well developed and widely applied. According to the literature most commonly used characterization techniques are electron microscopy based approaches (Tang et al. 2007; Wang et al. 2010; Tiraferri et al. 2011; Wei et al. 2011) and optical microscopy based techniques such as confocal laser scanning microscopy (CLSM) (Charcosset and Bernengo 2000; Suwarno et al. 2012; Wang et al. 2012). Though these methods can provide clear micrographs of the structures of the membranes and the foulant layer, they are only applicable to characterize the membrane
coupons at a post-filtration stage in most cases. Details such as the subtle interplay between the membranes and the dynamic filtration processes (e.g., the growth of a cake layer) remain unknown. As a result, there is an urge to develop novel techniques and/or to modify existing techniques which are tailored for characterizing the dynamic processes during the membrane filtration (Chen et al. 2004b). These characterization techniques are also labeled as ‘non-invasive’ and/or ‘in situ’ that can quantify and/or visualize the physico-chemical processes during the course of the membrane filtration (Chen et al. 2004a; Chen et al. 2004b).

2.3.1 Techniques for characterization of membrane structures

Membrane structures are closely associated with mass transfers especially for the osmotically driven membrane processes (e.g., FO/PRO) during which the membrane performance is adversely affected by the presence of ICP. ICP is a strong function of the membrane porous support structures (Wei et al. 2011; Wang et al. 2012). Microscopic techniques are most commonly employed to characterize membrane structures (Wang et al. 2010; Fane et al. 2011; Wang et al. 2012).

Wang and co-workers (Wang et al. 2012) employed confocal laser scanning microscopy (CLSM) to perform quantitative/semi-quantitative analysis of the pore structures of the FO support layer by imaging the membrane samples stained with the fluorescent dye. With this technique the depth-dependent pore size distribution can be obtained. This work also offers a comprehensive comparison of the porosity characterization methods, CLSM versus conventional approaches, i.e., TEM, SEM and dry-wet weighing method.

In addition to two dimensional characterizations of the membrane structure, there is increasing attention drawn to the characterization techniques which are able to acquire three dimensional information of the membrane structure. In particular, it allows acquisition of the spatial information such as the depth dependent porosity distribution and the interconnectivity of the membrane pores (Manickam et al. 2014). This kind of information plays a significant role in mass transfers during
filtration processes. It also allows a precise description of the pore morphology that is helpful to the membrane fabrication processes.

Manickam and co-workers demonstrated 3D reconstruction of the TFC RO membranes with the aid of the X-ray tomography (XRT) and a direct calculation of the structural parameter was also given based on the independent assessment of the porosity, the tortuosity and the thickness of the TFC membrane (Manickam et al. 2014). They also proposed that XRT is applicable to determine the interface between two layers. Viguié et al. demonstrated the use of XRT to characterize 3D macrostructures of the hollow fiber membranes (Viguié et al. 2013). They reported different processing conditions led to macrovoids with distinct morphologies. 3D reconstruction was also performed on the MF membranes via environmental SEM (ESEM) (Reingruber et al. 2011; Poelt et al. 2012). They were able to obtain the quantitative results (e.g., the volume porosity, the pore connectivity and etc.) from the 3D reconstruction of the membrane structures. It is unable to get quantitative results from simple 2D characterization. They also implied it might be possible to simulate the flow path of the fluid through the membrane with the technique (Reingruber et al. 2011).
Figure 2.9 3D reconstruction of the membrane structures via (a) and (b): X-ray tomography (XRT), and (c) environmental scanning electron microscopy (ESEM) (adapted from refs. (Manickam et al.; Reingruber et al. 2011; Viguié et al. 2013) with permission from Elsevier).
Another well developed characterization technique is electrochemical impedance spectroscopy (EIS). Different from the microscopic based techniques, EIS works on the basis that the impedance measurement can be related to the elements of the system using the Maxwell-Wagner model (Coster et al. 1996). EIS is based on the electrochemical relaxations related to the intrinsic properties of the systems of interest (Coster et al. 1996; Benavente 2005). It can potentially reveal the structural features of the order of a Debye length (Chilcott et al. 2002; Gaedt et al. 2002). The membrane – electrolyte system can be considered as a ‘black box’, by applying a small alternating current of known frequency $\omega$ and small amplitude $i_0$, the voltage and phase difference can be measured. The magnitude of the impedance can then be determined. The impedance is expressed in a complex form and it is a function of the conductance $G$, the capacitance $C$ and the angular frequency $\omega$. One convenient approach to study such system is to use equivalent circuits as models. For a homogeneous material it can be modeled as a parallel pathway of $G$ and $C$. Conductance and capacitance describe to what extent the homogeneous material can conduct and store electric charges, respectively (Coster et al. 1996). Here in the context of the EIS approach, the generalized forms of $G$ and $C$ can provide estimations which can be mapped with the physical geometries of the material of interest, from which information such as the thickness, the porosity and etc. can be determined (Kinzi 1990; Coster et al. 1996; Benavente 2005). Figure 2.10(a) gives an example of a UF membrane-electrolyte system and Figure 2.10(b) presents the equivalent circuits adopted to study this system. Some pioneer work of applying the EIS technique to study the pressure-driven membrane processes has been done by Coster and co-workers (Coster et al. 1996) in 1990’s. They employed EIS to probe the biological membranes and interfaces. In early 2000’s EIS-based characterization techniques were extended to study both porous and non-porous membrane structures (Kinzi 1990; Kinzi 1990; Hanai et al. 1991; Chilcott et al. 2002; Gaedt et al. 2002; Benavente 2005).
2.3.2 Techniques for characterization of fluid dynamics in a membrane channel

According to the literature the performance of a membrane is significantly limited by the presence of CPs and membrane fouling. Consequently, decrease in the permeate water and the solute rejection can be observed (Field et al. 1995; Hoek and Elimelech 2003; Le-Clech et al. 2006; Chong et al. 2008; Li et al. 2009; Lee et al. 2010; Tang et al. 2010; Tang et al. 2011; Wang and Tang 2011). Optimization of the hydrodynamic environment is considered as one of the most commonly used approaches to tackle problems like CPs and fouling (Sablani et al. 2001; Lau et al. 2009; Balster et al. 2010; Xiao et al. 2012; Xie et al. 2014). The effective boundary layer thickness is minimized by increasing the degree of turbulence in the vicinity of the membrane surface. This will lead to the enhanced mass transfers (In Seok and Ho Nam 1982; Da Costa et al. 1991; Cao et al. 2001; Balster et al. 2006;
The turbulence is commonly promoted in such a fashion that various types of spacers are installed in the feed channel (Schwinge et al. 2000; Geraldes et al. 2002; Li et al. 2004; Li et al. 2005; Balster et al. 2006; Fimbres-Weihs et al. 2006; Liu et al. 2013). A summary of different spacer studies reported in the literature and their major approaches of characterization are given in Table 2.1. The net-type spacer is commonly used in the spiral wound membrane modules and there are also novel types of spacers developed in order to enhance the mass transfers during the filtration processes (Gekas and Hallström 1987; Schwinge et al. 2004; Fimbres-Weihs and Wiley 2010). It is believed that the characteristics of the spacer (e.g., physical properties, filament arrangements and etc.) have profound influence on mass transfers during the filtration processes (Da Costa et al. 1991; Cao et al. 2001; Schwinge et al. 2004). Da Costa et al. examined a series of net-like spacers with different characteristic angles (Da Costa et al. 1991). They reported that with the presence of spacer the UF flux was enhanced meanwhile the pressure loss was also apparent. It was also observed that the spacer characteristics have influence on the membrane performance. Both permeate flux and pressure drop increased with the characteristic angle. Geraldes and co-workers investigated the effect of the ladder-type spacer in context of an NF process (Geraldes et al. 2002). They found that the concentration profiles near two membrane surfaces were distinct. The average CP near the membrane without the transverse filaments attached to the membrane surface increased with the channel length. In contrast, the average CP was independent of the channel length for the other side with direct contact of the transverse spacer filaments.
Table 2.1 Summary of various types of spacers.

<table>
<thead>
<tr>
<th>Spacer type and schematic</th>
<th>Main characterization method</th>
<th>Refs.</th>
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<tbody>
<tr>
<td><strong>Net</strong></td>
<td>CFD; direct numerical simulation</td>
<td>(Da Costa <em>et al.</em> 1991; Karode and Kumar 2001; Koutsou <em>et al.</em> 2007; Li and Tung 2008; Koutsou <em>et al.</em> 2009)</td>
</tr>
<tr>
<td><strong>Ladder</strong></td>
<td>CFD</td>
<td>(Geraldes <em>et al.</em> 2002; Geraldes <em>et al.</em> 2004)</td>
</tr>
<tr>
<td><strong>Multilayer</strong></td>
<td>CFD; experimental (evaluation of energy consumption)</td>
<td>(Balster <em>et al.</em> 2006; Fimbres-Weihs and Wiley 2008)</td>
</tr>
</tbody>
</table>
CHAPTER 2

Zigzag CFD; experimental (evaluation of membrane performance) (Schwinge et al. 2000; Fimbres-Weihs et al. 2006)

Sinusoidal CFD; experimental (evaluation of membrane performance) (Xie et al. 2014)

Integrated Experimental (evaluation of membrane performance) (Balster et al. 2010)
In virtue of development and advancement of numerical methods, computational fluid dynamics (CFD) has been widely employed as a handy tool to study the subtle interplay between the fluid and the spacer filaments (Cao et al. 2001; Schwinge et al. 2002; Ghidossi et al. 2006; Fimbres-Weihs and Wiley 2010). With such a more sophisticated approach information like the effects of the spacer filament configurations on the pressure drop along the membrane (Karode and Kumar 2001; Shakaib et al. 2009; Saeed et al. 2012), the velocity and the local shear stress distributions (Cao et al. 2001; Ahmad et al. 2005; Shakaib et al. 2009; Saeed et al. 2012), the concentration profiles (Ahmad et al. 2005; Park and Kim 2013; Xie et al. 2014) and the flow visualization in both 2D (Cao et al. 2001; Schwinge et al. 2003; Dendukuri et al. 2005; Fimbres-Weihs et al. 2006) and 3D (Karode and Kumar 2001; Fimbres-Weihs and Wiley 2007; Koutsou et al. 2007) contexts can be revealed.

Though CFD assisted approaches can provide interesting and sophisticated information and important implications for spacer designs and process optimizations, yet only a handful of direct experimental validations of the simulation results is available in the literature, especially the direct visualization of the fluid fields, which can be particularly important in bridging the gap between the model prediction and the experimentally measured mass transfers (e.g., the solute rejection, the permeate flux, the pressure drop, and etc.) (In Seok and Ho Nam 1982; Da Costa et al. 1991; Da Costa et al. 1994). Gaucher et al. employed the particle image velocimetry (PIV) technique to study the hydrodynamics in a UF module (Gaucher et al. 2002). The velocity field can be measured instantaneously by measuring the relative displacements (between two consecutive frames of images) of the tracer present in the fluid. The measurements are achieved by analyzing the images recorded by a digital camera with high resolutions. They showed the wall shear stress can be affected by factors such as the flow velocity, the channel height and the locations of the inlet and the outlet. Later, Gimmelshtein and co-workers applied the PIV technique to study the flow in the vicinity of the membrane wall in a spacer-filled channel (Gimmelshtein and Semiat 2005). They measured the velocity profile of a single phase flow within a spacer unit cell by using the setup shown in Figure 2.11. Willems et al. further developed the PIV method to study the
two-phase flow (i.e., liquid and gas) in the spacer-filled channels (Willems et al. 2010). Although the PIV technique is proved as a viable and non-destructive tool to study the fluid dynamics in the spacer-filled channels, it is only able to reveal the hydrodynamic information in the plane parallel to the membrane surface. Other important information such as the velocity profile along the plane perpendicular to the membrane surface is still undetectable.

Figure 2.11 PIV incorporated filtration system. This figure is reproduced from ref. (Gimmelshtein and Semiat 2005) with copyright permission.
Figure 2.12 Velocity maps of four successive frames of a bubble (the air phase) moving through a unit cell due to the flow (the liquid phase) in comparison with the velocity field of a single phase undisturbed flow. This figure is adapted from ref. (Willems et al. 2010) with copyright permission.
2.3.3 Techniques for characterization of membrane fouling

As discussed in Section 2.2.3, the main fouling mechanism for the non-porous membranes is the accumulation of solutes and particles on the membrane surface. Review on the fouling characterization techniques is therefore focused on those which are relevant to visualize and/or monitor the dynamic particle depositions and the cake layer build-up on the membrane surface.

Visualization of the foulant deposition and accumulation can offer an in-depth understanding of the complex interactions between the foulants, the fluid and the membrane structures during filtration processes. A major group of characterization techniques that can visualize the foulant deposition is optical based techniques, such as the direct observation through membrane (DOTM) technique (Chen et al. 2004b). This technique has been extensively applied to observe the particle deposition in the low pressure membrane processes (Li et al. 1998; Li et al. 2003; Wicaksana et al. 2012). In recent years, the DOTM technique has also been explored in the context of fouling observation during an FO process (Wang et al. 2010; Zou et al. 2013).

As depicted in Figure 2.13 the DOTM facility usually consists of an optical microscope on which a video camera is attached to record images. In terms of membrane applications, the objective lens is mounted above a cross-flow filtration cell. The cross-flow cell is modified by replacing the side close to the camera by a clear glass for the purpose of direct observation (Chen et al. 2004b). It is reported that for particles with a size greater than 1 μm they can be easily captured (Chen et al. 2004b) by the DOTM system. Researchers also coupled this technique with fluorescent components so as to improve the image resolution to identify submicron bacterial cells (Li et al. 2003).
Figure 2.13 (a) A cross-flow MF system incorporated with DOTM apparatus and (b) basic components of a DOTM apparatus (adapted from refs. (Li et al. 1998; Li and Fane 2000) with copyright permission).

With DOTM and its related techniques it is able to gain a better understanding and deeper insights of how the feed solutions interact with the membranes. In particular, it can provide valuable information on the particle transport, deposition and accumulation at the membrane-solution interface under various operating conditions. Li and co-workers employed a DOTM system incorporated with a fluorescent microscope to investigate the deposition and
removal of bacteria cells during an MF process (Li et al. 2003). It is suggested that the integrated DOTM system was more sensitive in terms of early fouling detection compared to monitoring the change of the TMP profile. Wicaksana et al. also had similar findings that they applied the DOTM facility to study the algae deposition during the MF processes (Wicaksana et al. 2012). The deposition rate of the microalgae increased with a decreased cross-flow velocity. In addition, they found it is possible to completely remove the algae layer by applying bubbling to the system. Wang et al. (Wang et al. 2010) and Zou et al. (Zou et al. 2013) also applied this technique to study the FO membrane systems fouled by the latex particles (3 μm) and the microalgae, respectively (Wang et al. 2010; Zou et al. 2013). Both studies suggested that the feed spacer had a positive effect on the FO permeate flux. Neal and co-workers also used the DOTM technique to investigate the effect of the spacer orientations on the critical flux as well as the latex particle deposition (Neal et al. 2003). This work was to simulate an SWM operating environment. They first confirmed that the critical flux of 6 μm latex particles can be enhanced by about two times in the presence of the net-like feed spacer. They further investigated how the spacer orientations affected the patterns of the particle deposition and the improvement of the critical flux. Distinct particle deposition patterns were observed under various filament orientations (refer to Figure 2.14). Huang et al. extended the scope of DOTM characterization to a high pressure operating environment to visualize the incipient deposition of the bacterial cells (Huang et al. 2010).

Though DOTM and derivative techniques are proved as a viable tool to study and to validate the particle transport and deposition at the membrane-solution interface, it is restricted to a 2D characterization of the plane parallel to the membrane surface (Chen et al. 2004b). It is not able to reveal the information on the plane perpendicular to the membrane surface such as the cake layer thickness, which is considered very important in order to understand the mass transfers in the boundary layer. In addition to this limitation, most of the DOTM applications require the membranes to be transparent (Chen et al. 2004b; Wang et al. 2010).
Figure 2.14 Patterns of the latex particle deposition under different spacer orientations (i) 0°, (ii) 90° and (iii) 45° (adapted from ref. (Neal et al. 2003) with copyright permission).
To address the limitation of the DOTM technique, that it is unable to reveal valuable information in the plane normal to the membrane surface, researchers also explored other techniques to fill this blank. Derlon et al. investigated the development of the biofilm structures in a gravity-driven membrane system with the aid of two optical techniques, confocal laser scanning microscopy (CLMS) and optical coherence tomography (OCT) (Derlon et al. 2012). Via the OCT technique they were able to perform the in situ visualization of cross-sectional view of the biofilm and to determine the physical properties of the biofilm (e.g., the mean thickness) by analyzing the in situ recorded OCT images. Similar to DOTM and CLMS, OCT is also an optical technique that utilizes a light source with a relatively long wavelength. The long wavelength allows a deeper penetration of micrometer resolutions (Huang et al. 1991; Tomlins and Wang 2005). A typical OCT system shown in Figure 2.15(a) includes a detector and a data acquisition system. In general, a low coherence light beam is emitted from the source and then split into the sample (SMP) and the reference (REF) arms as depicted in Figure 2.15(b). The reflected light is recombined to generate the interferograms which can be detected by the camera. For a medium of interest, the light reflected from different depths will interfere with a specific component of the reference light at different frequencies. As a result, the fringe signals are first obtained as a function of the optical frequency. Then, the recorded spectra are Fourier transformed to resolve the magnitude in a spatial domain. In addition to the magnitude, the phase angle is also obtained from the OCT signals. The change of phase angle is inherently related to the frequency shift which indicates the Doppler effect. When the object is moving toward the detector, the frequency of the detective wave will be increased and vice versa. Therefore, taking advantage of the Doppler effect, not only the sample structure but also the velocity profile could be obtained from the OCT characterization. Though the OCT technique has been extensively applied in fields of medical areas (Swanson et al. 1993; Chen et al. 1997; Yazdanfar et al. 1997; Yazdanfar et al. 2000; Andrews et al. 2008) and the flow measurements (Wang et al. 1997; Wu 2004), it has not been well exploited for membrane applications.
2.4 Summary of research gaps

As discussed previously the membrane performance is deteriorated by CPs and membrane fouling. It is crucial to develop techniques to characterize these dynamic processes so as to better understand the mechanisms. The majority of the existing characterization techniques target on the stationary characterization of the membranes and the foulant structures. On the other hand, many efforts have been spared on coupling the numerical modeling and the filtration process for a more
comprehensive appreciation of the hydrodynamics and the mass transfers. Other than that, it still requires direct observation and quantification to validate the dynamic processes related to the membrane filtration. In particular, the gaps lie in (i) very limited studies focus on the direct characterization of the ICP; (ii) visualization of the fluid field in the direction perpendicular to the membrane surface has not been realized and (iii) direct visualization and quantification of the cake layer formation and the effect of fluid dynamics on the cake layer growth are not well addressed.
CHAPTER 3

CHARACTERIZATION OF INTERNAL AND EXTERNAL CONCENTRATION POLARIZATIONS DURING FORWARD OSMOTIC PROCESSES

3.1 Introduction

Forward osmosis (FO) has been recently applied in fields of water/wastewater treatment, seawater desalination and energy harvesting, owing to its potentially low energy consumption (Lee et al. 1981; Cath et al. 2005; McCutcheon et al. 2005; Cornelissen et al. 2008; Skilhagen et al. 2008; Xu et al. 2010; Jin et al. 2011; Lay et al. 2011; Yip and Elimelech 2011; She et al. 2012). However, the application of FO processes is limited by the presence of severe concentration polarization (CP) (Lee et al. 1981; Loeb et al. 1997; McCutcheon and Elimelech 2008; Tang et al. 2010; Yaroshchuk 2010; Tang et al. 2011). Previous studies revealed that the CP process occurring near FO membrane surface, known as external CP (ECP) can be attenuated by hydraulic means, such as increasing cross flow velocity (Tang et al. 2010; Lay et al. 2012; Xiao et al. 2012). However, internal CP (ICP), a unique CP phenomenon occurring inside the porous support layer of the FO membrane, is much more detrimental to the FO processes due to the difficulty to control it (Cath et al. 2006). Severe ICP leads to the reduction of the effective driving force and thus the permeate flux (Loeb et al. 1997; Tang et al. 2010; Wei et al. 2011).

