Reverse osmosis desalination and reclamation : control of colloidal and biofouling

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**REVERSE OSMOSIS DESALINATION AND
RECLAMATION – CONTROL OF COLLOIDAL AND
BIOFOULING**

**CHONG TZYU HAUR
SCHOOL OF CIVIL AND ENVIRONMENTAL
ENGINEERING
2008**

Reverse Osmosis Desalination and Reclamation – Control of Colloidal and Biofouling

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School of Civil and Environmental Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

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SUMMARY

In this study, a novel sodium chloride tracer response technique coupled with the ultrasonic technique (ultrasonic time and frequency domain reflectometry) was employed to monitor the progress of fouling by silica colloids (model colloid), alginic acid (model bio-colloid) and *Pseudomonas fluorescens* (model bacteria species for biofouling). The study provided an insight into the interplay between critical flux, concentration polarization (through the enhanced osmotic pressure effect) and fouling. In colloidal fouling, critical flux and crossflow velocity (or shear) determined the deposition of particles on the membrane surface. It was found that the critical flux was proportional to the crossflow velocity, $J_{crit} \sim v^{0.4}$. Moreover, the critical flux for colloidal deposition was best described in terms of a Peclet number, defined as the ratio of the convective drag force to the back diffusive force. It was also found that the proportion of particles convected to the membrane that deposited was a function of crossflow velocity; at low crossflow the proportion was 100 % but at high crossflow the proportion was only about 10%. In addition, it was observed that the use of a spacer could enhance the critical flux by about 30 % compared to a slit channel.

The build up of deposit layer caused an additional hydraulic resistance, R_f , as well as the cake enhanced osmotic pressure (CEOP) effect. The CEOP effect arisen due to the hindered back diffusion of solutes through the tortuous path in the foulant layer. This resulted in an increase in the accumulation of solutes at the membrane surface, hence increasing the osmotic pressure, which caused a loss in the effective transmembrane pressure. For conventional constant flux operation the fouling in terms of rate of deposition, $\partial m_f / \partial t$, was a steady rise but the effect, observed as $\partial TMP / \partial t$, tended to be accelerating due to the non-linear contribution of CEOP. This happened at high net flux, low crossflow, high particle loading and high salt content. When the particle size was greater than 100 nm, the membrane performance loss due to the CEOP effect was dominant, regardless of other parameters mentioned above. It was also evident that the CEOP effect was greater at fixed flux operation than at fixed pressure operation simply due to the decline in flux, hence dropping the CP level, in the latter situation.

Whereas in biofouling, it was postulated that the role of CP was to control the levels of nutrient availability at the membrane surface for the growth of biofilm, which in turn caused the biofilm enhanced osmotic pressure (BEOP) phenomenon. The BEOP effect was more severe at higher flux operation due to the greater formation of biofilm, which was confirmed by the membrane autopsy data where greater amount of extracellular polymeric substances (EPS) were extracted from the membrane surface.

The outcomes of this study lead to a better understanding of the fouling mechanisms and the control of fouling process through the optimization of processes parameters. In addition, the non-invasive fouling monitors enable an early warning system that can assist in the fouling prevention and cleaning cycle.

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LIST OF SYMBOLS

<i>Symbol</i>	<i>Description (Units)</i>
A	Amplitude of ultrasonic wave (V)
A_H	Hamaker constant (J)
$A_{\text{Reflected}}$	Amplitude of reflected ultrasonic wave (V)
$A_{\text{Transmitted}}$	Amplitude of transmitted ultrasonic wave (V)
a_p	Radius of particle (m)
C	Concentration of solute (ppm or kgm^{-3})
C_{abs}	Concentration of light absorbing medium (kgm^{-3})
C_b	Concentration of solute in bulk solution (ppm or kgm^{-3})
C_{b, SiO_2}	Concentration of silica colloids in bulk solution (ppm or kgm^{-3})
C_{bio}	Concentration of biomass (kgm^{-3} or $\# \text{m}^{-3}$)
$C_{\text{bio-attached}}$	Concentration of biomass attached on the membrane (kgm^{-3} or $\# \text{m}^{-3}$)
C_c	Concentration of solute at cake layer surface (ppm or kgm^{-3})
C_{NaCl}	Concentration of sodium chloride (ppm or kgm^{-3})
C_p	Concentration of solute in permeate solution (ppm or kgm^{-3})
C_w	Concentration of solute at membrane surface (ppm or kgm^{-3})
CP	Concentration polarization modulus (dimensionless)
CP_{NaCl}	Concentration polarization modulus of NaCl (dimensionless)
CP_{NB}	Concentration polarization modulus of NB (dimensionless)
D	Diffusion coefficient of solute in bulk solution (m^2s^{-1})
D_{Br}	Diffusion coefficient of particle based on Brownian diffusion model (m^2s^{-1})
D_c	Diffusion coefficient of solute in cake layer (m^2s^{-1})
D_{NaCl}	Diffusion coefficient of NaCl in water (m^2s^{-1})
D_{NB}	Diffusion coefficient of glucose in water (m^2s^{-1})
$d_{F, \text{sp}}$	Diameter of filament of spacer (m)
d_h	Hydraulic diameter of membrane channel (m)
$d_{h, \text{sp}}$	Hydraulic diameter of spacer (m)
d_p	Diameter of particle (m)
d_{pen}	Penetration depth of evanescent wave (m)
d_s	Interfacial separation distance (m)
E_{EDL}	Electric double layer repulsion energy (J)