Numerous studies have investigated ICP mechanisms (Lee et al. 1981; Loeb et al. 1997; McCutcheon and Elimelech 2006; Tang et al. 2010; Li et al. 2011; Zhao and Zou 2011; Wei et al. 2013), yet only a handful of studies focused on direct characterization of ICP. The structural parameter, $S$, has been widely used as an indicator of the extent of the ICP (Tang et al. 2010; Yip et al. 2010; Wei et al. 2011). $S$ is of critical importance in FO studies, and smaller $S$ value is desirable for FO membranes due to the reduced ICP. In most of the existing FO studies, the $S$
value is obtained indirectly by fitting the FO water flux ($J_v$) curves using classical ICP models (i.e., Equation (3.1) for the active layer facing the feed solution (AL-FS) orientation and Equation (3.2) for the active layer facing the draw solution (AL-DS) orientation) (Loeb et al. 1997; Cath et al. 2013)

$$J_v = \frac{D_s}{S} \ln \left( \frac{A\pi_{\text{draw}} + B_s}{A\pi_{\text{feed}} + J_v + B_s} \right) (AL – FS)$$ (3.1)

$$J_v = \frac{D_s}{S} \ln \left( \frac{A\pi_{\text{draw}} - J_v + B_s}{A\pi_{\text{feed}} + B_s} \right) (AL – DS)$$ (3.2)

In Equations. (3.1) and (3.2), the membrane water permeability ($A$) and solute permeability ($B_s$) are obtained independently from filtration tests in a reverse osmosis (RO) mode. $D_s$ is the solute diffusion coefficient. $\pi_{\text{feed}}$ and $\pi_{\text{draw}}$ are the osmotic pressures of the feed solution and the draw solution, respectively. This method is based on the assumption that the transport properties are universally valid for RO and FO experiments (Tiraferri et al. 2013). Compared to the FO $J_v$-fitting approach, methods that directly characterize ICP and that measure $S$ values using independent tests are preferred. Up till now, there have been only limited attempts on the direct characterization of ICP (Wang et al. 2012; Gao et al. 2013). In addition, the existing FO $J_v$-fitting method does not allow independent assessment of ICP vs. ECP effects. Despite that ECP may play a significant role in FO (Tan and Ng 2008; Gruber et al. 2011; Yong et al. 2012; Zhao et al. 2012; Suh and Lee 2013), to the best knowledge of the authors, direct characterization of ECP in FO process is still lacking.

The objective of this study was to develop direct approaches to characterize FO membrane support structures. In this work, independent RO testing procedures were established to evaluate the structural parameter of FO membranes. Three approaches, relying on RO water flux measurements (the $J_v$-method), salt rejection measurements (the $R_s$-method) and trace contaminant (boron in the current study) rejection measurements (the $R_t$-method), were developed and compared. Particularly, the $R_t$-method provided a convenient solution to determine both the
structural parameter of the support layer and the separation properties of the rejection layer. Moreover, this method was feasible to resolve the effect of ECP from that of ICP experimentally.

3.2 Theory

3.2.1 RO water flux method ($J_v$-method)

In a conventional RO test, a membrane is placed with its active layer facing the concentrated feed solution and the support layer (SL) facing the permeate side (Figure 3.1(a)). Such membrane orientation is denoted as SL-permeate in the current study. The membrane water flux $J_v$ is described by the classical solution-diffusion model (Loeb et al. 1997; Baker 2004)

$$ J_v = A(\Delta P - \Delta \pi) $$

(3.3)

where $\Delta P$ represents the hydraulic pressure difference across the membrane active layer and $\Delta \pi$ is the osmotic pressure difference between the membrane surface $\pi_m$ and the permeate stream $\pi_p$. 
In the SL-permeate orientation, ICP is not important as there is no solute accumulation in the membrane porous support. However, ICP does occur when the membrane orientation is reversed in an RO test, i.e., the support layer is facing the feed solution (SL-feed, see Figure 3.1(a)). In this orientation, the solutes in the feed water entering the porous support layer are rejected by the membrane active layer,
leading to a concentration build-up inside the support. Consequently, the osmotic pressure inside the support is increased and the permeate flux is decreased. In addition to ICP, ECP occurring next to the porous layer where ICP occurs, may also have a negative effect on the permeate flux. By considering both ECP and ICP and applying the boundary layer film theory (Fane et al. 2011), we have:

\[
\frac{C_b - C_p}{C_b - C_p} = e^{j/k_{ef}}
\]

(3.4a)

where \(C_b, C_m, C_p\) are the concentrations of the bulk feed solution, the membrane surface and the permeate water, respectively. \(k_{ef}\) is the effective mass transfer coefficient, given by the ratio of effective solute diffusion coefficient \(D_{ef}\), to the effective boundary layer thickness \(\delta_{ef}\) (\(k_{ef} = D_{ef}/\delta_{ef}\)). Here the effects of both ICP (\(K_{m,s}\), mass transfer coefficient of the solute in the porous support layer) and ECP (\(k_s\), solute mass transfer coefficient outside the support) are lumped into a single term \(k_{ef}\), holding the relationship that \(1/k_{ef} = 1/K_{m,s} + 1/k_s\). By further assuming that the osmotic pressure is proportional to the solute concentration (Tang et al. 2010; Yip et al. 2011),

\[
\frac{\pi_m - \pi_p}{\pi_b - \pi_p} = e^{j/k_{ef}}
\]

(3.4b)

where \(\pi_b, \pi_m, \pi_p\) are the osmotic pressures of the bulk feed solution, the membrane surface and the permeate water, respectively. From Equation (3.4a), Equation (3.3) can then be expressed as:

\[
J_v = A \left[ \Delta P - e^{j/k_{ef}} \cdot (\pi_b - \pi_p) \right]
\]

(3.5)

It is worthwhile to note that Equation (3.5) is derived based on the assumption of linear concentration-osmotic pressure relation, which may not be valid for some concentrated solutions (Wilson and Stewart 2013) (see further discussion in Sections 3.4.1.1 and 3.4.1.4).
By re-arranging Equation (3.5), we can have the following relationship:

\[
\ln \left( \frac{\Delta P - \frac{J_v}{A}}{\pi_b - \pi_p} \right) = \frac{J_v}{k_{eff}}
\]  

(3.6)

By plotting experimental \(\ln[(\Delta P - J_v/A)/(\pi_b - \pi_p)]\) values as a function of \(J_v\), \(k_{eff}\) can be readily determined as the reciprocal of the slope of the curve.

Equation (3.6) is also applicable to the SL-permeate orientation by setting \(1/k_{eff} = 1/k_s\) (i.e., no ICP effect). Thus, one can determine the external mass transfer coefficient \(k_s\) in the SL-permeate orientation (ECP effect only) and the overall mass transfer coefficient in the SL-feed orientation (combined ICP and ECP effects). By comparing the two membrane orientations, the ICP related mass transfer coefficient \(K_{m,s}\) can be resolved.

Alternatively, one can obtain \(K_{m,s}\) directly from the SL-feed tests by applying a relatively high cross flow velocity to minimize the effect of ECP (see Section 3.4.2). By further assuming that the osmotic pressure of the permeate water is much less comparing to that of the feed solution (i.e., high membrane rejection), we can have:

\[
\ln \left( \frac{\Delta P - \frac{J_v}{A}}{A} \right) = \frac{J_v}{K_{m,s}} + \ln \left( \frac{\pi_b - \pi_p}{\pi_b} \right) \approx \frac{J_v}{D_s} \frac{1}{S} + \ln \pi_b
\]  

(3.7)

where \(D_s\) is the solute diffusion coefficient inside the porous support layer. \(S(=\tau_m \cdot l_m / \epsilon_m)\) is the structural parameter of the support layer given by the product of the tortuosity \((\tau_m)\) and thickness \((l_m)\) of the support layer over its porosity \((\epsilon_m)\) (Tang et al. 2010). Since the permeate flux and the pressure difference are available from RO measurements, Equation (3.7) thus allows us to evaluate \(S\) value from \(K_{m,s}\).
3.2.2 RO salt rejection method \((R_s\)-method\)

The presence of ICP in the SL-feed orientation not only adversely affects the permeate flux \((J_v)\) but also the membrane solute rejection \((R_s)\) (Jin et al. 2011). In this regard, the \(S\) value may also be determined from the membrane solute rejection measurements. The solute rejection of a membrane is typically evaluated as (Fane et al. 2011)

\[
R_s = 1 - \frac{C_p}{C_b} \quad (3.8)
\]

where the permeate concentration \(C_p\) is evaluated as the ratio of the solute flux \(J_s\) to \(J_v\) (Fane et al. 2011)

\[
C_p = \frac{J_s}{J_v} \quad (3.9)
\]

According to the solution-diffusion theory, \(J_s\) is determined by the product of the solute permeability \(B_s\) and the concentration difference across the membrane active layer, i.e., \(J_s = B_s \cdot (C_m - C_p)\) (Jin et al. 2011). When the FO membrane is examined in the SL-feed orientation, the effect of ICP shall be considered. Therefore, by applying the film theory (Equation (3.4)), we can obtain the following relationship:

\[
J_s = B_s \cdot e^{J_s/|k_{\alpha}|} \cdot \left(C_b - C_p\right) \quad (3.10)
\]

By substituting Equations (3.9) and (3.10) into Equation (3.8), we can have:

\[
R_s = 1 - \frac{B_s \cdot e^{J_s/|k_{\alpha}|}}{J_v} \cdot \left(C_b - C_p\right) = 1 - \frac{B_s \cdot e^{J_s/|k_{\alpha}|}}{J_v} \cdot R_s \quad (3.11)
\]

or

\[
\ln \left[J_v \cdot \left(\frac{1}{R_s} - 1\right)\right] = \frac{J_v}{k_{eff}} + \ln B_s = \frac{J_v}{D_{eff} / \delta_{eff}} + \ln B_s \quad (3.12a)
\]
Equation (3.12a) allows the determination of the ECP effect using the SL-permeate orientation and the combined ICP/ECP effect using the SL-feed orientation. By further assuming that the effect of ECP is minimized under a high cross-flow velocity (Tan and Ng 2008; Xiao et al. 2012; Zhao et al. 2012), one can obtain the following relationship:

\[
\ln \left( J_v \cdot \left( \frac{1}{R_s} - 1 \right) \right) = \frac{J_v}{K_{m,s}} + \ln B_s = \frac{J_v}{D_s / S} + \ln B_s 
\] (3.12b)

Therefore, by simply measuring the permeate water flux \( J_v \) and the solute rejection \( R_s \) of the membrane, values of \( K_{m,s} \) is readily achieved from the inverse of the slope. \( S \) value is then determined from \( K_{m,s} \). In addition, the solute permeability coefficient \( B_s \) can be estimated from the interception with y-axis, \( \ln B_s \). In addition, the solute permeability coefficient \( B_s \) can be estimated from the interception with y-axis, \( \ln B_s \). On the other hand, for scenarios that ECP is not negligible (under a relatively low cross-flow velocity), further discussion will be provided in Section 3.4.2.

### 3.2.3 RO trace contaminant rejection (\( R_t \)-method)

Instead of major solutes like NaCl one can also measure the rejection of trace compounds of interest (e.g., boron (Jin et al. 2011; Jin et al. 2012; Kim et al. 2012)). Equations (3.12a) and (3.12b) can be modified to,

\[
\ln \left( J_v \cdot \left( \frac{1}{R_t} - 1 \right) \right) = \frac{J_v}{k_{eff}} + \ln B_t = \frac{J_v}{D_{eff} / \delta_{eff}} + \ln B_t 
\] (3.13a)

\[
\ln \left( J_v \cdot \left( \frac{1}{K_{m,s}} - 1 \right) \right) = \frac{J_v}{K_{m,s}} + \ln B_t = \frac{J_v}{D_t / S} + \ln B_t 
\] (3.13b)
where $R_t$ and $B_t$ are the tracer rejection and the tracer permeability coefficient of the membrane, respectively. $K_{m,t}$ and $D_t$ are the mass transfer coefficient and diffusion coefficient of the trace contaminant in the support, respectively. This approach is similar to the $R_s$-method and it grants us the access to determine the values of $S$ and $B_t$ simultaneously.

3.3 Materials and experimental methods

3.3.1 FO membranes

Commercial FO membranes were supplied by Hydration Technology Inc. (Albany, OR). These membranes are made of cellulose triacetate (CTA) supported by a non-woven polyester mesh (denoted as CTA-NW according to our previous study (Wei et al. 2011)). Prior to each experiment, all membrane samples were soaked in ultrapure water (with a conductivity of 18.2 M$\Omega$·cm, Millipore Integral 10 Water Purification System) at 4 °C overnight.

3.3.2 RO filtration experiments

Two membrane orientations (SL-permeate and SL-feed, shown in Figure 3.1(a)) were examined in a pressurized cross-flow membrane filtration set-up, as depicted in Figure 3.1(b). The SL-permeate tests (conventional RO tests) were used to determine the active layer separation properties, including the water permeability coefficient $A$, the solute permeability coefficient $B_s$, and tracer permeability coefficient $B_t$. On the other hand, the SL-feed orientation was used to evaluate the effect of ICP and the structural parameter $S$. For all RO experiments, the pH of the feed solution was controlled at 7.0 ± 0.2 and the temperature was maintained at 24 ± 0.5 °C. The effective area of membrane samples was 42 cm$^2$. The feed solution was 10 mM NaCl and boron (in the form of boric acid) was spiked in the feed solution at a concentration of 5 mg/L as boron. Unless specified otherwise, a relatively high cross-flow velocity of 19.8 cm/s was used together with diamond-
pattern feed spacer to minimize the influence of ECP. A lower cross-flow velocity of 3.8 cm/s was also used in some experiments to evaluate the effect of ECP. Both cross-flow velocities were estimated using the feed flow rate divided by the gross cross-sectional area of the feed channel. The salt rejection was calculated based on conductivity measurements of the feed and permeate solutions. On the other hand, the boron rejection was evaluated based on boron concentration measurements by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin-Elmer Optima 2000). The water flux and conductivity of both the feed and permeate were collected over a relatively wide range of applied pressures, from 40 to 300 psi. Each measurement was repeated at least three times to ensure the consistency and the reproducibility. The same set of data was analyzed using three methods to assure the comparisons made among three methods more rational. In addition, to verify the mechanical stability of the FO membrane under high pressure the pure water flux of the membrane (CTA-NW) was tested under applied pressure ranging from 40 to 300 psi in both SL-feed and SL-permeate orientations (refer to Figure S1 in the Appendix A).

3.3.3 FO filtration experiments

A similar bench-scale FO cross-flow set-up employed in this work is described elsewhere (Tang et al. 2010). Both the active layer facing FS and active layer facing DS membrane orientations (AL-FS and AL-DS) were examined. The effective area (42 cm²) of the membrane coupon used in the FO tests was the same as that used in the RO experiments. The same diamond-patterned spacers were placed on both sides of the membrane so as to provide support of the membrane and to enhance mass transfer (McCutcheon and Elimelech 2006; Tang et al. 2010; Jin et al. 2011). The feed solution (FS) contained 10 mM NaCl and the draw solution (DS) concentrations varied from 0.1 to 2.0 M (NaCl). Counter-current flows controlled by peristaltic pumps (Cole-Parmer, Vernon Hills, IL) with a cross-flow velocity of 19.8 cm/s were applied to both sides of the membrane. The permeate flux was determined by the weight changes of the feed as a function of time for 2 h.
3.4 Results and discussion

3.4.1 Model prediction of S value

3.4.1.1 S value predicted by J_V-method

The left hand side of Equation (3.7) was designated as $Y_{J_V}$ for simplicity. Figure 3.2 plots $Y_{J_V} (= \ln(\Delta P - J_v / A))$ in SL-feed orientation as a function of water flux and it exhibited a relatively linear relationship as expected. Except the membrane water permeability coefficient, $A$, which was determined under regular RO testing mode (SL-permeate orientation), the rest of the parameters appeared in Equation (3.7) can be readily obtained under SL-feed orientation in which case the effect of ICP was considered. The reciprocal of solute mass transfer coefficient $K_{m,s}$ was given by the slope of the best fitting line, where $K_{m,s} = 9.90 \times 10^{-7}$ m/s for this FO membrane. $S$ value was then determined from $S = D_S / K_{m,s}$ and was therefore calculated to be 1.57 mm ($D_S = 1.54 \times 10^{-9}$ m$^2$/s). The value of $\pi_b$ determined graphically (the curve intercepted y-axis at $\ln\pi_b$) was $5.87 \times 10^4$ Pa, which was in the same order of magnitude of a theoretical value of $4.77 \times 10^4$ Pa calculated by OLI Stream Analyzer (OLI Systems Inc., Morris Plains, NJ).
Figure 3.2 $Y_{vt}$ as a function of water flux ($J_v$). Solute mass transfer coefficient ($K_{m,s}$) was obtained as the reciprocal of the slope. Osmotic pressure of the bulk feed solution ($\pi_b$) was determined from the y-axis interception. Experimental errors are reported as the standard deviation of at least three repeated measurements. The increasing permeate flux was achieved by increasing the applied pressure. $J_v$ was obtained at applied pressures of 40, 70, 100, 150, 200, 250 and 300 psi. Discussion on limitations of this approach is given in Section 3.4.1.4 Comparison of different methods.

However, Figure 3.2 shows a certain degree of scattering of data points from the straight fitting line (with relatively low $R^2$ value of 0.94). This may be partially attributed to the ideal solution assumption that the osmotic pressure is linearly dependent on the solute concentration. At a high solute concentration, the osmotic pressure can deviate significantly from such linear ideal behavior. In addition, the discrepancy might also arise from the assumption that the osmotic pressure of the permeate water was much less significant compared to that of the bulk solution. For an ideal case where ICP does not occur, $\pi_p$ tends to be relatively constant and it is negligible compared to $\pi_b$. However, when the SL-feed orientation was used in the $J_v$-method, the solute present in the feed solution entered the porous support layer of CTA-NW which led to a concentration build-up in the porous support and
therefore the solute concentration difference across the membrane was elevated. As a result, \((\pi_b - \pi_p)\) was varied at different applied pressures.