<i>Symbol</i>	<i>Description (Units)</i>
E_T	Total DLVO interaction energy (J)
E_{VDW}	van der Waals attractive energy (J)
F_X	Function as defined in Eq. (3.8), where X is TMP, feed conductivity or permeate conductivity (dimensionless)
H	Membrane channel height (m)
h_{sp}	Spacer height (m)
h_m	Thickness of medium (m)
I_S	Ionic strength of solution (molL^{-1})
J_{Br}	Flux based on Brownian diffusion model ($\text{Lm}^{-2}\text{h}^{-1}$ or $\text{m}^3\text{m}^{-2}\text{s}^{-1}$)
J_{crit}	Critical flux ($\text{Lm}^{-2}\text{h}^{-1}$ or $\text{m}^3\text{m}^{-2}\text{s}^{-1}$)
J_{IL}	Flux based on inertial lift model ($\text{Lm}^{-2}\text{h}^{-1}$ or $\text{m}^3\text{m}^{-2}\text{s}^{-1}$)
J_{SID}	Flux based on shear induced diffusion model ($\text{Lm}^{-2}\text{h}^{-1}$ or $\text{m}^3\text{m}^{-2}\text{s}^{-1}$)
J_s	Solute flux across membrane ($\text{kgm}^{-3}\text{h}^{-1}$ or $\text{molL}^{-1}\text{h}^{-1}$)
J_v	Permeate flux ($\text{Lm}^{-2}\text{h}^{-1}$ or $\text{m}^3\text{m}^{-2}\text{s}^{-1}$)
J_0	Initial permeate flux or flux at $t = 0$ ($\text{Lm}^{-2}\text{h}^{-1}$ or $\text{m}^3\text{m}^{-2}\text{s}^{-1}$)
ΔJ_v	Permeate flux drop ($\text{Lm}^{-2}\text{h}^{-1}$ or $\text{m}^3\text{m}^{-2}\text{s}^{-1}$)
K_N	Saturation constant of Nutrient Broth (ppm or kgm^{-3})
k_B	Boltzmann's constant ($1.3807 \times 10^{-23} \text{ JK}^{-1}$)
k_c	Mass transfer coefficient in cake layer (m/s)
k_{dc}	Spacer coefficient as defined in Eq. (2.11) (dimensionless)
k_{eff}	Effective mass transfer coefficient (ms^{-1})
k_m	Mass transfer coefficient (ms^{-1})
k_p	Mass transfer coefficient in polarized layer (ms^{-1})
L	Membrane channel length (m)
L_{clad}	Length of unclad portion of optical fiber (m)
$l_{M, sp}$	Spacer mesh length (m)
m_{bio}	Mass of biofilm per unit membrane area (kgm^{-2})
m_f	Mass of deposit per unit membrane area (kgm^{-2})
N	Concentration of Nutrient Broth (ppm or kgm^{-3})
N_b	Concentration of Nutrient Broth in the bulk (ppm or kgm^{-3})
N_{Re}	Reynolds number (dimensionless)
N_{Sc}	Schmidt number (dimensionless)

<i>Symbol</i>	<i>Description (Units)</i>
N_{Sh}	Sherwood number (dimensionless)
N_w	Concentration of Nutrient Broth at the membrane wall (ppm or kgm^{-3})
n_{clad}	Refractive index of fiber cladding (dimensionless)
n_{core}	Refractive index of fiber core (dimensionless)
n_{medium}	Refractive index of medium or analyte (dimensionless)
P_{abs}	Power transmitted by optical fiber with absorbing medium (mW)
P_{ref}	Power transmitted by optical fiber in the absence of evanescent wave absorption (mW)
P_0	Power transmitted by optical fiber without absorbing medium (mW)
ΔP_c	Trans-cake pressure (Pa or bar)
Pe	Peclet number (dimensionless)
$(Pe)_{crit}$	Critical Peclet number (dimensionless)
Q	Volumetric crossflow rate (Lmin^{-1} or m^3s^{-1})
R_f	Fouling layer or cake resistance (m^{-1})
R_g	Universal gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$)
R_m	Membrane resistance (m^{-1})
R_{obs}	Observed retention (dimensionless)
R_{real}	Real retention (dimensionless)
r_f	Effective fraction of the total guided power in the sensing region (dimensionless)
$S_{V, sp}$	Specific surface area of spacer (m^{-1})
T	Temperature (K)
t	Time (h or min or s)
t_m	Time for sound wave to travel through medium (s)
Δt_F	Shift in arrival time of fouling layer peak (s)
Δt_M	Shift in arrival time of membrane peak (s)
Δt_p	Difference in arrival time of fouling layer and membrane peak (s)
TMP	Transmembrane pressure (Pa or bar)
TMP_R	Relative change in transmembrane pressure (dimensionless)
TMP_s	Transmembrane pressure during sodium chloride tracer pulse (Pa or bar)
TMP_0	Initial transmembrane pressure or transmembrane pressure at $t = 0$ (Pa or bar)

<i>Symbol</i>	<i>Description (Units)</i>
ΔTMP	Transmembrane pressure increase (Pa or bar)
TRP	Total reflected power of sound wave (V MHz)
TRP_R	Relative total reflected power of sound wave (dimensionless)
v	Crossflow velocity (ms^{-1})
W	Membrane channel width (m)
X_i	Defined in Eq. (3.8), X is transmembrane pressure, feed conductivity or permeate conductivity at $t = 0$
X_{st}	Defined in Eq. (3.8), X is transmembrane pressure, feed conductivity or permeate conductivity at steady state
X_t	Defined in Eq. (3.8), X is transmembrane pressure, feed conductivity or permeate conductivity at $t = t$
$Y_{\text{bio/NB}}$	Yield coefficient for kg of biomass produced per kg Nutrient Broth (kg/kg)
Z	Acoustic impedance ($\text{Pa}\cdot\text{sm}^{-1}$)
<i>Greek Letters</i>	
δ_p	Thickness of polarised layer (m)
δ_c	Thickness of cake layer (m)
α_f	Specific cake resistance (mkg^{-1})
α_m	Bulk absorption coefficient of the absorbing species (dimensionless)
γ	Evanescent wave absorption coefficient (dimensionless)
γ_w	Wall shear rate (s^{-1})
μ	Viscosity of solution ($\text{Pa}\cdot\text{s}$)
μ_{bio}	Specific growth rate (h^{-1})
$\mu_{\text{bio-max}}$	Maximum specific growth rate (h^{-1})
ρ	Density of solution (kgm^{-3})
ρ_m	Density of medium (kgm^{-3})
ρ_p	Density of particle (kgm^{-3})
κ	Inverse Debye length (m^{-1})
ϕ	Molar osmotic coefficient (dimensionless)
ϕ_b	Particle volume fraction in the bulk solution (dimensionless)
ϕ_w	Particle volume fraction at the membrane wall (dimensionless)
ζ_m	Zeta potential of membrane (mV)

<i>Symbol</i>	<i>Description (Units)</i>
ζ_p	Zeta potential of particle (mV)
Φ	Fractional deposition constant (dimensionless)
ω_m	Sound velocity in medium (ms^{-1})
ω_f	Sound velocity in fouling layer (ms^{-1})
θ_{clad}	Incidence angle of light in fiber cladding (°)
θ_{core}	Incidence angle of light in fiber core (°)
θ_{crit}	Critical angle of incident light for total internal reflection (°)
θ_{inc}	Incidence angle of reflected light (°)
θ_{sp}	Hydrodynamic angle of spacer (°)
λ	Penetration depth of evanescent wave (m)
ε	Cake porosity (dimensionless)
ε_f	Permittivity of vacuum ($8.85 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$)
ε_{sp}	Voidage of spacer (dimensionless)
ε_0	Relative permittivity of water (78.4)
Π	Osmotic pressure (Pa or bar)
Π_b	Osmotic pressure of the bulk solution (Pa or bar)
Π_p	Osmotic pressure of permeate solution (Pa or bar)
Π_w	Osmotic pressure at the membrane wall (Pa or bar)
$\Delta\Pi_b$	Osmotic pressure difference between feed and permeate solution (Pa or bar)
$\Delta\Pi_{\text{bs}}$	Osmotic pressure difference between feed and permeate solution during sodium chloride tracer pulse (Pa or bar)
$\Delta\Pi_w$	Osmotic pressure difference between membrane wall and permeate solution (Pa or bar)
K	Conductivity of solution (mScm^{-1})
K_{feed}	Conductivity of feed solution (mScm^{-1})
K_{perm}	Conductivity of permeate solution (mScm^{-1})
ℓ_p	Permeability of membrane to solution flow ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)
ℓ_s	Solute transport constant (ms^{-1})