3.4.1.2 S value predicted by Rs-method

Another approached proposed in this work is based on the solute selectivity of the membrane in the SL-feed orientation. For simplicity, the left hand side of Equation (3.12b) was denoted as \(Y_R = \ln\left[\frac{J_v \cdot (1/R_s - 1)}{1/2}ight]\) and it was plotted against the permeate flux shown in Figure 3.3. Similar to the \(J_v\)-method, the \(S\) value was achieved readily from the corresponding solute mass transfer coefficient, \(K_{m,s} = 7.14 \times 10^{-7} \text{ m/s}\), which was the inverse of the plot slope. Here \(S\) was equal to 2.16 mm, in reasonable agreement with the value obtained from the \(J_v\)-method. Moreover, according to Equation (3.12b), the best fitting line intercepted y-axis at a value of \(\ln B_s\), from which \(B_s\) was determined \((3.60 \times 10^{-8} \text{ m/s})\). The value of \(B_s\) gained graphically was in excellent agreement with that experimental determined from the regular RO (SL-permeate) tests \((3.49 \times 10^{-8} \text{ m/s})\). The good agreement between the fitted \(B_s\) value and the experimentally determined value serves as an additional consistency check for the \(R_s\)-method. Furthermore, the \(R_s\)-method exhibited a better linear trend \((R^2 = 0.99)\) in contrast to the \(J_v\)-method, and the deviation of this approach was also minute. Unlike the \(J_v\)-method that requires the membrane permeability as a known input in order to determine the \(S\) value, this is not required for the \(R_s\)-method. In addition, we were able to determine the solute permeability graphically using the \(R_s\)-method.
CHAPTER 3

Figure 3.3 $Y_{Rs}$ as a function of water flux ($J_v$). Solute mass transfer coefficient ($K_{m,s}$) was obtained as the reciprocal of the slope. Solute permeability ($B_s$) was determined from the y-axis interception. Experimental errors are reported as the standard deviation of at least three repeated measurements. The increasing permeate flux was achieved by increasing the applied pressure. $J_v$ was obtained at applied pressures of 40, 70, 100, 150, 200, 250 and 300 psi.

3.4.1.3 S value predicted by Rt-method

In addition to previous methods, boron rejection in the SL-feed orientation was also used to determine the S value, namely the $R_t$-method. Here $Y_{Rs} \left( = \ln \left[ J_v \cdot (1/R_t - 1) \right] \right)$ represented the left hand side of Equation (3.13b) was plotted against $J_v$ and a relatively good linear relation was obtained ($R^2 = 0.99$, see Figure 3.4). Both boron mass transfer coefficient $K_{m,t}$ and boron permeability $B_t$ could be determined graphically. $B_t$ obtained from the figure was $4.29 \times 10^{-6}$ m/s, in good agreement to the value determined in the SL-permeate RO tests ($4.60 \times 10^{-6}$ m/s). In addition, by assuming that the S value is constant for a given FO membrane, $K_{m,t}$ can also be estimated from the following relation derived from $S = D_s / K_{m,t}$. 

- 57 -
\[
\frac{K_{m,t}}{K_{m,s}} = \frac{D_t}{D_s}
\] (3.14)

Using \(K_{m,s} = 7.14 \times 10^{-7} \text{ m/s} \) (estimated from \(R_t\)-method) and \(D_t = 1.46 \times 10^{-9} \text{ m}^2/\text{s} \) for boron and \(D_s = 1.54 \times 10^{-9} \text{ m}^2/\text{s} \) for NaCl (calculated using OLI Stream Analyzer), the \(K_{m,t}\) value was determined to be \(6.77 \times 10^{-7} \text{ m/s} \). This value followed closely to the one determined graphically in the \(R_t\)-method, which was \(6.41 \times 10^{-7} \text{ m/s} \). The \(S\) value obtained from the \(R_t\)-method was 2.28 mm, which corresponded well to that from the \(R_s\)-method (2.16 mm) but was higher than the value determined using the \(J_v\)-method (1.57 mm). Nonetheless, all three \(S\) values were in the same order of magnitude.

![Figure 3.4](image)

Figure 3.4 \(Y_{R_t}\) as a function of water flux \((J_v)\). Solute mass transfer coefficient \((K_{m,t})\) was obtained as the reciprocal of the slope. Tracer permeability \((B_t)\) was determined from the \(y\)-axis interception. Experimental errors are reported as the standard deviation of at least three repeated measurements. The increasing permeate flux was achieved by increasing the applied pressure. \(J_v\) was obtained at applied pressures of 40, 70, 100, 150, 200, 250 and 300 psi.
3.4.1.4 Comparison of different methods

In addition to the three methods discussed above (RO $J_v$-method, $R_s$-method, and $R_t$-method), we also evaluated the $S$ value indirectly by fitting the FO water flux using the classical ICP models for comparisons. In the latter method (Tang et al. 2010), the $A$ and $B_s$ values were determined by RO tests in the SL-permeate orientation, and the $S$ value was obtained by fitting the FO water flux values (Equations (3.1) and (3.2)). The $S$ values obtained by all four methods are summarized in Table 3.1. It shows that the $S$ values determined from the proposed approaches are on the same order of magnitude to the one achieved by the FO water flux fitting method. The RO $J_v$-method was considered less reliable owing to the facts that (i) the key assumptions of the linear osmotic-pressure-concentration relationship may not hold at high concentrations causing deviation from the linear behavior; (ii) the assumption of $\pi_p < \pi_b$ may also not be appropriate in many cases and (iii) the $J_v$-method presented a relatively large uncertainty (lower $R^2$ value). Both the $R_s$-method and $R_t$-method yielded similar results. Since NaCl rejection is much easier to measure compared to boron rejection, the $R_s$-method is recommended for routine measurements. The $S$ value obtained from the $R_s$-method was 2.16 mm, which was greater than that from FO water flux fitting method ($S = 1.63$ mm under the AL-FS orientation and $S = 1.80$ mm under the AL-DS orientation). In the FO method, the parameters used to fit the $K_{m,s}$ value from Equations (3.1) and (3.2) were collected under different experimental conditions, i.e., $A$ and $B_s$ were determined from RO experiments and $J_v$ was measured in FO tests. In addition, this method also requires the key assumption of linear osmotic-pressure-concentration relationship. Since relatively high solute concentrations are generally encountered in FO applications, this ideal solution assumption may not be applicable (Tang et al. 2010) and it can lead to potential deviations in the $S$ value prediction. An added advantage of the $R_s$-method is that it allows the determination of both ECP and ICP effects (Section 3.4.2), while the FO water flux fitting method does not allow such discrimination explicitly.
Membrane separation parameters determined are also tabulated in Table 3.1. The first column summarizes the performance parameters, $A$, $B_s$, and $B_t$ of CTA-NW obtained by conventional RO tests (the SL-permeate orientation). The water permeability was $1.24 \times 10^{-12}$ m/s·Pa and the salt permeability was $3.49 \times 10^{-8}$ m/s, which are consistent with previous research (Wei et al. 2011). In addition, $B_s$ and $B_t$ obtained graphically (using the SL-feed orientation) are also presented in Table 3.1 for comparisons. The $B_s$ and $B_t$ values determined in the two membrane orientations were consistent with each other, ensuring a good quality insurance of the $R_s$ and $R_t$ fitting procedures introduced in the current study.
Table 3.1 Intrinsic properties of CTA-NW were measured under RO testing mode either experimentally under SL-permeate orientation or graphically under SL-feed orientation. Experimental results were obtained over a pressure range from 40-300 psi, with the feed solution of 10 mM NaCl and 5 mg/L boron. Experimental errors are reported as the standard deviation of multiple repeated measurements.

<table>
<thead>
<tr>
<th>Testing method</th>
<th>Conventional FO water flux fitting method*</th>
<th>J_v-method</th>
<th>R_s-method</th>
<th>R_t-method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>A = ( \frac{J_v}{\Delta P - \Delta \pi} ) (RO)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( B_s = \left( \frac{1}{R_p} - 1 \right) J_v ) (RO)</td>
<td>( \ln \left( \frac{\Delta P - J_v}{A} \right) = \frac{J_v}{D_j / S} + \ln \pi_s )</td>
<td>( \ln \left[ J_v \left( \frac{1}{R_p} - 1 \right) \right] = \frac{J_v}{D_j / S} + \ln B_s )</td>
<td>( \ln \left[ J_v \left( \frac{1}{R_p} - 1 \right) \right] = \frac{J_v}{D_j / S} + \ln B_t )</td>
</tr>
<tr>
<td>+ ICP models for FO (Eqs. 1 &amp; 2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Testing mode/orientation

- RO: SL-permeate **
- FO: AL-FS and/or AL-DS
- (and SL-permeate for A value**)
- RO: SL-feed
- RO: SL-feed

<table>
<thead>
<tr>
<th>Solute permeability ( B_s ) (× 10^{-8} m/s)</th>
<th>3.49 ± 0.02</th>
<th>—</th>
<th>3.60 ± 0.20</th>
<th>—</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron permeability ( B_t ) (× 10^{-6} m/s)</td>
<td>4.60 ± 0.71</td>
<td>—</td>
<td>—</td>
<td>4.29 ± 0.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S value (mm)</th>
<th>1.63 ± 0.10 (AL-FS)</th>
<th>1.57 ± 0.20</th>
<th>2.16 ± 0.02</th>
<th>2.28 ± 0.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80 ± 0.05 (AL-DS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes:

* Details of the FO water flux fitting method can be found in Tang et al. (Tang et al. 2010).

** Water permeability A, determined from conventional RO method (SL-permeate orientation) was (1.24 ± 0.03) × 10^{-12} m/s·Pa.
3.4.2 Observed and predicted solute rejection

In this section, RO salt rejections obtained under both SL-permeate and SL-feed orientations are compared. Cross-flow velocity was further reduced to 3.8 cm/s under both membrane orientations in order to investigate the effect of ECP. The linearized rejection results using Equation (3.12a) are elucidated in Figure 3.5(a). Relatively linear relationships were obtained regardless the value of cross-flow velocity for both membrane orientations. The effect of ECP can be determined for the SL-permeate orientation. In this orientation a membrane is not subjected to the effect of ICP. Therefore, the external boundary layer thickness $\delta_{ECP}$ can be determined directly in accordance to Equation (3.12b). At a cross-flow velocity of 19.8 cm/s, the fitting line is nearly flat, yielding to an ECP boundary layer thickness $(\delta_{ECP})$ of ~0.05 mm. This supports our early assumption that ECP is relatively mild at the high cross flow (19.8 cm/s) condition. When the cross-flow velocity was reduced to 3.8 cm/s, the best fitting line yielded a slightly steeper slope. The $\delta_{ECP}$ value was ~0.25 mm, signaling a more severe ECP. In contrast to the relatively flat slopes in the SL-permeate orientation, the corresponding slopes obtained in the SL-feed orientation were much steeper due to the effect of ICP. From this comparison, it is evident that ICP plays a more dominant role in the SL-feed orientation. Nevertheless, the effective boundary layer thickness was increased from 2.16 to 2.24 mm when the cross-flow velocity was reduced from 19.8 to 3.8 cm/s, suggesting that ECP can still be important when a low cross-flow velocity.
Figure 3.5 (a) Linearization of salt rejection as a function of permeate flux. Two cross-flow velocities (3.8 cm/s and 19.8 cm/s) were examined under both SL-feed and SL-permeate orientations; (b) Observed and predicted salt rejections by the CTA-NW membrane as a function of permeate flux under various operating pressures. Experimental errors are reported as the standard deviation of at least three repeated measurements. The increasing permeate flux was achieved by increasing the applied pressure. $J_v$ was obtained at applied pressures of 40, 70, 100, 150, 200, 250 and 300 psi.

The values of $K_{m,s}$ determined graphically from Figure 3.5(a) were used to model salt rejections (see Equation (3.11)). Both modeled and experimental salt
rejections as a function of water flux are illustrated in Figure 3.5(b). Experimental results were consistent with the predicted values. In the SL-permeate orientation, salt rejections increased at increasing permeate flux regardless of cross-flow velocities. This trend can be explained by the dilution effect predicted by the classical solution-diffusion theory; more permeate water passing through the membrane at higher applied pressures will dilute the permeate concentration (Cath et al. 2006; Tang et al. 2010). On the other hand, in the reversed membrane configuration (SL-feed), the salt rejection was increased initially with increasing water flux owing to the dilution effect. Nonetheless, at a permeate flux >0.5 μm/s, the rejection decreased at increasing water flux. The latter trend is due to the more significant influence of ICP under the SL-feed orientation at a higher water flux level. Since the level of ICP increases exponentially with water flux, a high water flux can lead to the severe solute accumulation in the membrane support layer and thus significantly reduced the solute rejection. Similar behavior (increased and then decreased rejection at higher water flux) was previously reported in the context of FO testing in the AL-DS orientation, which is also attributed to the effect of ICP (Jin et al. 2011). In the current study the maximum rejection in SL-feed orientation occurred at a water flux of ~0.5 μm/s. This value closely matches with the $k_{eff}$ values ($\sim 7 \times 10^{-7}$ m/s or 0.7 μm/s) in this orientation. The current study therefore suggests that the concentration polarization starts to play a dominant role when the water flux is on the same order of magnitude as the mass transfer coefficient, which is in good agreement with the classical film theory (Fane et al. 2011).
Figure 3.6 Experimental and simulated boron rejections ($R_t$) by the CTA-NW membrane as a function of water flux under different applied pressures. Eq. (11) was used to simulate $R_t$ for different $J_v$, where $K_{m,t}$ was determined graphically by the $R_t$-method, $K_{m,t} = 6.41 \times 10^{-7}$ m/s. Experimental errors are reported as the standard deviation of at least three repeated measurements. The increasing permeate flux was achieved by increasing the applied pressure. $J_v$ was obtained at applied pressures of 40, 70, 100, 150, 200, 250 and 300 psi.

The boron rejections of CTA-NW in two membrane orientations are presented in Figure 3.6. For the SL-permeate orientation, the boron rejection results were improved at higher applied pressures which are in good agreement with the predicted results (shown as the dashed line in Figure 3.6). Approximately 30% of the boron rejection was achieved when the permeate flux was ~2 μm/s, which was comparable to the value reported by early study (Jin et al. 2011). The slight difference might be attributed to a different FO membrane and different experimental protocols were used in the current study. On the other hand, when the SL-feed orientation was examined, boron rejection results increased initially then decreased when further increasing the permeate flux. The experimental results are
well corresponded to the predicted values

\[
R_s = \frac{J_v}{J_v + B_s \exp\left(\frac{J_v}{K_{m,s}}\right)}
\]

(Equation (3.11)) shown by the solid line in Figure 3.6.

3.4.3 Model validation in FO processes

Feasibility of the \( R_s \)-method was further verified in the FO process. The experimental water flux under both AL-FS and AL-DS orientations are plotted as a function of simulated water flux using Equations (3.1) and (3.2), respectively, with \( K_{m,s} \) determined from the \( R_s \)-method. A 45° line is also depicted in the Figure 3.7 as a reference to represent the case when the measured water flux is the same as the simulated value. In general, reasonably good agreement was obtained between the FO experimental and modeling results, suggesting the direct \( S \) value determination method (particularly, the \( R_s \)-method) can be reliably applied to the characterization and performance prediction of an FO membrane.
Figure 3.7 Experimental and simulation results of water flux in the FO process. Both AL-FS and AL-DS orientations were evaluated with 10 mM NaCl as the feed solution and the draw solution concentrations varying from 0.1 - 2.0 M without pH adjustment. Cross flow velocity was 19.8 cm/s on both sides of the membrane. Temperature was maintained at 24 ± 0.5 °C. Experimental errors are reported as the standard deviation of at least three repeated measurements.

3.5 Conclusions

In the current work three approaches were developed to characterize the ICP and ECP effects directly. All three methods were realized in the RO operation mode and experimental results demonstrated a well fit with the theoretical models. Thus, these methods allow independent assessment of the structural parameter of an FO membrane. Among three methods, the $R_s$-method is generally preferred. This method is relatively easy to perform, and it had smaller deviation compared to the $J_v$-method. Meanwhile, the accurate determination of the solute permeability coefficient $B_s$ from this method serves as an independent reliability check. The
method was also demonstrated to be a handy tool to study ICP and ECP interpretively.

Although the current paper has primarily focused on forward osmosis characterization, the methods developed here are versatile and can be applied to characterize concentration polarization in other membrane processes. As demonstrated in the study the method can be useful to characterize the external concentration polarization and to determine the boundary layer thickness in an RO process. In addition, the method can be potentially extended to characterize the cake enhanced concentration polarization (CECP) effect in the context of RO membrane fouling (Hoek and Elimelech 2003; Chong et al. 2008). In the latter case, solutes entering the porous foulant cake layer are retained by the dense rejection layer of an RO membrane, causing a severe concentration polarization in the unstirred cake layer. CECP is an important fouling mechanism for dense membranes and it can lead to severe flux reduction as well as reduced solute rejection in both RO (Hoek and Elimelech 2003; Chong et al. 2008; Tang et al. 2011) and FO (Lay WC 2010; Lee et al. 2010; She et al. 2012) processes. The methods presented in the current paper can provide a handy tool for charactering the CECP effect. The solute/tracer rejection models also provide a convenient framework for understanding the effect of concentration polarization (including fouling induced CECP) on membrane rejection performance.

On the other hand, a great concern lies in the mechanical stability of FO membranes characterized in RO testing mode. It was demonstrated that the mechanical strength of FO membranes under pressurized conditions are highly dependent on the choice of spacers/carriers, that membranes are better supported with finer spacers/carriers and mechanical damage can be minimized (She et al. 2013). It is therefore recommended to perform pure water tests (refer to Figure S1 in Appendix A) first in order to confirm mechanical stability of the membranes. With careful selection of permeate carries, it is also interesting to see if the proposed methods are applicable to characterize FO membranes with unconventional structures, i.e., a membrane with double rejection layers, in which case the flux fitting with classical ICP method may not be applicable.
CHAPTER 4

CHARACTERIZATION OF FORWARD OSMOSIS MEMBRANES BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

In previous chapter, we reported a novel approach to characterize internal and external concentration polarizations separately during a filtration process. In this chapter we focused on resolving the complex interplay between the forward osmosis membrane structures and transport processes. In particular, the electrochemical impedance spectroscopy technique was employed to characterize the filtration process and to reveal the subtle relationship between various membrane substructures and the concentration polarizations.

4.1 Introduction

Forward osmosis (FO) has been attracting significant attention for desalination and water/wastewater treatment (McCutcheon et al. 2006; Holloway et al. 2007; Cornelissen et al. 2008). Instead of utilizing an externally-applied hydraulic pressure, FO processes are driven by an osmotic pressure difference across the membrane (Cath et al. 2006). However, previous studies (Cath et al. 2006; McCutcheon and Elimelech 2008; Tang et al. 2010) revealed that significant flux reduction can be caused by the concentration polarization across the porous FO membrane substrate, i.e., the internal concentration polarization (ICP). Further studies (Tang et al. 2010; Li et al. 2011; Tiraferri et al. 2011) also highlighted the interplay between the ICP and the complex substrate structure. It is therefore critical to develop a better understanding of the FO membrane substrate to account for the effect of ICP during the FO processes.