LIST OF PUBLICATIONS

Journal Publications:

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Chong, T. H., Liew, J. B., Wong F. S. and Fane, A. G. (2006). “The effect of fouling on concentration polarization in reverse osmosis at constant flux operation: NaCl tracer response technique”, In: Stuetz, R. and Lim, T.-T. (Eds.), Young Researchers 2006, London, IWA Publishing, ISBN: 1843395134, pp. 393 – 400.

CHAPTER 1

Introduction

1.1. Problem Statement

Since the development of the first asymmetric cellulose acetate reverse osmosis (RO) membrane in the early 1960's by Loeb and Sourirajan, RO is widely used to convert seawater, brackish water and municipal wastewater to potable water. For example, the government of Singapore, in a joint project between the Public Utilities Board (PUB) and Ministry of Environment (in year 2004, Ministry of Environment has been renamed to Ministry of the Environment and Water Resources (MEWR), which consists of two statutory boards, the National Environment Agency (NEA) and PUB) has initiated application of the NEWater process since 1998 that transforms secondary effluent from an activated sludge treatment process, through a series of steps involving microfiltration/ultrafiltration, reverse osmosis and ultraviolet disinfection, to yield high quality water (Public Utilities Board, 2002). NEWater can be mixed and blended with reservoir water and then undergo conventional water treatment to produce drinking water. It is inevitable that RO technology will play a crucial role in supplying water to water scarce countries. The pivotal advantage of the RO membrane is its uniqueness in transport properties such that water can pass through with little hindrance while presenting a virtually impermeable barrier to salts and other components. However, the major challenge in RO technology is the fouling of the membrane.

Fouling is defined as the accumulation of unwanted materials such as biological/organic, colloidal, particulate and crystalline matters on the surface of process equipment (Epstein, 1983), in this case the surface of the membrane which deteriorates the performance. Normally, feed water to a RO system has a turbidity of less than 1 Nephelometric Turbidity Units or NTU, which is caused by particles of sub-micron sizes. Examples of the commonly encountered colloidal matter in water treatment processes include colloidal silica, clay, iron oxide, humic substances, and organic macromolecules. These particles are difficult to remove by conventional pre-treatment processes and can even pass through micro-filtration (MF), as MF membranes have pore sizes (0.45 or 0.2 μm) larger than some colloids.

They can easily deposit and form a compact cake layer on the RO membrane surface. In addition, biofouling is probably the most prevalent and problematic type of fouling in a RO system; e.g. from the autopsies of 150 membrane samples collected all over the world, it was observed that more than 50 % of the deposits removed from the membrane surface were biological/organic foulants (van Hoof *et al.*, 2002). Many precautionary and preventative steps have been developed to combat biofouling, among them, the use of biocides to eliminate the microorganisms at source and the use of cleaners to remove the biofilm. These strategies have had mixed results; thus the former may actually break down the complex organic molecules into simple molecules that could act as carbon sources for the metabolism and reproduction of microorganisms (LeChevallier, 1991); while the latter may fail to completely remove the biofilm even though an improvement in permeability may be observed (McDonogh *et al.*, 1994), due to the fact that the cleaners are not targeting the extracellular polymeric substances (EPS) which are the foundation of a biofilm (Flemming *et al.*, 2000).

Colloids are transported to the membrane by permeation drag force, and accumulate on the surface of membrane. This creates a concentration gradient, known as concentration polarization (CP), where the concentration at the wall is greater than the bulk concentration. Colloids will diffuse back into the bulk solution due to this concentration gradient. Tangential crossflow is normally applied to reduce the concentration gradient. Colloids will deposit on the surface once the drag force is sufficient to overcome the back diffusion as well as the particle-surface interaction forces, e.g. electrostatic repulsion and van der Waals attraction. Therefore, colloidal fouling is also linked to concentration polarization, which is related to the permeation flux (J_v) and mass transfer (k_m) in the RO system, via the Film Model, $CP = \exp(J_v/k_m)$. Thus, by proper control of CP, or in other words flux and mass transfer, colloidal fouling can be controlled or avoided. Hence, this gives rise to the concept of 'critical flux' (Field *et al.*, 1995), where there is no continuous deposition of particles below this flux and fouling occurs when operating above this flux. The concept of critical flux has been widely applied in MF/UF operations, but its direct application to RO process has been limited. As a result, it is desirable to study further the critical flux phenomena in a RO system as

it determines the commencement of fouling as well as the extent of fouling. A related topic of interest is the effect of feed spacers (as used in the spiral-wound module) on fouling. It is generally recognised that spacers can improve mass transfer and therefore reduce the CP level, but its direct link to the fouling process is not well studied. So far there has been only one work reported on the effect of spacers upon critical flux improvement for particles (Neal *et al.*, 2003).

Furthermore, the formation of the colloidal layer on the membrane surface will provide an additional hydraulic resistance to permeation. Apart from that, the solutes (e.g. sodium and chloride ions) now have to diffuse through the tortuous path in the cake layer, so the effective back diffusion is greatly reduced. This will further exacerbate the CP level, and elevate the concentration as well as osmotic pressure of solutes at the membrane wall. This phenomenon is known as the cake enhanced osmotic pressure (CEOP) effect (Hoek and Elimelech, 2003). The increase in osmotic pressure means a loss in the effective driving force for filtration. Thus, the extent of fouling is determined by the interplay between the CP and the deposit layer. This issue has been overlooked in the past, and hence the fouling predictive models underestimated the severity of fouling. A fouling model that includes both the critical flux concept and CEOP effect is essential to predict the long-term performance of a RO membrane under the influence of colloidal fouling.

Biofouling is much more complex than colloidal fouling and is the formation of a biofilm on the RO membrane surface, which is developed through a series of successive events such as surface conditioning, transport, attachment, growth and detachment (Characklis, 1990b). However, in order to simplify the problem, microorganisms are commonly treated as colloids as they also have sub-microns sizes, surface charge etc. So it is reasonable to relate biofouling to flux-mass transfer or concentration polarization of a membrane system as in the case of colloidal fouling. Since the growth of microorganisms is nutrient dependent, the higher concentration of nutrient at the membrane surface due to the CP effect not only supports the survival of the microorganisms, but could also accelerate the biofilm formation rate. This means by proper control of these parameters, biofouling in the RO system can be avoided or inhibited. Unfortunately, there is a lack of information available that relates biofilm development to flux-mass transfer

properties of a membrane system. In addition, the CEOP phenomenon could also exist in biofouling. Similar to colloidal deposit, the solutes also need to diffuse through the tortuous path within the heterogeneous structure of the biofilm. Therefore the effective mass transfer is less than for the bulk fluid and CP is greatly enhanced. However this postulation needs to be validated.

Currently, there is a lack of a simple technique to measure the critical flux and to monitor the transient CP in a RO system. Furthermore, in order to combat fouling, e.g. through optimization of frequency and duration of cleaning, one needs to monitor the development of the fouling process. However, conventional methods that are based solely on the rise in transmembrane pressure (TMP) in constant flux operation or decline in flux in constant pressure operation are insufficient to provide detailed information about fouling behaviour. An alternative monitoring technique is through membrane autopsy performed on a fouled membrane, but this is an undesirable destructive method where the membrane has to be sacrificed. Therefore, to gain a fundamental understanding of the fouling mechanisms, as well as insight into formation of the deposit layer, an effective non-invasive fouling monitoring tool is crucial. In this study, a sodium chloride tracer response technique has been developed to elucidate the interplay between concentration polarization and fouling as well as to determine the critical flux of colloidal fouling in an RO system. In addition to that, the ultrasonic time domain reflectometry (UTDR) method has been selected to monitor the build up of deposit layers as it has been proven to be versatile and shows great potential for use as a fouling monitor for large scale spiral wound RO modules (Chai *et al.*, 2001; Mairal *et al.*, 2000; Mairal *et al.*, 1999). Most previous work has involved the detection of deposits of scale such as calcium sulphate. In this study, the application of the UTDR method for detection of sub-micron colloidal deposits (solid and soft cake) as well as biofilms has been critically assessed. Another method, the fiber optical sensor (FOS) was also investigated for biofilm detection in the RO process.