FO membranes generally have an asymmetrical structure, with a thin selective layer (the active layer) on top of a porous substrate (the support layer) (Cath et al. 2006; Wei et al. 2011). Despite the critical importance of the substrate
in controlling ICP, there have been only a handful number of studies on the systematic characterization of its structure (Wang et al. 2010; Tiraferri et al. 2011; Wei et al. 2011). Existing characterization methods reported in the literature are mainly based on electron microscopy (Wang et al. 2010; Tiraferri et al. 2011; Wei et al. 2011) and light microscopy (Wang et al. 2010). Whereas these techniques are able to produce clear micrographs of FO membranes, the complex interaction between the substrate structure and the transport processes is difficult to be resolved. Therefore, in situ characterization of FO processes is entailed to investigate the underlying transport mechanisms.

As one of the important non-invasive characterization techniques, electrochemical impedance spectroscopy (EIS) has been widely used to study the structure of filtration membranes (Asaka 1990; Coster et al. 1992; Benavente et al. 2000; Fortunato et al. 2006) and to investigate membrane fouling and concentration polarization in pressure-driven membrane processes (Hanai et al. 1991; de Lara and Benavente 2009; Kavanagh et al. 2009; Luo et al. 2010). EIS is based on the electrochemical relaxations related to the intrinsic properties of the studied systems (Coster et al. 1996; Benavente 2005). It can potentially reveal structural features of the order of a Debye length (Chilcott et al. 2002; Gaedt et al. 2002). For a membrane with several structural layers, it is also possible to determine the structural properties (e.g., thickness, porosity, etc.) of each layer using an equivalent circuit modeling (Asaka 1990; Coster et al. 1996; Benavente 2005).

In the current study, we were motivated to incorporate the EIS characterization with the FO processes. The objective of the study was to develop a novel EIS-based approach for investigating FO membrane structures and ICP in real time. A commercial EIS system was modified to accommodate FO membranes with a variety of substructures. The equivalent circuits were proposed to interpret impedance spectra. Particularly, the impedance spectra were obtained in both static tests (without osmosis) and dynamic tests (with osmosis) for a comprehensive understanding of the characteristic electric responses pertaining to the FO systems. To the best knowledge of the authors, this is the first systematic EIS study for
characterizing FO membrane structures and concentration polarization during FO processes.

4.2 Theory of EIS characterization

EIS measurements are usually performed by imposing an alternating current $I = I_0 \sin(\omega t + \phi_i)$ into the system of interest, and the voltage response $V = V_0 \sin(\omega t + \phi_v)$ is measured (where $I_0$ and $V_0$ are the amplitudes of the current and the voltage, respectively) (Coster et al. 1996). The impedance $Z$ is then defined as a phasor, of which magnitude $|Z|$ is equal to $V_0/I_0$, and phase angle $\phi$ is given by $\phi_v - \phi_i$:

$$Z = \frac{V_0}{I_0} (\cos \phi + j \sin \phi) \quad (4.1)$$

Where $j$ is the imaginary unit which satisfies $j = \sqrt{-1}$.

The measured system can be approximated by an equivalent circuit having a conductance element in parallel with a capacitance element. Therefore, the impedance is in turn recast into:

$$Z = \frac{1}{G + j\omega C} \quad (4.2)$$

$$G = \frac{1}{|Z|} \cos \phi \quad (4.3)$$

$$C = -\frac{1}{\omega |Z|} \sin \phi \quad (4.4)$$

where $G$ and $C$ are the parameters describing the ability of the system to conduct and store electric charges, respectively; and $\omega$ is the angular frequency of the alternating current.
For a system with a homogeneous structure, both the conductance $G$ and capacitance $C$ are independent of the probing frequency $f$ (or angular frequency $\omega = 2\pi f$) and they are determined by the electric properties of the material (electric conductivity $\sigma$, and dielectric permittivity $\varepsilon$). For a sample cross-sectional area of $A_m$ and a thickness of $L$, the impedance of this homogeneous structure can be evaluated by:

$$Z = \frac{L}{A(\sigma + j\omega \varepsilon)} \quad (4.5)$$

In a system where the electric properties are non-homogenous, the equivalent circuit can be treated as a combination of sub-circuits. Each sub-circuit corresponds to a portion of the system with infinitesimal thickness. Then, the total impedance is expressed by the integral of these sub-circuits:

$$Z = \int_{0}^{L} \frac{dx}{A_m(\sigma + j\omega \varepsilon)} \quad (4.6)$$

where $dx$ represents an infinitesimal thickness, corresponding to an individual substructure. Both theoretical and experimental studies (Hanai et al. 1991; Coster et al. 1992) revealed that the spatial variation of the electric properties might render the strong correlations between the global element parameters ($G$ and $C$) and the probing frequency. By interpreting the resultant dispersion curves, one will be able to obtain information about the substructures of the system.

In the current study, we focused on the system of FO membrane immersed in electrolytes. According to the analysis of the equivalent circuit (Coster et al. 1992), we can distinguish the electric properties of the membrane ($G_m$ and $C_m$) from the electrolyte ($G_e$ and $C_e \approx 0$) by invoking the characteristic dispersions of the global parameters $G$ and $C$:

$$G = \frac{G_e G_m (G_e + G_m) + \omega^2 G_e C_m^2}{(G_e + G_m)^2 + \omega^2 C_m^2} \quad (4.7)$$
\[ C = \frac{C_m G_r^2}{(G_r + G_m)^2 + \omega^2 C_m^2} \] (4.8)

In writing Equations (4.7) and (4.8), it is implicitly assumed that both the membrane and the electrolyte have spatially uniform electric properties such that the global properties can be evaluated by piecewise integral.

When internal concentration polarization occurs, the electric properties of the membrane are spatially varied as the concentration profile is developed. In particular, we optionally lump the spatial variation into $G_m$ and $C_m$ by using the logic of effective medium approximation (EMA) (Li et al. 2011). Technically, this approximation relegates the mathematical complexity and facilitates capturing the key points as we initiate the work to investigate the role of the internal concentration polarization on the electric response.

4.3 Materials and experimental methods

4.3.1 FO membranes

Three commercial FO membranes (denoted as CTA-HW, CTA-W, and CTA-NW in the current study) were supplied by Hydration Technology Inc. (Albany, OR). These asymmetric FO membranes are made of cellulose triacetate (CTA) supported by polyester mesh (Wei et al. 2011). Prior to membrane characterization, all membrane samples were soaked in Milli-Q water (conductivity of 18.2 MΩ·cm, Millipore Integral 10 Water Purification System) at 4 °C overnight. The area of membrane samples used in the EIS characterization was 5.4 cm².

4.3.2 SEM characterization

Scanning electron microscope (SEM, Zeiss EVO 50) was used to characterize FO membrane morphologies. All membrane samples were freeze-
dried (Christ Alphr 1-4 LD, Germany) and cracked after being immersed in liquid nitrogen to obtain cross-sections. The samples were then sputter-coated with a uniform layer of gold (Emitech SC7620 sputter coater) before characterization. An accelerating voltage of 10 kV was used for all scanning.

4.3.3 EIS characterization

An INPHASE™ EIS system (INPHAZE, Australia) was employed to measure electrical properties of the FO membranes. The EIS systems are schematically depicted in Figure 4.1. It has four terminals that one pair of electrodes is used for injecting alternating current into the system while the other pair is to measure the voltage across the sample of interest. Such four-terminal configuration has the advantage that the impedance of the interface between the current-injecting electrodes and the aqueous phases can be compensated (Kavanagh et al. 2009). Additionally, the adopted EIS system has the current electrode pair with a relatively large area, which ensures the uniform distribution of current over the membrane sample. In contrast, the voltage electrodes have a smaller area, thereby minimizing the current through these electrodes. The impedance spectra were scanned in a frequency range from $1 \times 10^{-1}$ to $1 \times 10^4$ Hz, and each measurement was repeated three times to ensure the consistency and the reproducibility.
Figure 4.1 Schematic of two-chamber, four-terminal EIS apparatus for (a) static tests and its equivalent circuit and (b) dynamic tests and its equivalent circuit.
In the current study, the FO membranes were characterized by the EIS system in both static and dynamic testing modes. For the static tests (Figure 4.1(a)), an FO membrane sample was inserted between two electrolyte solutions of identical composition (10 mM NaCl). There was no osmosis occurring during the static tests since the osmotic pressure difference across the membrane was zero. The dynamic tests were performed to investigate the effect of ICP on the electrochemical impedance spectra. Accordingly, the two chambers of the EIS system were filled with electrolyte solutions of different concentrations (Figure 4.1(b)). The feed solution contained 10 mM NaCl, while the draw solution contained a 0.5 M NaCl. The FO water flux was determined by measuring the weight changes of the draw solution at a time interval of ~20 min. Both the-active-layer-facing-the-feed-solution (AL-FS) and the-active-layer-facing-the-draw-solution (AL-DS) orientations were evaluated.

4.4 Results and discussion

4.4.1 Characterization of FO membranes by SEM

The SEM micrographs of the FO membranes are presented in Figure 4.2(a-c) for CTA-HW, CTA-W, and CTA-NW, respectively. All these images clearly show that the membranes had an asymmetric structure. CTA-HW and CTA-W were supported by a woven fabric, whereas CTA-NW was supported by a non-woven fabric. According to prior studies (Tang et al. 2010; Li et al. 2011; Tiraferri et al. 2011), the FO substrate has significant impact on ICP whose length scale is given by the structural parameter $S$, where:

$$S = \frac{\tau_m \lambda_m}{\varepsilon_m}$$  \hspace{1cm} (4.9)

In Equation (9), $\tau_m$, $\varepsilon_m$, and $\lambda_m$ denote the tortuosity, porosity and thickness of the FO substrate, respectively. The values of $S$ parameter and membrane porosity, obtained from our previous study (Wei et al. 2011), are also indicated in the corresponding SEM images. Membrane CTA-HW (Figure 4.2(a)) had a support
layer with finger-like structures (thus low tortuosity), consistent with its relatively low $S$ parameter ($0.72 \pm 0.15$ mm). In comparison, CTA-W had a less porous substrate ($\varepsilon_m = 0.46$), which gives rise to a larger $S$ parameter ($1.00 \pm 0.54$ mm) in spite of its smallest substrate thickness (~40 µm, Figure 4.2(b)). Membrane CTA-NW had the highest $S$ value of $1.38 \pm 0.26$ mm, due to the additional mass transfer resistance resulting from its thick non-woven fabric support.
Values of $\varepsilon_m$ and $S$ were obtained from ref. (Wei et al. 2011).

Figure 4.2 SEM micrographs of cross-sections of (a) CTA-HW, (b) CTA-W, and (c) CTA-NW.
4.4.2 EIS characterization of FO membranes

4.4.2.1 Static EIS tests

In the static tests, the FO membranes were characterized in a 10 mM NaCl electrolyte solution. The impedance modulus $|Z|$ and the phase angle $\phi$ were determined based on the difference between the imposed current and the corresponding voltage response over a wide frequency range ($1 \times 10^{-1}$ to $1 \times 10^4$ Hz). In addition, the impedance spectra of the electrolyte solutions (without membrane sample) were also measured independently to provide a baseline for comparison. Figure 4.3(a) plots the impedance modulus $|Z|$ as a function of the frequency $f$ (i.e., $\omega/2\pi$). For the 10 mM NaCl electrolyte solution alone (baseline case), a constant $|Z|$ value (~0.1 $\Omega\cdot\text{m}^2$) was observed, which is typical for homogenous systems. In contrast, the EIS spectra for the membrane/electrolyte system showed frequency-dependent dispersions. Specifically, the magnitude of the impedance was significantly decreased within a narrow range of the frequencies ($1 \times 10^2$ to $1 \times 10^3$ Hz), whereas it remained nearly constant at both the high frequency regime and the low frequency regime. At low frequencies, the spectra differences between the membranes can be clearly observed (Figure 4.3(a)), where the CTA-NW system had the highest modulus value whereas the CTA-HW system had the lowest value. All these dispersion curves approached the baseline asymptotically at high frequencies, indicating that the response at high frequency range was mainly governed by the electrolyte solution and it had little dependence on the membrane properties.
Figure 4.3 (a) The impedance magnitude as a function of frequency and (b) the Nyquist plot. Error bars were obtained the average and standard deviation of multiple measurements.
In the current study, the Nyquist diagram (Macdonald 1987) was also employed by resolving the impedance phasor into the imaginary part $Z_{\text{img}}$ ($|Z| \sin \phi$) and the real part $Z_{\text{real}}$ ($|Z| \cos \phi$). As discussed in previous works (Macdonald 1987; Benavente 2005), a perfect semi-circle in the Nyquist diagram indicates that the corresponding system is composed of an ideal conductance element and an capacitance element in a parallel manner. The semi-circles observed in the current study were slightly depressed as shown in Figure 4.3(b), with their aspect ratio $\frac{2 \text{Max}(-Z_{\text{img}})}{\text{Max}(Z_{\text{real}}) - \text{Min}(Z_{\text{real}})}$ ranging from 0.75-0.89. The depressed semi-circles were likely due to the ion diffusion in the membrane substrate (Macdonald 1987; Benavente 2005). Consistent with this explanation, membrane CTA-HW with the lowest $S$ value (thus lowest mass transfer resistance to ion diffusion in the substrate) also had the highest aspect ratio. In the Nyquist diagram, the left intersections between the semi-circles and the horizontal axis were nearly identical, which was dominated by the electrolyte solution behavior. In contrast, the right intersections were different, reflecting the differences between the three FO membranes. It is also interesting to note that the system containing only the 10 mM electrolyte solution (Figure 4.3(b)) exhibits deviant behaviors at the low frequencies, as indicated by the decreasing modulus. This was likely due to the diffusion effects that are dominant in the system in the regime low frequency (Benavente 2005).

To better understand the subtle differences between the FO membranes, the equivalent circuit approach was adopted. This allows us to distinguish the systems’ abilities to conduct and store charges. In addition, the dispersion of the global parameters $G$ and $C$ are usually more sensitive to the variation of the probing frequency, and hence offers more reliable analysis (Coster et al. 1996). According to Equations (4.3) and (4.4), the impedance spectra were transformed into the plots of the global $G$ and $C$ with respect to the frequency (Figure 4.4). In the current study, the system for static test was approximated by an equivalent circuit having ideal elements for the membrane ($G_m$ and $C_m$) and the electrolyte solutions ($G_e$). This explanatory circuit was schematically depicted on the lower panel of Figure
4.1(a). The correlations between the ideal elements and the global elements were given by Equations (4.7) and (4.8). However, the non-ideal behaviors of the electrolyte may restrict the accuracy of fitting the individual elements by implementing the conventional algorithm of complex nonlinear least squares (CNLS) (Macdonald 1992). Therefore, we instead resolved the global circuit by invoking the limit formulations:

\[
\lim_{f \to 0} G = \frac{G_e G_m}{G_e + G_m} \approx G^L \quad (4.10)
\]

\[
\lim_{f \to 0} C = \frac{C_m G_e^2}{(G_e + G_m)^2} \approx C^L \quad (4.11)
\]

\[
\lim_{f \to \infty} G = G_e \approx G^H \quad (4.12)
\]

\[
\lim_{f \to \infty} C = 0 \quad (4.13)
\]

The superscripts \( L \) and \( H \) denote the electric properties measured in the low frequency and high frequency regimes, respectively.
In Figure 4.4(a), it is observed that the values of global $G$ of the systems containing FO membrane were lower than that of the solitary electrolyte system at the low frequencies, and these values remained nearly unchanged at low frequency regions. As predicted by the limit formulation (Equation (4.12)), both the systems having CTA-HW and CTA-W membrane samples yield the asymptotes merging into the electrolyte baseline near the limit probing frequency ($1 \times 10^4$ Hz). An
exceptional transition curve was observed for the system of CTA-NW membrane sample, which had the highest $S$ value. This deviation was perhaps caused by the severe discontinuity between the membrane sample and the external solutions, which amplifies the diffusion effects of the electrolyte species in the high-end frequency regime.

The corresponding values of global $C$ are presented in Figure 4.4(b). When the value of $G_e$ is much greater than that of $G_m$, Equation (4.11) predicts that the limit value of the global $C$ would approach the same value of $C_m$. We note that the non-ideal behavior of the electrolyte solution at the low frequencies was noticeably projected onto the capacitive component, of which value was remarkably greater than zero below the frequency of 1 Hz. In comparison with the relative consistence of the conductive component illustrated by Figure 4.4(a), the severe deviation of $C_e$ puts obstacle to estimating the values of $C_m$ for the FO membranes according to the limit formulation given by Equation (4.11), which is based on the assumption of $C_e = 0$. In spite of the low-frequency inconsistency, all the dispersion curves are approaching a vanishingly small value at the extremely high frequencies underscoring the prediction by Equation (4.13).

The relative consistency of the experimental $G$ values enables us to estimate the membrane conductive elements $G_m$ by exploiting Equation (4.10). In particular, instead of using the value from the electrolyte solutions, the value of $G_e$ was approximated by the corresponding conductance at the high-end frequency $G^{''}$ as to minimize the effects of non-ideal solution behaviors. The calculated values of $G_m$, together with the experimental values of $G^{\prime}$ and $G^{''}$, are listed in Table 4.1. It shows that membrane CTA-HW had the greatest $G_m$ value of 21.7 S/m² while the smallest $G_m$ value of 1.4 S/m² was given by membrane CTA-NW. This is consistent with the fact that the membrane with higher value of $S$ parameter would decrease the mobility of the electrolyte species within the porous matrix, thereby
reducing the membrane conductance, which is mainly contributed by the moving electrolyte phase.

4.4.2.2 Dynamic EIS tests

The concentration level of the electrolyte species was kept constant in the membrane structures during the static tests since the osmosis processes were not involved. When there is a concentration difference across the active layer of the FO membrane, the osmosis process takes place, and the concentration profile is subsequently developed to yield a balance between the diffusive solute flux and the convective solute flux. The dynamic tests were therefore designed to verify the ability of the EIS system to capture the information about the polarization phenomena during FO processes.

As introduced in the experimental section, the EIS system was modified to incorporate the osmosis process. The electrolyte solution in one chamber was 10 mM NaCl (feed solution) as that for the static tests, whereas that in the other chamber was 0.5 M NaCl (draw solution). As a result, the average concentration level of the overall system was significantly increased compared to that of the static tests, which in turn overwhelmed the changes of the membrane electric properties caused by the polarization phenomena. In order to minimize the effects of the variation of the solution environments on the circuit analysis, two membrane orientations (AL-FS and AL-DS) were employed in the dynamic tests.

The impedance modulus $|Z|$ and phase angle $\phi$ were measured as the osmosis was proceeding, and the probing frequency was varied from about $10^{-1}$ to $10^4$ Hz. As discussed in the static tests, the EIS spectra of $G$ versus $f$ are usually superior to those based on the values of $C$, which is a strong function of the diffusion effects. Therefore, the circuit analysis for the dynamic tests was restricted to the conductive component of the impedance phasor.