1.2. Objectives and scope

The objectives and scope of this research study and the breakdown of the thesis structure are outlined as follows:

- i. Critically review the available literatures on colloidal and biofouling in RO as well as the fouling detection methods (Chapter 2).
- ii. Develop a simple sodium chloride tracer response technique to elucidate the cake enhanced osmotic pressure (CEOP) effect (Chapter 3) and to measure the critical flux of colloids in the RO process (Chapter 4). Also, the effect of the spacer on critical flux is investigated (Chapter 4). In this thesis, mono-dispersed silica colloid and alginic acid as surrogate for EPS of biofilm are used.
- iii. Develop a predictive model for the performance of the RO system that incorporates the critical flux and cake enhanced osmotic pressure (CEOP) effect (Chapter 5). The fouling mechanism in fixed flux and fixed transmembrane pressure operation is studied.
- iv. Critically assess the applicability of ultrasonic time domain reflectometry (UTDR) as a non-invasive, in-situ and real time fouling monitoring tool for nano-sized colloids and macromolecule gel layer (Chapter 6) and biofilm (Chapter 7). In addition, the UTDR is used in conjunction with the tracer response technique to correlate results obtained from these two methods.
- v. Investigate the relationship between biofilm formation and flux-mass transfer of a RO system as well as the existence of CEOP effect in biofouling (Chapter 7). Assess a novel fiber optic sensor (FOS) for biofilm detection; a biofilm of *Pseudomonas fluorescens* was selected as a model biofilm in the study.

1.3. Significance

The significant outcomes of this research are:

- i. A fundamental understanding of the colloidal and biofouling mechanisms.
- ii. A fouling model that can be incorporated into dynamic operational models of a plant for performance optimization and control of fouling.
- iii. Assessment of non-invasive, in-situ and real time fouling monitors that can provide early detection and detailed information of fouling in the RO process. These monitors could also assist in the cleaning cycle of the membrane.

CHAPTER 2

Literature Review

This chapter provides the basic principles of the operation of reverse osmosis, the fundamentals of colloidal and biofouling and various tools or techniques to monitor the fouling process.

2.1. Fundamentals of reverse osmosis

Osmosis is a natural phenomenon in which water (solvent) passes through a semi-permeable membrane from the side with lower solute concentration to the higher solute concentration side until equilibrium of water (solvent) chemical potential is reached (Bhattacharyya and Williams, 2001b). At equilibrium the pressure difference between the two sides of the membrane is equal to the osmotic pressure difference. In reverse osmosis (RO), a pressure difference greater than the osmotic pressure difference has to be applied in order to reverse the flow.

2.1.1. Membranes and membrane modules

An ideal RO membrane consists of an ultra-thin imperfection-free film of a polymeric material, having transport properties such that water can easily pass through while it is impermeable to other solutes. In addition, the membrane must be strong enough to withstand the high operating pressure, e.g. up to 70 bars for seawater desalination. Most commercially available RO membranes are composite membranes, where a porous matrix (support) is topped by a thin film (active layer). The support layer is optimized for maximum strength and compression resistance, and the active layer is optimized for the maximum solvent flux and solute retention (Petersen, 1993). These composite membranes are cast from a variety of polymers such as polyamides and poly(ether/amide).

There are four types of membrane modules available: spiral wound, hollow fiber, tubular, and plate and frame. Table 2.1 summarizes the general characteristics of RO membrane modules. The spiral wound module, as shown in Figure 2.1, is the most commonly used configuration in the desalination and reclamation industry because of its large surface to volume ratio and therefore its high productivity per

unit volume. It also offers a good balance between fouling resistance and ease of cleanability. In addition, the feed spacer can be optimized to minimize the pressure drop as well as to improve the hydrodynamic conditions to make it less susceptible to fouling.

Table 2.1: General characteristics of RO membrane modules (Bhattacharyya and Williams, 2001a; Wagner, 2001)

Characteristics	Module Type			
	Spiral Wound	Hollow Fiber	Tubular	Plate - Frame
Packing density (m^2/m^3)	800	6000	70	500
Feed flow rate (m/s)	0.25 – 0.50	~ 0.005	1 – 5	0.25 – 0.50
Feed side pressure drop (bar)	3 – 6	0.1 – 0.3	2 – 3	3 – 6
Feed stream filtration requirement	10 – 25 μm	5 – 10 μm	Not required	10 – 25 μm
Tendency of fouling	Average	Very High	Low	Average
Cleanability	Good	Poor	Good	Good

Figure 2.1: Cut away view of a multi-leaf spiral wound module (Bhattacharyya and Williams, 2001a; Wagner, 2001)

2.1.2. Performance of membrane

Typically membrane performance is represented in terms of flux and selectivity. The term permeate flux, J_v , which is the rate of permeate collected per unit membrane area, is used to characterize the performance of a membrane; and is linked to the applied pressure and osmotic pressure as given by the solution-diffusion model (Lonsdale *et al.*, 1965; Merten, 1966):

$$J_v = \ell_p (\text{TMP} - \Delta\Pi_w) \quad \text{Eq. (2.1)}$$

where TMP is the applied pressure across the membrane and is referred to as the transmembrane pressure; $\Delta\Pi_w = (\Pi_w - \Pi_p)$ is the osmotic pressure difference of the solution between the wall and the permeate, which takes into account the effect of concentration polarization (refer to Section 2.1.3.); ℓ_p is the permeability of membrane to solution flow. Eq. (2.1) is commonly represented in another form:

$$J_v = \frac{\text{TMP} - \Delta\Pi_w}{\mu R_m} \quad \text{Eq. (2.2)}$$

where μ is the viscosity of the permeate solution and R_m is the membrane resistance. Eq. (2.1) and (2.2) are for a clean membrane. If fouling occurs, an additional term is required and the modified form will be introduced in Section 2.2.1.5. The solute permeation across the membrane can be represented by the solute flux, J_s ,

$$J_s = \ell_s (C_w - C_p) = J_v C_p \quad \text{Eq. (2.3)}$$

where C_w and C_p is the concentration of solute at the membrane surface and in the permeate, respectively and ℓ_s is the solute transport constant.

Another way to represent the performance of the membrane is via its selectivity, which is the fraction of solute rejected or retained by the membrane. The observed solute retention, R_{obs} , is the relative change in concentration of solute from the feed side, C_b , to the permeate side, C_p , and is given by

$$R_{\text{obs}} = \frac{C_b - C_p}{C_b} \quad \text{Eq. (2.4)}$$

To include the effect of concentration polarization, the real retention coefficient, R_{real} , is

$$R_{\text{real}} = \frac{C_w - C_p}{C_w} \quad \text{Eq. (2.5)}$$

2.1.3. Concentration polarization

When the solute is rejected by the membrane, the solute concentration near the membrane surface increases, since the convective flow of the solute to the membrane surface must be balanced by the back diffusion of solute to the bulk feed solution. The build up in concentration in this boundary layer region is referred to as concentration polarization (CP). This is schematically represented in Figure 2.2.

Figure 2.2: Concentration polarization in reverse osmosis

Concentration polarization is undesirable for three reasons. Firstly, the osmotic pressure near the membrane surface is increased due to the higher solute concentration, which means $(\Pi_w - \Pi_p)$ is increased and therefore flux will decline unless additional pressure is applied to compensate for the increase in osmotic pressure. Secondly, as more solutes are present at the membrane wall, the solute passage across the membrane is increased since the driving force for solute transport is the concentration gradient across the membrane. The third effect is the promotion of fouling (refer to Section 2.2.). The accumulated solutes, e.g. such as Ca^{2+} and CO_3^{2-} , form insoluble salts when the solubility limit is exceeded; or particles like silica colloids transit from the solution phase (particle polarisation layer) to the solid phase (deposit layer) on the membrane surface (Bacchin *et al.*, 2002a; Chen *et al.*, 1997).

At steady state, the flux of solute to the membrane, $J_v C$, the flux of solute through the membrane, $J_v C_p$, and the solute back diffusion, $-D(\partial C / \partial x)$, are balanced and can be written mathematically as the convective-diffusion equation (Dickson, 1988):

$$J_v C_p = J_v C - D \frac{\partial C}{\partial x} \quad \text{Eq. (2.6)}$$

with boundary conditions at the solution boundary layer interface: $x = \delta$, $C = C_b$; and at membrane surface: $x = 0$, $C = C_w$; solving Eq. (2.6) yields:

$$CP = \frac{C_w - C_p}{C_b - C_p} = \exp\left(\frac{J_v}{D/\delta}\right) = \exp\left(\frac{J_v}{k_m}\right) \quad \text{Eq. (2.7)}$$

where D is the solute diffusivity, δ is the CP layer thickness, and k_m is the mass transfer coefficient. Although k_m is only exactly equal to D/δ when the flux tends to zero, D/δ is written as k_m , which is a common assumption. From Eq. (2.7), it is seen that the magnitude of CP increases exponentially with either an increase in J_v or a decrease in k_m .