The values of the parameter $G$ were calculated by using Equation (4.11) and plotted in
Figure 4.5(a) for both membrane orientations. All the dispersion curves had a wider stagnant regime over the frequency domain compared to those resulted from the static tests (Figure 4.4(a)). This is in agreement with the fact that the characteristic frequency of the system might be enhanced by increasing the concentration level of the electrolytes (Hanai et al. 1991). The value of the global $G$ was significantly increased as the frequency was above the characteristic value. However, the desired plateau regime was not detected at the upper limit of the probing frequency.
Figure 4.5(a) the results of AL-DS orientation were marked by the solid symbols, whereas the void symbols are for the results from the AL-FS orientation. The interesting aspect of these paired plots is that the curves of AL-FS orientation were consistently lower than those of the reversed orientation at the low frequencies. It is also noted that, based on the same axis scale, the apparent differences between the curves of opposite orientations were reduced when the system had the lower limit value of $G$ (e.g., CTA-NW). In order to achieve a better inspection without the influence of the coordinate scaling entails, the quantitative analysis based on the limit behaviors of the equivalent circuit is entailed.
Figure 4.5 (a) The conductance as a function of frequency, and (b) water flux. The plots were obtained under dynamic testing conditions for both AL-DS and AL-FS orientations. Error bars were obtained the average and standard deviation of multiple measurements.

The explanatory circuit for the dynamic system was depicted in the lower panel of Figure 4.1(b). In particular, the conductive elements for the feed solution
and draw solution are denoted by $G_{eF}$ and $G_{eD}$, respectively. Then, the limit formulations for the static system are extended to account for the difference of the electrolyte solutions by invoking the recursive algorithm:

$$\lim_{f \to b} G = \frac{G_{eF} - G_{eD} - \bar{G}_m}{G_{eF} + G_{eD} + \bar{G}_m} \approx G^L$$ \hspace{2cm} (4.14)

$$\lim_{f \to \infty} G = \frac{G_{eF} G_{eD}}{G_{eF} + G_{eD}} \approx G^H$$ \hspace{2cm} (4.15)

The group $\frac{G_{eF} G_{eD}}{G_{eF} + G_{eD}}$ can be viewed as the average value of the electrolyte conductance, and was approximated by the value of $G^H$ for resolving the average value of the membrane conductance $\bar{G}_m$.

Table 4.1 Values of conductive elements for static and dynamic tests.

<table>
<thead>
<tr>
<th></th>
<th>Static test</th>
<th>Dynamic test</th>
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<tbody>
<tr>
<td></td>
<td>-</td>
<td>AL-FS</td>
</tr>
<tr>
<td>CTA-HW</td>
<td>$G^L$</td>
<td>6.9 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$G^H$</td>
<td>10.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$G^m$</td>
<td>21.7 ± 0.2</td>
</tr>
<tr>
<td>CTA-W</td>
<td>$G^L$</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$G^H$</td>
<td>10.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$G^m$</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>CTA-NW</td>
<td>$G^L$</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$G^H$</td>
<td>8.9 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$G^m$</td>
<td>1.4 ± 0.1</td>
</tr>
</tbody>
</table>

Note: Unit for all values is S/m²; values of $G_m$ for dynamic tests are the averaged values $\bar{G}_m$ over the membrane profile.

The calculated values of $\bar{G}_m$ were listed in Table 4.1. It is evident that the values of $\bar{G}_m$ measured in the tests with AL-DS orientation were significantly
greater than the corresponding values of $G_m$ from the reversed orientation. However, as discussed in the previous studies (Cath et al. 2006; Tang et al. 2010), when the active layer is facing the feed solution, the dilutive ICP occurs indicating a more conductive support layer as the concentration level in the porous structures is dominated by the draw solution. This discrepancy may be explained by the fact that the overall conductance of the FO membrane is more sensitive to the active layer, which is contacting with the solution with the opposite concentration level. The bulk flux measured during the dynamic tests is also plotted in

![Diagram](image.png)

**Figure 4.5(b).** It clearly shows that the bulk flux yielded in the AL-FS orientation was significantly lower than that from the reversed orientation. This is consistent with the previous work (Jin et al. 2011; Wei et al. 2011) stating that the
dilutive ICP in the AL-FS orientation gives rise to a more severe loss of driving force across the active layer. The convective diffusion of the electrolyte species, which is not taken into account by the current models, may have considerable impact on the electric properties of the membrane during the FO processes.

4.5 Conclusions

In this work, we proposed a new application of EIS characterization to the FO processes. The electric properties carrying the information of the membrane substructures were successfully identified by exploiting the limit behaviors of the impedance spectra. The effects of the ICP on the impedance spectra were clearly observed as the osmosis processes were scanned by the EIS system in real time. Although the values of FO membrane conductance $G_m$ were estimated by the developed limit formulations, the contributions of the active layer and support layer were not distinguished without catching the corresponding characteristic frequencies in the impedance spectra. Furthermore, the mechanisms accounting for the effects of the convective diffusion on the electric responses are still ambiguous.

As the first step to explore a novel characterization method, the potential of the EIS for characterizing the FO systems was justified by the current work. However, more systematical studies are required to improve both the EIS system and the approach to interpreting the impedance spectra, so as to obtain more accurate and extensive information relating to the complex polarization phenomena during the FO processes.
CHAPTER 5

CHARACTERIZATION OF FLUID DYNAMICS IN SPACER-FILLED CHANNELS FOR MEMBRANE FILTRATIONS USING DOPPLER OPTICAL COHERENCE TOMOGRAPHY

In previous chapter we discussed the subtle interplay between substrate structures and ICP. On the other hand, the effect of ECP is usually determined by the hydrodynamics of the fluid. In this chapter, a new application of Doppler optical coherence tomography (OCT) technique was employed to characterize the flow patterns in spacer-filled channels.

5.1 Introduction

Membrane filtration is one of the emerging separation technologies that has extensive application in water/wastewater treatment (Mulder 1996; Cath et al. 2005; Le-Clech et al. 2006; Tang et al. 2006; Cornelissen et al. 2008), desalination (Fritzmann et al. 2007; Greenlee et al. 2009; Jin et al. 2011; Lay et al. 2011), and others (Li et al. 2005; She et al. 2012; Li et al. 2013). Previous studies indicate that the performance of membrane processes is adversely affected by the coupled phenomena of concentration polarization (CP) and membrane fouling (Field et al. 1995; Hoek and Elimelech 2003; Chong et al. 2008; Li et al. 2009; Tang et al. 2010; Tang et al. 2011; Wang and Tang 2011). The resulting concentration profiles and foulant layers could significantly reduce the membrane throughput and decrease the membrane selectivity (Mulder 1996; Fane et al. 2011). Therefore, novel characterization techniques are of crucial importance to mitigate these negative impacts, especially when the optimization of filtration membranes is focused on achieving a higher water permeability and higher solute rejection (Mulder 1996).

Considerable effort has been devoted to improving the hydraulic environment in various membrane configurations such as plate-and-frame and spiral wound modules. The basic idea is to enhance the degree of turbulence near the
membrane surface so that the thicknesses of the hydrodynamic and concentration boundary layers can be reduced (Da Costa et al. 1994; Cao et al. 2001). One of the most efficient ways of promoting turbulence is to fill the fluid channels with well-designed spacers, which are usually meshes fabricated from polymer filaments (Da Costa et al. 1991; Da Costa et al. 1994; Neal et al. 2003). Previous studies have shown that the spacer-filled fluid channels provide less space for the fluid streams, thereby increasing the local fluid velocity on the membrane surface; on the other hand, the presence of the spacer filaments also creates tortuous fluid paths that usually result in eddies of various magnitude (Neal et al. 2003). It is also recognized that increasing the packing density and tortuosity is accompanied by a reasonably large pressure drop through the membrane modules (Schock and Miquel 1987; Da Costa et al. 1991; Da Costa et al. 1994). The optimization of membrane spacers to promote a higher degree of turbulence and a lower pressure drop necessitates the study of characterizing the fluid dynamics in a more subtle fashion.

Both theoretical and experimental approaches have been adopted to investigate the flow behavior in spacer-filled fluid channels. Owing to the advancement of numerical techniques, computational fluid dynamics (CFD) has come to play an important role in revealing the detailed flow patterns resulting from the interaction between the fluid and the filaments that form periodic barriers in the narrow channels. Cao et al. for the first time adopted the approach of CFD to investigate the effects of the spacer configurations on the velocity and local shear stress distributions in a two-dimensional spatial domain (Cao et al. 2001). This numerical approach then was extended to simulate more complicated cases involving three-dimensional flow patterns (Karode and Kumar 2001; Fimbres-Weihs and Wiley 2007; Koutsou et al. 2007; Fimbres-Weihs and Wiley 2010). Although several interesting simulation results were obtained from these CFD studies, direct experimental support was rarely reported in the open literature. Furthermore, a very large computational effort can be required for simulating complicated configurations that could be of particular value in designing novel spacers with better performance. Most of the experimental studies focused on assessing the spacer performance that was interpreted based on some hypothesis. Several empirical and semi-empirical correlations have been obtained for predicting
the mass-transfer rate and pressure drop in terms of the operating conditions and the
basic geometrical characteristics of the spacer-filled channels (Schock and Miquel
1987; Da Costa et al. 1991; Da Costa et al. 1994; Karode and Kumar 2001; Ghidossi et al. 2006).

Gaining a better understanding of the underlying mechanisms accounting for
the spacer performance and bridging the gap between the model predictions and
experimental observations require direct visualization of the velocity field within
the spacer interstices. Recent experimental studies have employed some novel
techniques to detect the detailed behavior of the fluid flowing through a spacer-
filled channel. The particle image velocimetry (PIV) technique was introduced by
Gimmelshtein et al. to investigate the velocity distribution within a membrane cell
(Gimmelshtein and Semiat 2005). The PIV method was further modified to
accommodate two-phase flows by Willems and co-workers (Willems et al. 2010).
The direct observation through the membrane (DOTM) technique was also explored
to reveal the interplay between the feed solution and the spacer; the movement of
the tracer particles (latex beads (Neal et al. 2003; Wang et al. 2010), micro-
organisms (Wicaksana et al. 2012; Zou et al. 2013) or micro-bubbles (Willems et al. 2009)) within the spacer network was recorded to analyze the streamlines relating to
the velocity field. However, in general these visualization techniques are unable to
resolve the variation of the velocity field in the direction perpendicular to the
membrane wall, which is of great importance to elucidate the hydrodynamic
environment adjacent to the membrane surface.

Optical coherence tomography (OCT) is an optical technique that employs
near-infrared light of relatively long wavelength so that a deeper detection with
micrometer-resolution can be achieved relative to techniques such as confocal
microscopy (Huang et al. 1991; Tomlins and Wang 2005; Wang et al. 2012). In
Fourier Domain OCT interference fringe signals are first obtained as a function of
optical frequency; both the magnitude and phase angle of the signals then are recast
in the spatial domain via a Fourier transform (Brezinski 2006). In addition to the
structural image derived from the signal intensity, the velocity profile is obtained by
detecting the variation of the phase angles between two consecutive scans via the
Doppler effect (Wu 2004). Doppler OCT is one of the most powerful non-invasive imaging techniques and has been successfully applied to the *in vivo* observation of blood flow (Chen *et al.* 1997; Yazdanfar *et al.* 2000; Larina *et al.* 2008).

This study adapts the Doppler OCT technique to the investigation of the effect of the spacer characteristics on the flow patterns during a membrane filtration process. A membrane cell was modified to accommodate the Doppler OCT system so that the optical scans could be implemented within the spacer network on the membrane surface. In particular, the detection was aimed at visualizing the velocity profiles in a two-dimensional plane normal to the membrane surface, while the spacer orientation was changed in relation to the bulk flow direction. The Doppler images were used to describe the transport phenomena within the spacer interstices; these analyses provided insight to interpret the filtration performance during the reverse osmosis (RO) process with the same spacer configurations. To the best of our knowledge, this is the first study of the application of the Doppler OCT system to the characterization of the fluid dynamics during a membrane filtration process.

### 5.2 Experimental methods

#### 5.2.1 Doppler OCT imaging

The visualization of the velocity field within the spacer network was achieved by integrating a Doppler OCT system (TELESTO 1325 nm OCT System, Thorlabs Inc., Newton, NJ) with a cross-flow filtration system as schematically depicted in Figure 5.1. The dynamic flow patterns within the filtration cell are directly detected by the OCT camera; the optical signals then are resolved to show the OCT images.
Figure 5.1 Schematic of the OCT incorporated system for detecting the velocity field in a spacer-filled channel during membrane filtration processes. In the OCT system, the SD-OCT engine contains a superluminescent diode (SLD) light source with a central wavelength of 1325 nm and a linear InGaAs array-based spectrometer. A video camera is integrated in the probe which offers live imaging during data acquisition. The data acquisition system (TELESTO Software) is provided by Thorlabs Inc. (Newton, NJ).

The spectral domain OCT (SD-OCT) system has a higher mechanical stability and lower phase noise compared to swept-source OCT (SS-OCT) systems (Yaqoob et al. 2005). In the SD-OCT a light beam of low coherence is emitted from a broadband light source and split into sample and reference arms. Interference patterns then are obtained by recombining the reflected light from the sample and the reference; in particular, the light reflected from different depths interferes with a specific component of the reference light at different frequencies.
The acquired frequency domain interferograms then are Fourier transformed to obtain the signals as a function of the sample depth. The magnitude of the complex signals is used to generate the structural image of the scanned region; the changes rates of the phase angles contain the information pertaining to the local movement. Specifically, the variation of the phase angle $\Delta \phi$ in an incremental time interval $\Delta t$ is related to the frequency shift $f_D$ by:

$$f_D = \frac{\Delta \phi}{\Delta t \cdot 2\pi}$$  \hspace{1cm} (5.1)

In terms of the Doppler Effect (Tomlins and Wang 2005; Kundu and Cohen 2008) the local velocity $v$ then is evaluated with this frequency shift as:

$$v_p = v \cos \theta = \frac{\lambda f_D}{2n}$$ \hspace{1cm} (5.2)

where $\lambda$ is the center wavelength, and $n$ is the index of refraction. The local velocity can be obtained only when the Doppler angle $\theta$ is known, which is defined as the angle between the light beam and the moving direction of the fluid particles. For the cases in which the value of the Doppler angle is not available, the optical signals by themselves give rise to the velocity component $v_p$ that is parallel to the direction of the light beam.

The Doppler OCT was adapted to observe the flow pattern in the fluid channel of a membrane filtration module by modifying an acrylic filtration cell with a rectangular channel of 3.8 cm $\times$ 9.2 cm. The upper wall of the cell channel was replaced with a thin transparent glass plate (3.2 cm $\times$ 6.4 cm) so as to introduce the light beam from the OCT into the channel. The observation cell was mounted onto the sample station of the OCT system. As introduced by Equation (5.2), only the movement parallel to the light beam is detected by the Doppler OCT system. Therefore, the observation cell was slightly inclined so that the sample light was introduced into the filtration cell with an angle $\alpha$ that is formed by the observation cell surface (the direction to the fluid outlet) and the light beam (the direction towards the membrane). In particular, this inclination angle is specified by the
positive direction of the bulk flow (pointing to the flow outlet) and the positive direction of the light beam (away from the detector) as shown schematically in Figure 5.2(a). It therefore forms an angle greater than 90° when the outlet side of the observation cell is slightly raised from the horizontal station, whereas an acute angle is generated by lifting the inlet side. This inclination angle needs to be carefully chosen so that the Doppler OCT signal would not be overwhelmed by the noise.

The feed water was circulated into the filtration cell via an electromagnetic pump. The flow rate was controlled at ~180 mL/min so that the nominal fluid velocity in the fluid channel (3.8 cm × 9.2 cm × 0.2 cm) was ~3 cm/s. In the current study the trans-membrane pressure was very low so as to prevent the thin glass wall from being cracked and to avoid leaking (because the glass plate was glued onto the cell frame). Therefore, the impact of the permeate flux on the flow field in the channel can be neglected. Ultra-heat treatment (UHT) milk with 1.5% fat was added into the feed water with a volume ratio of about 1:100. The micro-particles of the milk facilitated the OCT imaging by improving the scattering properties of the feed fluid. The acquired Doppler data were imaged by using a user-defined color mode as shown by the color map in Figure 5.2(b). A black color indicates that there is no local movement in the observation direction; the change of color from black to blue (red) corresponds to the relative increase of the local velocity towards (away from) the OCT detector.
Figure 5.2 Schematic of different measurement angles in OCT scans: (a) $\alpha$ is the angle between the observation surface (the direction to the fluid outlet) and the light beam (the direction to the membrane surface); (b) $\theta$ is the angle between the velocity vector and the light beam (the direction to the membrane surface) at a certain location in the fluid (the motion towards the detector is color-coded by the blue band, whereas the red band is for the motion away from the detector).

The net-like spacer used in this study is commercially available from GE Power & Water (GE Osmonics, SEPA); a photo of this spacer is shown in Figure 5.3(a). A typical unit cell of the spacer is schematically shown in Figure 5.3(b) and its major dimensions are indicated. The spacer is composed of two groups of filaments with a nominal diameter of ~0.6 mm; one group of filaments lies on top of the other group with an internal angle of 90°. All filaments are evenly distributed with a distance of ~3 mm; the intersected filaments are partially merged into each
other to form knots with a thickness of ~1.2 mm. The spacer was fixed between the observation window (upper wall) and filtration membrane (lower wall). In this paper the filaments touching the membrane surface (denoted by grey) are in particular defined as the attached filaments, which are exploited to identify the orientations of the spacer in the fluid channel; the filaments close to the observation window (denoted by green) are correspondingly designated as the detached filaments.

The OCT characterization was carried out with three spacer orientations as illustrated by Figure 5.3(b): (i) the axial configuration in which the attached filaments were parallel to the direction of the bulk flow; (ii) the transverse configuration in which the attached filaments were orthogonally intersected with the bulk flow; (iii) the diamond configuration in which the attached filaments were inclined to the bulk flow at an angle of 45°. In addition, the flow pattern without the installment of the spacer was also examined so as to serve as a baseline for comparative studies.

In each OCT characterization the scans were carried out at room temperature (~20 °C) and initiated about 10 min after circulating the feed water through the filtration cell. The scans were focused on different cross-sections in a single unit of the spacer; the two-dimensional Doppler images were consecutively recorded with a frame rate of 10 fps. The recorded image data in a time interval of 5 s then were used to obtain the time-averaged Doppler images with reduced random noise, which are shown in this paper. The OCT scans were carried out in more than two different unit cells of the spacer to ensure the reliability of the results.
Figure 5.3 The structure of the spacer used in the current study: (a) microscopic image of the spacer; (b) schematic of a unit cell in the spacer with major geometric dimensions. The spacer orientation is determined by the relative arrangement of the attached filaments (in direct contact with the membrane surface) to the bulk flow direction.
5.2.2 RO filtration

For a parallel study the performance of RO filtration with the same spacer configurations was evaluated with a laboratory scale RO setup. Specifically, the filtration fluxes and the salt rejections were measured as the spacer orientation was changed in the same way for the OCT characterization. The membrane was placed in a cross-flow filtration cell (CF042 Membrane Cell, Sterlitech, WA) with an effective area of 42 cm². The feed solution (0.01 mol/L NaCl) was pumped with a variable speed diaphragm pump (Model D-03, HydraCell, Minneapolis, MN) at a fixed trans-membrane pressure of ~1.3 MPa. The cross-flow rate was adjusted by a needle valve and maintained at a constant value of 200 mL/min (the corresponding nominal cross-flow velocity was about 3 cm/s). The temperature of the feed solution was kept at 24 °C with a refrigerated water circulating bath (BL-710, YIHER). The permeate flux was measured using a digital flow meter (Bronkhorst, Netherlands) and the salt rejection was obtained by measuring the conductivities of both the feed and permeate streams with a conductivity meter (MYRON L 4PII, Cole-Parmer). All the RO filtrations were repeated three times to ensure consistency and reproducibility of the measurements.

5.3 Results and discussion

5.3.1 Imaging the flow pattern in the channel with no spacer

The color-coded Doppler image in Figure 5.4 shows the velocity profiles in the channel without a spacer. As was mentioned in Section 5.2.1, the observation cell was intentionally inclined at an angle \( \alpha \) with respect to the incident light so as to increase the magnitude of the velocity component parallel to the light beam. In the first case the outlet side of the cell was slightly raised to create an obtuse inclination angle of 95° as shown in Figure 5.4(a). The observation cell then was inclined by lifting the inlet side to make an acute inclination angle of 85° as shown in Figure 5.4(b). It was assumed for that the flow was guided by the channel and that all streamlines were parallel to the channel walls since there were no
obstructions present. Therefore, the Doppler angles in both cases were expected to constantly equal to the inclination angle $\alpha$.

The assumption of laminar flow is validated by the color patterns in Figure 5.4. It clearly shows that raising the outlet side results in a color band in the blue region, whereas the opposite inclination yields a color band in the red region. This is consistent with the color map given in Figure 5.2(b) defining that the motion towards the camera is indicated by blue, whereas the color band is red for the motion away from the camera. It is also evident that both color bands gradually fade as the detection point is getting closer to the channel walls from the channel center. Owing to the invariant Doppler angle $\theta$ the magnitude of the fluid velocity should be proportional to that of the parallel component that was detected by the OCT. Therefore, both color patterns indicate a parabolic velocity distribution, which is consistent with the classical model for laminar flow between two parallel flat plates (Kundu and Cohen 2008). The results from these baseline cases also verify the ability of the Doppler OCT to resolve the velocity variation in the direction normal to the membrane surface.
Figure 5.4 Doppler images of the velocity field in the channel without spacer. The fluid inlet is on the right side: (a) the inclination angle $\alpha$ of the observation cell is 95°; (b) the inclination angle $\alpha$ of the observation cell is 85°.
5.3.2 Imaging the flow pattern in the spacer-filled channel (the attached filaments parallel to the flow direction)

In this study the arrangement of the attached filaments (in direct contact with the membrane surface) in relation to the bulk flow direction is used to designate the spacer orientation, which is schematically shown in the left panels of each Doppler image. The lower wall of the observation cell is referred to as the membrane side for defining the attached filaments that are denoted by grey, while the detached filaments (touching the upper wall or the observation window) are represented by green. The flow direction is given by the blue arrows in these plots. Specifically, the scanned cross-sections are indicated by the red sectioning lines with two-end bars towards the viewpoint. All OCT scans for the spacer-filled channel were implemented with the inlet of the observation cell slightly lifted to create an inclination angle $\alpha$ of 85°.

In the first case the spacer was arranged to make the attached filaments parallel to the bulk flow direction (the axial configuration). The Doppler OCT scans were focused on a unit cell of the spacer; two typical cross-sections were scanned to obtain the time-averaged Doppler images as shown in the right panel of Figure 5.5. The direction of the incident light beam is indicated by the orange arrow by the Doppler images. In particular, the sectioned filaments are circled by white dashes in terms of the structural images in which the filament regions could be easily distinguished from the surrounding fluid.
Figure 5.5 Doppler images of the velocity field in the channel filled with a spacer; the attached filaments are parallel to the bulk flow direction (axial configuration). Schematics for demonstrating the spacer orientation (grey for the attached filaments, and green for the detached filaments) and the scanned cross-sections (red sectioning lines) are given in the left panel: (a) the cross-section parallel to the bulk flow direction and (b) the cross-section perpendicular to the bulk flow direction in the center of the unit cell. The inclination angle \( \alpha \) of the observation cell is 85°; the filament cross-sections are circled with dashes in terms of the corresponding structural images. The color map is given in Figure 5.2.

The first cross-section is located in the center of the unit cell and parallel to the bulk flow as depicted in the left panel of Figure 5.5(a). It is evident in the corresponding Doppler image that the two filaments are in contact with the upper wall, whereas the filaments contacting the lower wall are absent from this view. In comparison to the result from the channel without spacer in Figure 5.4(b), in which the observation cell was inclined in the same way (the inclination angle \( \alpha \) is 85°), complex color patterns with circular structures are created within the spacer interstices. The presence of the spacer resulted in secondary flows of which directions were deviated from the bulk flow. Therefore, the local Doppler angle is
CHAPTER 5

not available for evaluating the local velocity; the color patterns in this case only indicate the variation of the velocity component parallel to the light beam.

The Doppler image in Figure 5.5(a) clearly indicates that the movement of the fluid behind and in front of the filaments is significantly curved. The fluid entered the unit cell from the slit formed by the upstream filament and the lower wall; part of the fluid was directed to flow towards the upper wall and then entrained by the gap between the upper wall and the filament as shown by the rounded blue band behind the upstream filament. A smaller curved band of red color is found inside the blue one indicating that an eddy might be formed in this region. In the region in front of the downstream filament, the curved band of red color represents the flow away from the camera after being reattached onto the upper wall.

Although the multi-layer circular bands with alternating colors somehow provide an evidence of the existence of vortical structures, it is interesting to note that the fluid path indicated by the Doppler image is roughly consistent with those predicted by the CFD results in previous studies (Cao et al. 2001; Schwinge et al. 2002; Shakaib et al. 2007) though there are some irregularities. It is intuitively expected that the rotating motion of a vortex should create a rounded band with the opposite sides having different colors (red or blue). To resolve this discrepancy, further study is needed to figure out the exact velocity field via the Doppler OCT approach that involves a dual-beam system (Iftimia et al. 2008; Daly et al. 2012) or an additional measurement relating to the Doppler bandwidth (Piao and Zhu 2003).

It is also evident that there are some dark regions in the Doppler images. The regions adjacent to the boundary walls were likely filled with liquid almost at rest and therefore are referred to as the absolute dark regions. In contrast, flows with significant momentum can be present in the dark regions between the ring-shaped structures and through the gaps between the detached filaments and lower wall. This is because the Doppler OCT with single incident light is unable to detect motion perpendicular to the light beam. There is also a possibility that the local velocity components are too high to be detected by the OCT, since the maximum detectable velocity in the beam direction is limited by the axial scan rate and the
OCT wavelength. These undetectable regions are referred to as the pseudo-dark regions, in which the shear force may be dominant.

The Doppler image of the cross-section normal to the bulk flow direction is shown in Figure 5.5(b). It clearly shows that the velocity field is symmetric about the center of the unit cell. Referring to the color pattern in Figure 5.5(a), this scan gives a sectioned view of the circular structure in front of the downstream filament. It shows that the convective flux normal to the boundary walls is most likely in the regions above the attached filaments, whereas the pseudo-dark regions are confined by the neighboring attached filaments and the lower surface. The shear flow (tangent to the boundary walls) and the normal flow (perpendicular to the boundary walls) can play different roles in the transport phenomena during concentration polarization or membrane fouling; their development in the spacer-filled channel is strongly influenced by the subtle interaction between the filaments and the fluid as shown by the Doppler images.

5.3.3 Imaging the flow pattern in the spacer-filled channel (the attached filaments perpendicular to the flow direction)

In the second configuration the attached filaments were arranged to be perpendicular to the bulk flow (the transverse configuration) as shown by the schematics in the left panel of Figure 5.6. It is expected that the fluid would experience the same channeling as in the first configuration (the axial configuration) since the upper and lower walls are indistinguishable to the fluid. From the perspective of an OCT observation, the second configuration is equivalent to scanning the same flow field in the first configuration with an incident light beam introduced from the lower surface (the membrane side).
Figure 5.6 Doppler images of the velocity field in the channel filled with a spacer; the attached filaments are perpendicular to the bulk flow direction (transverse configuration). Schematics showing the spacer orientation (grey for the attached filaments, and green for the detached filaments); the scanned cross-sections (red sectioning lines) are given in the left panel: (a) the cross-section parallel to the bulk flow direction and (b) the cross-section perpendicular to the bulk flow direction in the center of the unit cell. The inclination angle $\alpha$ of the observation cell is 85°; the filament cross-sections are circled with dashes in terms of the corresponding structural images. The color map is given in Figure 5.2.

Similarly, a cross-section was first scanned in the direction parallel to the bulk flow as shown in Figure 5.6(a). In contrast to the Doppler image in Figure 5.5(a), the sectioned filaments are in contact with the lower wall. A multi-layer circular structure with a red outer layer is found behind the upstream filament while another one with a blue outer layer is in front of the downstream filament. The cross-section normal to the bulk flow in the second configuration is shown by the Doppler image in Figure 5.6(b). This scan sectioned the ring-shaped structure in front of the downstream filament through the region dominated by the flux normal to the detection light beam, thereby generating the color pattern mostly occupied by black, i.e., the pseudo-dark region.
If the surface touching the filaments in Figure 5.6(a) is considered from the perspective of a reflecting surface, the resulted velocity field is a mirror image of that in the same cross-section for the first spacer configuration shown in Figure 5.5(a). It is observed that similar ring-shaped structures are created in the positions that are of planar symmetry in these two Doppler images. The corresponding bands are shown to have opposite colors since the detection light beam was introduced from different surfaces in terms of this planar symmetric system. However, it is also evident that the size of these band pairs is changed in a complementary sense; that is, the size of the blue bands is expanded while the color is changed to red and vice versa. This discrepancy of the color pattern symmetry can be understood by taking into account the fact that the observation cell was inclined to the OCT station surface at a small angle by slightly lifting the inlet side of the cell in both cases.

Instead of a rigorous mathematical argument, a schematic is given in Figure 5.7 to illustrate how this inclination angle affects the color patterns in the Doppler images. The solid blue line represents the OCT station surface in the first
configuration; the detection light beam (light beam 1) is introduced from surface 1 (the upper wall in this case) into the cell with an inclination angle $\alpha_1$, which is less than $90^\circ$ due to the higher level on the inlet side. A local velocity vector $v$ is shown by the black arrow; its parallel component $v_{pl1}$ with respect to the light beam 1 is shown by the red arrow. As mentioned at the beginning of this section, the second spacer orientation can be viewed as if the detection light beam (light beam 2) was introduced from the opposite surface (surface 2) while the velocity field remains unchanged; i.e., the local velocity $v$ is invariant. Considering the fact that the inlet side of the cell was consistently raised for all OCT scans, the inclination angle $\alpha_2$ should be equal to $\alpha_1$. As a result, the same velocity vector is resolved relative to the direction of light beam 2 as $v_{pl2}$ (the blue arrow) with an opposite phase shift (moving to the negative direction of light beam 2) and a relatively small magnitude in comparison to the parallel component $v_{pl1}$ for the first configuration. The reversal of the phase shift explains the exchange of the color bands in the Doppler images; the magnitude variation of the parallel components is responsible for the asymmetric effect of the eddy size.

The size variation of the ring-shaped structures in these two configurations should be minimized when the local velocity vector is normal or parallel to the cell wall. When the local velocity vector is perpendicular to either of the two incident light beams (i.e., the undetectable cases), its parallel component with respect to the other light beam could still be of significant magnitude. It is for this reason that the dark regions surrounding the curved bands are partially filled with color in their mirror images. This also substantiates that these dark regions are pseudo-dark regions. For example, the dark regions between the filaments and the lower wall in Figure 5.5(a) are shown with clear color bands by their corresponding parts in the mirror reflection in Figure 5.6(a), i.e., the gaps between the filaments and the upper wall. According to the color patterns in Figure 5.6(a), the tangential flows close to the wall were significantly accelerated when passing through the filament gaps; this acceleration effect was confined within a narrow region, beyond which the absolute dark regions are observed. This is consistent with modeling results in the literature.
(Cao et al. 2001) that predict a pulse-like distribution of the shear stress on the membrane surface.

The comparison of the visualization of the two spacer orientations indicates that the interpretation of the Doppler images is dependent on the coordinate system that accounts for the interrelationship between the bulk flow direction, the inclined cell surface, and the incident light beam. Correctly identifying the regions with different dominant momentum transfer mechanisms is of great value in understanding CP or fouling phenomena during a membrane filtration process.

5.3.4 Imaging the flow pattern in the spacer-filled channel (the attached filaments inclined to the flow direction)

The diamond configuration is more complex in that all the spacer filaments intersected the bulk flow at an angle of 45°. More cross-sections were scanned in comparison to the first two configurations so that the variation of the velocity field along the transverse direction could be resolved. The sectioning positions are schematically shown in the left panel of Figure 5.8.

The Doppler image in Figure 5.8(a) was taken in the diagonal plane sectioning two filament knots; the sectioning plane was normal to the channel walls. It clearly shows that the merging of two filaments results in larger sectioning areas of the filaments. The fluid was unable to cross the knots in the direction parallel to this cross-section, since the height of the channel is theoretically defined by the filament knot. Instead, the fluid was split into two streams that entered the unit cell from different directions and height levels. One stream was mainly guided by the detached filaments and flowed across the attached filaments before entering a unit cell; the other stream was coming from a direction almost perpendicular to the first stream and through the gap between the lower wall and the detached filaments. These two streams partially merged along the diagonal axis and were hindered by the downstream filaments before leaving the unit cell.
Figure 5.8 Doppler images of the velocity field in the channel filled with a spacer; the attached filaments are inclined to the bulk flow direction at an angle of 45° (diamond configuration). Schematic showing the spacer orientation (grey for the attached filaments, and green for the detached filaments); the scanned cross-sections (red sectioning lines) are given in the left panel: (a) the cross-section parallel to the bulk flow direction and sectioning the filament knots; (b) the cross-section parallel to the bulk flow direction and sectioning the part with the attached filament downstream; (c) the cross-section parallel to the bulk flow direction and sectioning the part with the attached filament upstream; (d) the cross-section perpendicular to the bulk flow direction and sectioning the filament knots. The inclination angle $\alpha$ of the observation cell is 95°; the filament cross-sections are circled with dashes in terms of the corresponding structural images. The color map is given in Figure 5.2.
These complex interactions create two pairs of circular structures attaching onto the upstream and downstream filament knots in Figure 5.8(a). The circular structures above the mid-plane have the opposite colors compared to those below the mid-plane indicating conflictive fluid movements at the merging surface. Previous 3D CFD study (Koutsou et al. 2007) predicts that a central free vortex with spiral 3D structures could be generated along the diagonal axis in the diamond configuration. However, such a vertical movement cannot be clearly derived from this view; further observation is required to verify this free vortex. Nevertheless, both approaches elucidate that the diamond configuration is able to generate more complex flow patterns in relative to the other configurations.

In order to elucidate the whole picture of the velocity field in this complex case, two more cross-sections parallel to the first one were scanned by shifting the sectioning line to two opposing directions. The sectioning line was first shifted to the part in which the attached filament was upstream as shown by the left panel in Figure 5.8(b), while the cross-section in Figure 5.8(c) intersected the part with the attached filament downstream. Similar to the relationship between the axial and transverse spacer configurations, the velocity fields in these two cross-sections should be the mirror images of each other. However, the color patterns shown in the Doppler images are not in good agreement with the expectation of planar symmetry. This deviation of the OCT Doppler imaging stems from the same reason discussed in section 5.3.3; i.e., the inclined observation cell could significantly affect the magnitude of the phase shift signals. Regardless of these asymmetric effects, these color patterns clearly demonstrate the complex interactions between the fluid and the filaments. It is observed that some ring-shaped structures are spanning the space between the two filaments; relatively small ones are found in the corners that are restricted by the filaments and the channel walls. Furthermore, the average distances between two filaments in the direction of the bulk flow are substantially decreased in this case. As a result, combining these two cross-sections shows that the absolute dark regions near the walls are reduced in contrast to those in the axial and transverse configurations.
Figure 5.8(d) shows the cross-section that sectioned the filament knots but normal to the bulk flow direction. The inclination of the observation cell had no influence on this view for imaging the planar symmetric parts. The Doppler image demonstrates two similar rounded patterns with opposite color bands; the counter flows by the central axis indicate a rotated current that is free to the filaments. This is consistent with the simulation results from CFD studies (Fimbres-Weihs and Wiley 2007; Koutsou et al. 2007), though the free vortex may not be fully developed (Fimbres-Weihs and Wiley 2007) (Reynolds number is approximately 50 in the current study). Besides, the regions with significant normal flows (red or blue regions) are almost sweeping the entire profile of the channel. Intense flow mixing might occur in the pseudo-dark regions, which can significantly improve the degree of turbulence, thereby accelerating the mass-transfer rate in this configuration.

5.3.5 Interpretation of the filtration performance based on the Doppler images

The Doppler images reveal that there are two major mechanisms inside the spacer interstices, which could be relevant to the mass transport phenomena during membrane filtration. The first is the tangential flows mainly driven by the bulk motion of the feed fluid; the other is the development of eddies, which could generate significant flows normal to the membrane surface and create disturbance in these regions. Their development and spatial distribution in the channel are primarily governed by the geometrical characteristics and orientation of the spacer in relation to the channel. The current study was also intended to correlate the observations from the OCT characterization with the filtration performance during a membrane separation process. In particular, the filtration flux and solute rejection were evaluated during RO with the filtration cell filled with the same spacer.

As revealed by previous studies (Fane et al. 2011), the filtration flux and solute rejection during RO processes are a strong function of the CP phenomenon that in essence is an indicator of the effective solute transport rate on the membrane.
surface. In general, as the filtration process proceeds, water continuously permeates through the membrane while solute is being partially or completely rejected; therefore, a concentration profile of the solute is developed on the membrane surface, which is referred to as external concentration polarization (ECP). This complex transport phenomenon is usually described by a film theory model (Fane et al. 2011), and mathematically expressed as:

$$\frac{C_m - C_p}{C_f - C_p} = \exp \left( \frac{J_v}{k_s} \right) \tag{5.3}$$

in which $C_f$ and $C_p$ are the solute concentrations of the feed solution and permeate stream; $C_m$ is the solute concentration on the membrane surface and a function of the degree of CP; $J_v$ is the filtration flux, i.e., the flow rate of the permeate per unit area of the membrane; $k_s$ is the mass transfer coefficient in the concentration boundary layer and usually defined as:

$$k_s \equiv \frac{D_s}{\delta_{eff}} \tag{5.4}$$

where $D_s$ is the solute diffusion coefficient and $\delta_{eff}$ is the effective boundary layer thickness. The impact of the hydrodynamics on the mass-transfer rate is therefore lumped into this mass-transfer coefficient, or more specifically, the effective thickness characterizing the concentration boundary layer.

The RO performance was evaluated by using a filtration cell filled with the same spacer; the spacer orientation was varied in the same way as for the OCT characterization. The experimental results are shown in Figure 5.9(a) and (b) for the normalized filtration flux ($J_f / J_w$, $J_w$ is the filtration flux with pure water as the feed) and the apparent solute rejection ($R_s \equiv 1 - C_p / C_f$), respectively. These data clearly show that the existence of the spacer in the filtration channel substantially mitigated the adverse effects of the CP on both the filtration flux and solute rejection. Basically, the spacer-filled channel provided a better hydraulic
environment for enhancing the mass transfer on the membrane surface (increasing the value of $k_s$), thereby reducing the difference between solute concentrations in the bulk flow and on the membrane surface as indicated by Equation (5.3); minimizing the surface concentration then reducing the trans-membrane osmotic pressure difference (resulting in a higher filtration flux) and the permeate concentration (resulting in a higher solute rejection). Moreover, a variation of the RO performance as a function of the spacer orientation was observed; accounting for these differences requires the knowledge of the interplay between the fluid and the spacer, which can be provided by the Doppler OCT characterization in this study.
As discussed in section 5.3.3, the axial and transverse configurations gave rise to the same velocity field. However, the local hydraulic environment on the channel walls was different as elucidated by the Doppler images. These differences
resulted in the variation of the filtration performance when replacing the lower channel wall with a membrane in the RO tests. In the axial configuration the membrane surface was dominated by the shear flow as indicated by the pseudo-dark regions near the lower wall in Figure 5.5(a). However, the influence of the shear force was mostly confined within the narrow regions underneath the filaments, whereas the remaining parts of the membrane were in contact with the absolute dark regions, in which the flow was moving at an extremely low rate. The effect of cell inclination on the Doppler OCT observation is verified by comparing the color pattern near the upper wall in Figure 5.5(a) and Figure 5.6(a).

In contrast, the opposite channel wall was mainly influenced by swirling flows of a size that covered a relatively large membrane area; the flow near the membrane surface contained a significant velocity component towards the bulk flow as indicated by the region near the upper wall in Figure 5.5(a). Although both the shear and normal flows benefited the mass transfer on the membrane surface, the relatively narrow regions affected by the shear flow are probably responsible for the lower RO performance of the axial configuration. It is also noted that the results of solute rejection have relatively narrow confidence intervals compared to those for the flux measurements; the confident regions of the flux results for the cases with a spacer are partially overlapping. This is because the varied magnitude of external mass-transfer rate in this experimental investigation has less impact on the permeate flux than the apparent solute rejection during the RO filtration, which can be mathematically verified by the film theory model.

In the diamond configuration (the filament inclined 45° to the bulk flow) a more complex velocity field was revealed by the Doppler images in Figure 5.8. The color patterns indicate that more swirling flows with a broader size range were predominantly present in the spacer interstices; the degree of turbulence could be significantly increased due to the merging of the flows from different directions. Furthermore, the high shear force regions underneath the filaments were able to cover more membrane area because the average distances between the filaments in the bulk flow direction were substantially reduced as shown in Figure 5.8(b) and (c).
By combining these positive effects the diamond configuration yielded the highest RO performance in the current filtration tests.

Numerous studies have been reported to compare the mass-transfer efficiency in the filtration with different spacer configurations, including CFD simulations (Cao et al. 2001; Karode and Kumar 2001; Schwinge et al. 2003; Fimbres-Weihs and Wiley 2007) and experimental investigations (Da Costa et al. 1994; Neal et al. 2003; Koutsou et al. 2009; Suwarno et al. 2012). Especially, the coupling between the velocity and concentration fields was quantitatively evaluated by the numerical approach; some simulation results (Schwinge et al. 2002; Schwinge et al. 2002) even provide numerical evidence supporting that the diamond configuration is superior to some other configurations. In current study the OCT technique is unable to directly provide the information about the solute concentration field; additional approach, like the RO tests used in this study, is needed to verify the effect of the flow pattern on the mass transfer. Although deeper insights about the mass transfer adjacent to the membrane surface cannot be derived from the current OCT results, the approach presented in this paper was verified as an efficient way to directly explore the complex transport phenomena during membrane filtration. Another novel aspect of the current study is that the asymmetric effect of flow patterns in a zigzag filament array on the local mass transfer are elucidated by distinguishing the axial configuration from the transverse configuration. Such a study may result in a better understanding about the mass-transfer mechanism in membrane modules.

5.4 Conclusions

In this work a new application of Doppler OCT was explored to characterize the fluid dynamics in a channel filled with a spacer. The Doppler images of different cross-sections in a unit cell of the spacer were successfully obtained while the orientation of the spacer was varied with respect to the bulk flow direction. Specially, the effect of the observation cell inclination on the color patterns was discussed to present a more precise interpretation of the Doppler images. The
interactions between the fluid and the spacer filaments were clearly visualized by these images with a well-defined color mode; the development of eddies and the spatial variation of the shear flow then were discussed in terms of the color patterns in the Doppler images for different cross-sections. These observations provided useful information for understanding the mass-transfer mechanisms during membrane filtration with spacer-filled modules. Further study is recommended to improve the interpretation of Doppler OCT images so that the gap between the results from OCT characterization and other approaches could be minimized.

In the current study the OCT characterization results also provided a reasonable explanation for the effect of the spacer orientation on the filtration performance during an RO process; the influence of the CP was successfully correlated to the velocity profiles near the membrane surface in a heuristic manner. This characterization approach could be extended to other scenarios related to membrane filtration, such as fouling processes in which the subtle flow patterns could play an important role in forming the fouling layer on the membrane surface.
CHAPTER 6

CHARACTERIZATION OF CAKE LAYER GROWTH IN A SPACER-FILLED CHANNEL FOR MEMBRANE FILTRATION USING OPTICAL COHERENCE TOMOGRAPHY

In previous chapter we have demonstrated the feasibility of using the Doppler OCT technique to study the fluid dynamics in a spacer-filled channel. In this chapter the OCT technique was further exploited to visualize and to quantify the dynamic growth of a foulant layer and to systematically investigate the effect of fluid dynamics on the cake layer formation.

6.1 Introduction

Membrane fouling is commonly assessed by performing membrane autopsy studies using microscopy approaches, such as scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM) and atomic force microscopy (AFM) (Tang et al. 2006; Suwarno et al. 2012). Although these methods can provide important information (e.g., clear micrographs) they are unable to reveal the dynamic process during the membrane filtration such as the particles transport and deposition on the membranes. In addition, it is apparent that such approaches are rather destructive and the membranes fail already by the time when the information on fouled membrane is acquired. As a result, there is an urge to develop novel, in situ and non-destructive techniques to characterize these dynamic processes (Chen et al. 2004a; Chen et al. 2004b). In particular, numerous efforts are given to the incipient detection and monitoring of membrane fouling (Mairal et al. 1999; Chong et al. 2007; Kavanagh et al. 2009) as well as the visualization of the particle depositions during filtration processes (Huang et al. 2010; Wang et al. 2010; Wicaksana et al. 2012).

Membrane fouling is inevitable in both pressure-driven and osmotically driven membrane processes. However, it can be controlled by improving the hydrodynamic environment during operations such as using the feed spacers and
increasing the cross-flow velocities (Schwinge et al. 2004; Chong et al. 2007; Picioreanu et al. 2009; Wang et al. 2010). Therefore, it would be useful to explore other options to directly study the subtle interactions between the hydrodynamic environment, foulant particles and the membrane surface. Wang et al. employed the direct microscopic observation to observe FO membrane fouling by micro-latex particles (Wang et al. 2010). With this technique more severe fouling was observed at high flux levels (above the critical flux). It also suggests that the feed spacer has a positive influence on the membrane performance. The microscopic observation techniques have also been applied to study other membrane processes, such as MF fouling by bacterial cells (Li et al. 2003). These findings revealed that the microscopic observation technique is a viable tool to investigate the particles transport and deposition in the membrane-solution interface. However, the characterization is limited to a two dimensional plane parallel to the membrane surface. It also requires the membrane to be transparent in some cases (e.g., direct microscopic observation through membranes (Li et al. 1998; Wang et al. 2010; Wicaksana et al. 2012)). The valuable information in the plane normal to the membrane surface is still missing. In Chapter 5 we proved that the Doppler optical coherence tomography (OCT) is effective in resolving the fluid fields normal to the membrane surface. Derlon and co-workers studied the bio-film development during the UF processes (Derlon et al. 2012) by using CLMS and OCT to characterize the micro-scale and meso-scale structures of the bio-film, respectively. However, the variation of the fouling layer during the filtration was not recorded since the OCT system was not integrated into the membrane filtration system in their study.

It was the first time that an OCT system was used to characterize the fluid dynamics in a spacer-filled channel by exploiting the Doppler imaging technique in Chapter 5. Therefore, we were motivated to further modify this system so that the growth of a cake layer during membrane filtration could be investigated using OCT structural imaging. This study was aimed at exploring the feasibility of applying OCT techniques to visualize and quantify the growth of a cake layer during membrane filtration. Specifically, it was intended to incorporate the OCT facility with a membrane filtration system so as to implement real-time scans to the foulant
layer that is being developed during a filtration process. A series of structural OCT images was obtained as a function of filtration time under different flow conditions.

6.2 Experimental methods

6.2.1 Structural imaging by OCT

A spectral domain OCT (SD-OCT) facility (TELESTO 1325 nm OCT System, Thorlabs, Inc., Newton, NJ) was adopted in this study. In this SD-OCT system the incident light is emitted from a broadband and low-coherent light source (a superluminescent diode) and divided into the sample and reference arms. The light penetrating the sample is partially reflected owing to the variation of the refractive index through the sample structure. The light reflected from the different depths then interferes with the reference light to obtain the interferograms as a function of frequency. Subsequently, these frequency-dependent interferograms are Fourier-transformed to generate the intensity signals as a function of the sample depths (Greenbaum et al. 2008).

The process of obtaining a depth profile at a certain point is commonly known as an A-scan (Leitgeb et al.). For an SD-OCT system the rate of an A-scan is mainly controlled by the speed of the digital camera in the spectrometer. In this study the A-scan rate was set at 28 kHz. The axial resolution is determined by the centre wavelength and the bandwidth of the light source. The used light source had a centre wavelength of 1325 nm, and the bandwidth was fixed at 100 dB. As a result, a depth profile with 450 pixels for a penetration depth of approximately 1.67 mm was achieved for each A-scan. A series of scans at different points can be continuously carried out in a straight line on the sample surface. Such a collection of sequential A-scans is called a B-scan (Leitgeb et al.). Compared to the axial resolution of an A-scan, the lateral resolution (i.e., the spatial density of the sequential A-scans in one B-scan) depends on the focusing performance of the probe adopted in the OCT system. In this work each B-scan was composed of 1364 A-scans covering a line distance of about 8.00 mm. As a result, the resultant OCT structural images were 1364 pixels × 450 pixels (width × depth) for a physical
 profile of approximately 8.00 mm × 1.67 mm; the spatial resolution was of the order of 10 μm. All the OCT images were acquired and processed by the ThorImage OCT software (Version 4.0, Thorlabs, Inc., Newton, NJ).

6.2.2 Fouling characterization

The key point to realize real-time imaging of fouling processes via an OCT system is to introduce the detection light beam into the channel of the filtration module. Such a combination of the OCT facility and membrane filtration system has been accomplished in the work reported in Chapter 5 by replacing the top channel wall with a transparent window. In order to guarantee the optical transparency of this observation window, a very thin glass plate (2 mm) was adopted. Therefore, a membrane process with low pressures is preferable so as to avoid potential failure of the glass window. In this study forward osmosis (FO) was selected as the model membrane process since FO processes are driven by the osmotic pressure difference across the membrane (Cath et al. 2006). The general principles developed in this work can be easily adapted to other membrane processes, such as microfiltration (MF) and reverse osmosis (RO).
The OCT-FO system is schematically shown in Figure 6.1. The observation cell used in this work has the same size (3.8 cm × 9.2 cm) as the one for the fluid dynamics characterization. The glass window (3.2 cm × 6.4 cm) was glued onto the acrylic plate. In order to accommodate the FO filtration, the lower compartment of the observation cell was modified such that the draw solution, i.e., the solution with a higher salinity (2 M NaCl), could be circulated through the channel beneath the
membrane. When the feed solution, i.e., the solution with a lower salinity (1 mM NaCl), was flowing through the upper channel, a water flow was osmotically driven from the feed solution side to the draw solution side. The cross-flow velocity for each channel was controlled at about 3 cm/s in all the filtration experiments. In particular, thin film composite (TFC) FO membranes (Hydration Technology Inc., Albany, OR) were used in this work; the active layer was exposed to the feed solution (AL-FS mode) during the filtration.

Bentonite micro-particles with a size range of 1 to 10 μm were chosen as the model foulant. The foulant particles were added into the feed solution to give a concentration of 2 g/L. A foulant layer was gradually formed on the membrane surface facing the OCT probe, and the process of the growth of the cake layer was recorded by the OCT system. In each fouling experiment OCT scans were carried out as the fouling occurred. The scan interval was gradually increased with an initial scan interval 1 min that was increased to 2 min after half hour (eventually, the interval was 5 min after 50 min). In addition, the variation of the permeate flux (i.e., the water flux) was monitored by weighing the tank that contained the draw solution during the filtration. The membrane was fouled for 1 h in all the fouling experiments.

Two modes of the fluid channel were employed for the fouling characterization. In the first mode there was no spacer in the fluid channel whereas a commercial spacer (GE Osmonics, SEPA) was placed between the glass window and the FO membrane in the second mode. The detailed specifications of the spacer were described in Chapter 5. In particular, three spacer orientations same as those presented in Chapter 5 were adopted. It was expected that different fouling layers would be formed in each channel mode due to the different hydrodynamic environments. The flow patterns in the fluid channel were obtained by exploring the Doppler effects, which were evaluated in terms of the phase angle variation of the OCT signals. In this study the bentonite micro-particles were not only used as the foulant, but also played the role of tracers for the Doppler imaging.
The thickness of the cake layer was quantitatively analyzed by post-processing the structural images. The original structural images were first cropped so as to focus on the region mainly showing the cake layer. Image subtraction then was applied to each cropped image with the initial one (for the clean membrane) as the subtrahend. Higher values of the pixels were rendered in the regions having more significant changes, that is, the region showing the cake layer. With the aid of a well-designed pixel filter, the cake layer was digitally separated from the background in the subtracted images. The separated pixels with a value indicating the gray scale were polarized to generate a binary image, in which the white pixels denote the cake layer whereas the background is covered by the black pixels. All these post-treatments of the images were automatically performed using MATLAB codes developed in-house.

6.3 Results and discussion

6.3.1 Characterization of the growth of a fouling layer without a spacer

The fouling characterization was first carried out by using the filtration cell without a spacer in the channels. It was expected that the simplest flow pattern would be generated since a very low value of Reynolds number (about 30) was used in the filtration, which was evaluated based on the hydraulic diameter of the channel cross-section. The schematic in the upper left panel of Figure 6.2 demonstrates the spatial domain characterized by the OCT, and the scanned cross-section is denoted by the surface with red color. This cross-section is parallel to the direction of the bulk flow, and a Doppler image was first obtained to verify the flow pattern in the channel as shown in Figure 6.2(a).

A dash-dot curve is added into the OCT images to help distinguish the membrane surface. It shows that the membrane surface is inclined at a small angle. This is because the inlet of the filtration cell was slightly raised so as to increase the intensity of the velocity components parallel to the light beam, which can be detected by the Doppler OCT (Wojtkowski 2010). As discussed in Chapter 5 the
single color band in Figure 6.2(a) indicates a laminar flow completely guided by the channel, and the velocity profile evaluated from the color gradients (Figure S2 in Appendix B) are consistent with the parabolic distribution of the velocity predicted by the classical fluid hydrodynamic model.

Figure 6.2 OCT images of the in the channel without a spacer. The cross-section scanned by the OCT was parallel to the direction of the bulk flow as indicated by the red area in the upper left schematic. The images obtained in this cross-section include: (a) the Doppler image of the velocity field in the channel at $t = 0$ min, (b) the structural image in the channel at $t = 0$ min, and (c) the structural image in the channel at $t = 60$ min.
The Doppler imaging is dependent on the variation of the phase angle resulting from the motions of the sample particles, whereas the intensity (modulus) of the interference signals is used to resolve structural images showing the cake layer at a certain instant. In comparison to the color bands in Doppler images, structural images are composed of gray-scaled pixels, of which values reflect the variation of the refractive index of the material in the scanned section. Therefore, the quality of visualizing the cake layer mainly depends on the differences of the optical properties between the fouling particles and the ambient fluid.

During the fouling a series of structural images were continuously recorded in the primary cross-section. In particular, the structural images at the beginning (t = 0 min) and end (t = 60 min) of the fouling are shown in Figure 6.2(b) and (c), respectively. When compared with the image for the clean membrane in Figure 6.2(b), the profile of the fouling layer can be easily identified in Figure 6.2(c).

In the structural images it is intriguing to note that there are some discernible, though not very clear, changes of the gray scale from the center of the channel to both the membrane surface and the upper channel wall (i.e., the observation window). The variation of the gray scale indicates the change of the scattering characteristic of the fluid. In this study the only reason responsible for this change is the variation of the concentration of the foulant particles (i.e., the bentonite micro-particles). Therefore, the distribution of the particles can be evaluated from the structural image (an example is given in Figure S3 in Appendix B). Similar observations were obtained in the work by Saarinen et al. studying the rheology of suspensions via OCT, and the concentration gradient near the wall is attributed to the shear-induced diffusion (Saarinen et al. 2014). In terms of the literature (Leighton and Acrivos 1987; Acrivos 1995) flows of suspended particles could be induced by the gradient of the shear rate, and the direction of the particle migration is from the regions of a higher shear rate to the regions of a lower shear rate. At the steady state this shear-induced particle flux is balanced by the counter-flux driven by the concentration gradient. During membrane filtration a thicker concentration boundary layer could be generated near the membrane surface due to the net convective transfer of the particles toward the membrane surface. The
presented results suggest that the OCT characterization can be potentially applied to investigate concentration polarization (CP) phenomena in membrane filtration, though further systematic studies are needed.

As introduced in Section 6.2.2, by using the image subtraction and pixel polarization, all the structural images were digitally converted into binary images showing the cake layer isolated from the background. These binary images are of higher visualization quality that is more suitable for a quantitative analysis compared to the original structural images. Some characteristic binary images at different moments are displayed in Figure 6.3. Specially, the images of the cake layer (the white pixels) were partially truncated at both ends for convenience of observation; image rotation was also applied so as to reduce the effects of the inclination angle on the quantitative analysis. The images in Figure 6.3 evidently illustrate the uniform growth of the cake layer along the membrane surface. This is consistent with the result of the Doppler imaging indicating a hydrodynamic environment in which the flow is constantly laminated in the direction of the bulk flow. At each point of the membrane surface the fouling particles were deposited with the same probability, thereby giving rise to a uniform cake layer at all times.
Figure 6.3 Binary images of the foulant layer in the channel without a spacer at different filtration times. The cake layer is denoted by the white pixels whereas the background is shown by the black pixels. The original structural images were scanned in the primary cross-section, and the post-treatment was implemented by using the self-developed Matlab codes.
With the aid of the binary images, the thickness of the cake layer can be easily evaluated by counting the number of the white pixels in a line perpendicular to the membrane surface. In particular, the small fluctuations at different locations are accounted for by averaging the thickness of the cake layer over the entire cross-section. The average thickness of the cake layer is plotted as a function of the filtration time in Figure 6.4(a). The variation of the permeate flux is shown in Figure 6.4(b) for a comparative study.

A simple way to describe the formation of a foulant layer is the classical cake filtration model stating that the rate of the particle deposition is approximately proportional to the flux normal to the membrane surface (She et al. 2009). In spite of the coupled effects of the CP and fouling during the FO filtration, a typical fouling process of cake filtration is indicated by both the plots in Figure 6.4. During the initial filtration the permeate flux was relatively high, thereby resulting in higher growth rates of the cake layer (i.e., the slope of the thickness-time curve in Figure 6.4(a)). As the cake layer was getting thicker, the hydraulic resistance of the cake layer is increased. Therefore, a gradual reduction of the permeate flux is observed in Figure 6.4(b), which in turn decreases the growth rate of the cake layer in the long term filtration as indicated by Figure 6.4(a).
Figure 6.4 Characteristic curves of the fouling in the channel without a spacer: (a) the average thickness of the cake layer as a function of the filtration time, and (b) the water flux as a function of the filtration time. Experimental errors are reported as the standard deviation of at least two repeated measurements.

6.3.2 Effect of the fluid dynamics on the growth of a fouling layer

As validated in Section 6.3.1, the OCT technique is effective in visualizing the cake layer growth during membrane filtration processes. In a realistic process of membrane filtration the channels of the membrane module are usually filled with net-like spacers, which could give rise to some secondary flows in the interstices.
The formation of the cake layer in the spacer-filled channels could be significantly affected by the complex hydrodynamic environment. Therefore, it is of great interest to verify the ability of OCT to explore these coupled phenomena during membrane fouling. In this section, systematic studies on the effect of fluid dynamics on the growth of a foulant layer were conducted. In particular, various flow patterns were generated by manipulating the spacer orientations as presented in Chapter 5. A three dimensional schematic of the filament orientation is given for each case. The attached filaments are in direct contact with the membrane surface and they are represented by gray. The detached filaments on the other hand are denoted by green. The sectioning plane for imaging is denoted by red color. Noted that the same color-code as presented in Chapter 5 was adopted here to interpret the flow patterns.

6.3.2.1 Characterization of the growth of a fouling layer in the spacer-filled channel with attached filaments parallel to the flow direction

In the first case the attached filaments were arranged parallel (0°) to the bulk flow direction (axial configuration) as depicted in Figure 6.5(a). Figure 6.5(b) and (c) present the Doppler and structural images taken when the membrane was fouled for an hour. It is apparent from the OCT images that the detached filaments are in direct contact with the upper wall forming narrow slits right beneath these filaments. It is obvious that the build-up of the cake layer was more intense toward the middle of the unit cell compared with those spots beneath the detached filaments. This is presumably due to the fact that the fluid was accelerated when passing through the narrow slits, thereby yielding a strong shearing effect near the membrane surface. As a result, it is hardly to discern any particle deposition beneath the detached filaments. On the other hand, two standing eddies with different size were formed within the unit cell. The upstream swirling structure had an outer layer moving away from the membrane surface (indicated by blue), whereas the downstream one had an inverse outer layer (denoted by red). These two vortices with opposite circulation partially merged and created a zone having relatively low shearing. By simply measuring the location of the foulant peak (approximate 60% of the overall
cake layer span in this view taken the downstream side as reference), it is confirmed that the foulant bump formed on the membrane surface was attributed to the non-uniform deposition. Similar foulant pattern was reported by Suwarno et al. (Suwarno et al. 2012) using confocal scanning electron microscopy (CLSM) to examine the effect of spacer on biofouling. They presented the confocal images of a unit cell covered by biofilm at different fouling period. It is evident that the biofilm tended to be initiated near the attached filaments rather than the detached filaments.

It is more evident from the binary images presented in Figure 6.6. The peak of this foulant bump is slightly shifted toward the upstream side. In order to quantify the thickness of the cake layer change with time, specific spots were selected. Measurements of the cake layer thickness at the peak and the trough (5% of the span with reference of the downstream) are plotted against the filtration time as illustrated in Figure 6.7. It shows that the thickness of the peak attains a value of approximate 170 μm after the one-hour fouling. On the contrary, barely any growth was observed at the trough. This quantitative result is in good agreement with the observation and interpretation from both Doppler and structural images.
Figure 6.5 The attached filaments are parallel to the flow direction (the axial configuration). (a) Schematic of a spacer unit cell showing the axial configuration; (b) Doppler image of the velocity field at $t = 60$ min at the cross-section indicated by the light red wall in (a), and (c) structural image of the specific cross-section at $t = 60$ min. The membrane surface is indicated by the green dash-dot line. The spacer filaments are highlighted with the white dashes.
Figure 6.6 Binary images of the foulant layer in a unit cell under the axial configuration at different filtration times. The cake layer is denoted by the white pixels whereas the background is shown by the black pixels. The original structural images were scanned in the primary cross-section, and the post-treatment was implemented by using the self-developed Matlab codes. D - downstream (approximate 0.05 of the span) and P - peak (approximate 0.6 of the span from downstream).
Figure 6.7 The thickness of the foulant layer as a function of the filtration time at two locations, peak and downstream (marked as P and D in Figure 6.6).

6.3.2.2 Characterization of the growth of a fouling layer in the spacer-filled channel with attached filaments perpendicular to the flow direction

In the second case that the attached filaments were placed normal (90°) to the bulk flow (transverse configuration) as illustrated in Figure 6.8(a). Comparing to the first case, the attached filaments were visible from this view and they were directly on top of the membrane surface. The arrangement here kept the shear layers of eddies away from the membrane surface. As indicated by the dark region, the valley formed by the attached filaments (in transverse direction) and the membrane surface was filled with liquid having relatively low velocity. This is especially true at both upstream and downstream corners. Therefore, it is expected that the movement of the foulant particles was dominated by the permeate flux along the whole membrane surface. Such hypothesis is evidently verified by the binary images shown the morphology of the cake layer at different times (refer to Figure 6.9). It is apparent that a relatively uniform cake layer was gradually formed on the membrane surface. In particular, it seems that the growth at both corners had
higher rates compared to the central part. The growth rates of one location toward the downstream as well as the valley are given in Figure 6.10. It is confirmed by the plots that for location D (same as axial configuration, the spot distanced 5% of the span from downstream was selected), a much steeper slope at the initial period was observed in contrast to the axial case, suggesting a relatively fast growth of the cake layer toward the downstream corner. On the other hand, the growth rate of the valley (location V, found to be about 0.4 of the overall span with reference of the downstream) was relatively low during the course of membrane fouling as shown by the solid inverse triangles in Figure 6.10.
Figure 6.8 The attached filaments are perpendicular to the flow direction (the transverse configuration). (a) Schematic of a spacer unit cell showing the transverse configuration; (b) Doppler image of the velocity field at \( t = 60 \) min at the cross-section indicated by the light red wall in (a), and (c) structural image of the specific cross-section at \( t = 60 \) min. The membrane surface is indicated by the green dash-dot line. The spacer filaments are highlighted with the white dashes.
Figure 6.9 Binary images of the foulant layer in a unit cell under the transverse configuration at different filtration times. The cake layer is denoted by the white pixels whereas the background is shown by the black pixels. The original structural images were scanned in the primary cross-section, and the post-treatment was implemented by using the self-developed Matlab codes. D - downstream (approximate 0.05 of the span) and V - valley (approximate 0.4 of the span from downstream).
6.3.2.3 Characterization of the growth of a fouling layer in the spacer-filled channel with attached filaments inclined to the flow direction

In the third case all filaments were inclined to the bulk flow at an angle of $45^0$ and it is denoted as the diamond configuration. As discussed in Chapter 5, such spacer configuration led to a more complicated velocity field. The imaging was focused on a diagonal plane sectioning two knots and parallel to the bulk as indicated by red in Figure 6.11(a). In terms of the Doppler imaging, two pairs of vortices were created around both knots, and the vortex regions were very close to the membrane surface. It is also noted that two dead zones were formed at the corners where the filament crossing were in contact with the membrane. It seems that the micro-hydraulic environment within this cross-section carries some features from both axial and transverse configurations. As a result, the growth of the cake layer also shares some characteristics from these two cases: (i) a foulant bump was formed in the central area, and (ii) particles preferably deposited at the downstream corner. Such pattern is more evident from the binary images (refer to Figure 6.12).
Figure 6.11 The attached filaments are inclined to the flow direction at 45° (the diamond configuration). (a) Schematic of a spacer unit cell showing the diamond configuration; (b) Doppler image of the velocity field at $t = 60$ min at the cross-section indicated by the light red wall in (a), and (c) structural image of the specific cross-section at $t = 60$ min. The membrane surface is indicated by the green dash-dot line. The spacer filaments are highlighted with the white dashes.
Figure 6.12 Binary images of the foulant layer in the channel with a spacer (diamond configuration) at different filtration times. The cake layer is denoted by the white pixels whereas the background is shown by the black pixels. The original structural images were scanned in the primary cross-section, and the post-treatment was implemented by using the self-developed Matlab codes.
Instead of some specific locations, here the thickness of the cake layer was averaged over the whole cross-section. The change of the averaged cake layer thickness is shown by the red curve for the diamond configuration as presented in Figure 6.13(a). The same analysis was performed for the first two cases. The blue curve is for the axial configuration, while the green curve is for the transverse configuration. It shows that the averaged growth of the cake layer from the diamond configuration is close to that from the axial configuration. After the one-hour filtration, both cases yielded a cake layer having an averaged thickness significantly lower than that in the transverse configuration. It is worth noting that the cake layer formed in the diamond configuration might have a non-uniform distribution in the direction normal to the bulk flow. This is because some studies reported the uneven distribution of the velocity field over a unit cell (Koutsou et al. 2007; Picioreanu et al. 2009). Therefore, by averaging the cake layer thickness over the whole membrane surface, it is expected that the diamond configuration might have a smaller value of the averaged cake layer thickness. This hypothesis is somehow verified by the experimental data of the permeate flux (refer to Figure 6.13(b)) which reflects the change of the averaged hydraulic resistance. This is in a way verified by previous work (Suwarno et al. 2012). A slower TMP rise was observed under the diamond configuration compared with that in the axial configuration. However, as revealed by some previous studies (Hoek and Elimelech 2003; Chong et al. 2007), the fouling process may be coupled with the concentration polarization phenomena. Therefore, a complete explanation of the fouling behaviour from these different cases is required in the future.
Figure 6.13 Characteristic curves of the fouling in a spacer-filled channel under different spacer configurations: (a) the average thickness of the cake layer as a function of the filtration time, and (b) the water flux as a function of the filtration time. Experimental errors are reported as the standard deviation of at least two repeated measurements.
6.4 Conclusions

In current study the application of the OCT technique was further extended to visualize and quantify the cake layer growth during membrane filtrations. It successfully demonstrates that the growth of a fouling layer during membrane filtration can be observed non-invasively and in real time via the structural imaging of an OCT system. The depth profiles of the cake layer can be resolved in the structural images. When the process of the cake growth is recorded, the evolution of the morphology of the cake layer can be clearly demonstrated by a series of binary images. It is difficult for conventional approaches to achieve this real-time observation of the depth profiles. Moreover, the concentration field of the suspension particles can also be visualized by the structural imaging, which has great value in understanding the underlying fouling mechanisms.

The ability to measure velocity profiles gives the OCT system extra benefit for characterizing membrane fouling. Without the need for additional independent measurements, Doppler images can be obtained simultaneously from the same interference signals. Therefore, the dependence of the fouling process on the micro-hydrodynamic environment can be analyzed by comparing the structural images with the Doppler images. In this regard, this work provides an in-depth understanding on how fluid dynamics would affect the formation of the cake layer. This dual-function characterization brings a new perspective to the study of membrane fouling, and more possibilities can be explored in other applications concerning water technologies.
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

This chapter addresses the major findings and limitations with regards to the characterization techniques reported in Chapters 3-6 and based on those findings and limitations, recommendations of the future work are also provided herein.

7.1 Conclusions

In this study three novel approaches with specific focus were developed and explored to characterize the mass transfer during membrane filtrations. First, the methods established in Chapter 3 addressed the importance of direct characterization of ICP and ECP based on newly established theoretical models and experimental protocols. Then in Chapter 4, focus was given to in situ characterization of ICP using the EIS technique. Chapter 5 highlighted the direct visualization of the flow fields (i.e., ECP) using the Doppler OCT technique and Chapter 6 further explored the application of the OCT technique to visualize and quantify the dynamic cake layer growth during membrane filtrations. The major findings from this research together with the current limitations are summarized as follows:

Firstly, three experimental approaches relying on measurements of the permeate water \( J_v \)-method, salt rejection \( R_s \)-method and boron rejection \( R_b \)-method) were developed based on proposed theoretical models to directly characterize the effects of ICP and ECP under RO testing mode. With these methods direct and independent assessment of the structural parameter of an FO membrane can be achieved. Prima facie, there are concerns associated with the mechanical stability of FO membranes under the RO testing mode. However, it was demonstrated that by using finer spacers/carriers the mechanical damage can be minimized (refer to Figure S1 in Appendix A). Among the aforementioned methods, the RO \( J_v \)-method was considered less reliable owing to the facts that a) the key assumptions of the linear “osmotic-pressure vs. concentration” relationship may not hold at high concentrations, b) the assumption of \( \pi_p \ll \pi_b \) may also not be
appropriate in many cases, and c) the $J_r$-method presented a relatively large uncertainty (lower $R^2$ value, refer to Figure 3.2). On the other hand, both the $R_s$-method and $R_t$-method yielded similar results. Since NaCl rejection is much easier to measure compared to boron rejection, the $R_s$-method is recommended for routine measurements. In addition, the $R_c$-method is also relatively easy to perform, and is able to resolve the effect of ECP from that of ICP interpretively by manipulating the cross-flow velocities. Another bonus point of this method is that the solute permeability $B_s$ can also be determined graphically with a high accuracy. This can serve as an independent reliability check. Furthermore, this method was demonstrated to be useful in determining boundary layer thickness in an RO process. The solute/tracer rejection models also provide a convenient framework for understanding the effect of concentration polarization (including fouling induced CECP) on membrane rejection performance.

Secondly, a brand new application of the EIS technique was explored to characterize the FO process. The potential of using the EIS technique to characterize FO membrane-electrolyte systems was demonstrated. The effect of FO structures on CP was systematically investigated by in situ measuring the impedance spectra of both static and dynamic membrane-electrolyte systems. The electric properties carrying the information of the membrane substructures were successfully identified by exploiting the limit behaviors of the impedance spectra. The effects of the ICP on the impedance spectra were clearly observed as the osmosis processes were scanned by the EIS system in real time. However, mainly due to the fact that the skin layer and the substrate layer of the FO membranes are made of the same material (thus the dielectric constant is the same), it is difficult to resolve the electrical properties of the skin layer from that of the porous substrate with the current models, which is considered of great importance in studying the mass transfer during an FO process. It is therefore necessary to develop more sophisticated models to better represent the FO systems so that it is able to separate the electrical properties of the skin layer from that of the substrate.

In contrast to ICP which is closely associated with the physical properties of the substrate structure, the fluid hydrodynamics has profound influence on the mass
transfer in the boundary layer. Thereby, another effort was devoted to developing an OCT-based characterization system to investigate the dynamic processes during membrane filtrations. In particular, the Doppler OCT was first successfully employed to characterize the fluid dynamics in a channel filled with a spacer as reported in Chapter 5. The interactions between the fluid and the spacer filaments were clearly visualized by these images with a well-defined color mode and the development of eddies and the spatial variation of the shear flow then were discussed in terms of the color patterns in the Doppler images for different cross-sections. These observations provided useful information for understanding the mass-transfer mechanisms during membrane filtration with spacer-filled modules. This technique was further confirmed to be feasible to visualize the growth of a cake layer during a filtration process (see Chapter 6). Distinct cake layer formations were also observed by changing spacer orientations with respect to the bulk flow direction. It was shown that subtle flow patterns were very important to the formation of a foulant layer on the membrane surface. However, there are also limitations of the current OCT-based characterization system such as the response of OCT to turbulent flow still remains unknown. This is mainly because the filtration experiments could not be implemented with higher cross-flow rates owing to the current observation cell. In addition, to visualize the full velocity field, a dual-beam OCT system or additional measurements relating to the Doppler bandwidth maybe required. With the knowledge of the exact velocity field, one could therefore better understand the mass transfers during the course of membrane filtrations. As such, studies to explore the limitations of the OCT-based characterization for membrane processes are of critical importance for adopting this novel technique in more applications.
7.2 Recommendations

In regards to the major findings stated in Section 7.1, several future studies are recommended here in order to further explore the capability of each technique proposed in this research.

First, the $R_s$-method was successfully applied to characterize the CTA-NW FO membrane. However, by careful selection of permeate carriers this method may be applicable to characterize FO membranes with unconventional structures such as a membrane with double rejection layers. As in such case the common flux fitting with classical ICP models approach may fail. In addition, there is potential to apply this method to characterize the cake enhanced concentration polarization (CECP) effect in the context of RO membrane fouling (Hoek and Elimelech 2003; Chong et al. 2008).

Second, with regard to the EIS-based characterization system, future work on developing more sophisticated equivalent circuit models to account for the complex polarization phenomena during FO processes is necessary. On the other hand, it is also worth studying the mechanisms accounting for the effects of the convective diffusion on the electric responses. Since physical properties of the membranes can be determined from the impedance spectra, it is worth exploring the possibility to couple this technique with other characterization methods (e.g., X-ray tomography which can provides 3D information of the membranes (Viguié et al. 2013)) to acquire more extensive information on the membranes.

Furthermore, in view of the significant implications of the OCT study, it is interesting to apply this technique to characterize novel types of spacers. It is also recommended to correlate the particles transport and deposition with the critical flux using the OCT technique. In addition, more sophisticated fouling models are required to better interpret the foulant layer formation in the presence of spacers.
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APPENDIX A

VERIFICATION OF MECHANICAL STABILITY OF FO MEMBRANES IN RO TESTS

In order to verify the mechanical strength of CTA-NW membrane tested in the RO mode, experiments were performed by measuring the permeate flux at various applied pressures under both SL-feed and SL-permeate orientations using pure water as feed (refer to Figure S1). For both orientations the permeate flux was first measured at increasing applied pressure of 40, 70, 100, 150, 200, 250 and 300 psi (note: 1 psi = 6.895 kPa) and then measured again by reducing the applied pressure from 300 to 40 psi to ensure the stability of the FO membrane performance. As seen from Figure S1 (dotted lines) the permeate flux was linearly correlated with the applied pressure within the pressure range of 40-300 psi under both membrane orientations. This linear trend was further confirmed by correlating various fluxes measured at decreasing applied pressures (represented by dashed lines).
Figure S1. Water flux of CTA-NW membrane at various applied pressures in RO tests (a) under SL-feed orientation and (b) under SL-permeate orientation. Experimental errors are reported as the standard deviation of at least two repeated measurements.
APPENDIX B

VELOCITY AND CONCENTRATION PROFILES IN THE CHANNEL WITHOUT A SPACER

Figure S2. Velocity profile in the channel without a spacer at t = 0 min (the values are normalized by the maximum).

Figure S3. Concentration profile in the channel without a spacer at t = 0 min (the values are normalized by the maximum).
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