2.1.4. Mass transfer coefficient in membrane channel

The flow in an “empty” membrane channel can be treated as flow through a thin slit channel. The mass transfer correlation for laminar flow in a membrane feed channel with height, h , based on the Graetz-Lvque equation is related to the Sherwood number, N_{Sh} , by (Rautenbach and Albrecht, 1989):

$$N_{Sh} = \frac{k_m d_h}{D} = 1.62 \left(N_{Re} N_{Sc} \frac{d_h}{L} \right)^{1/3} \quad \text{Eq. (2.8)}$$

where $d_h \approx 2H$ is the channel hydraulic diameter, N_{Re} is the Reynolds number, N_{Sc} is the Schmidt number, and L is the channel length.

The major disadvantage of the slit channel is the low value of k_m (although some modules are based on this design). An improvement in mass transfer can reduce the CP effect. This can be achieved by increasing crossflow velocity or using a feed spacer. To increase the crossflow velocity, the volumetric feed input to the process needs to be increased. This method has an adverse consequence, as the feed is increased, the amount of concentrate with high salt content that requires treatment or disposal is increased simultaneously. Therefore, a flow-channel spacer

is introduced to improve the hydrodynamic conditions. Installation of spacers and good spacer design has been proven to significantly reduce the CP effect (Da Costa *et al.*, 1991; Geraldles *et al.*, 2002a; b; 2003; Schwinge *et al.*, 2004b). There are many types of spacer available, but the most commonly used spacers in commercial membrane modules are the ladder and diamond type spacers. Both spacers are illustrated in Figure 2.3. They are distinguished by the orientation of the spacers in touch with the flow direction. The mass transfer correlation for a channel filled with spacers can be estimated as follows (Da Costa *et al.*, 1991; Da Costa *et al.*, 1994; Schock and Miquel, 1987):

$$\text{For ladder type: } N_{Sh} = 0.664 N_{Re}^{0.5} N_{Sc}^{0.33} (d_{h,sp} / l_{M,sp}) \quad \text{Eq. (2.9)}$$

$$\text{For diamond type: } N_{Sh} = 0.664 k_{dc} N_{Re}^{0.5} N_{Sc}^{0.33} (2d_{h,sp} / l_{M,sp}) \quad \text{Eq. (2.10)}$$

where

$$k_{dc} = 1.65 (d_{F,sp} / h_{sp})^{-0.04} \epsilon_{sp}^{0.75} (\sin \theta_{sp} / 2)^{0.09} \quad \text{Eq. (2.11)}$$

$$d_{h,sp} = \frac{4\epsilon_{sp}}{\left[(2/h_{sp}) + (1 - \epsilon_{sp}) S_{V,sp} \right]} \quad \text{Eq. (2.12)}$$

$$\epsilon_{sp} = 1 - \frac{0.5\pi d_{F,sp}^2 l_{M,sp}}{l_{M,sp}^2 h_{sp}} \quad \text{Eq. (2.13)}$$

$$S_{V,sp} = 4/d_{F,sp} \quad \text{Eq. (2.14)}$$

θ_{sp} is the hydrodynamic angle of spacer; $l_{M,sp}$ is the mesh length; $d_{F,sp}$ is the filament diameter; and h_{sp} is the spacer thickness

Figure 2.3: Feed spacers (a) ladder type, and (b) diamond type

Undoubtedly, the spacer can improve the mass transfer in a membrane channel. However, the link between spacer and fouling has not been well established and the aid of the spacer in reducing fouling needs further study. So far, only one experimental work has been reported to evaluate the spacer efficiency for improving the critical flux (refer to Section 2.2.1.4.), which is related to the onset of fouling (Neal *et al.*, 2003). It was found that the critical flux of a model particle (6.4 μm latex beads) was enhanced by up to 2 times in the presence of spacers, but the degree of enhancement was dependent on the spacer orientation. Also, it is important to recognise that the shear field is rather uneven around the spacer filaments as revealed by sophisticated hydrodynamic analysis of spacers using the Computational Fluid Dynamics (CFD) technique (Schwinge *et al.*, 2002b; c; d). This leads to non-uniform distribution of the fouling layer around the filament as reported in Neal's work (Neal *et al.*, 2003). In addition, the improvement in mass transfer comes with the penalty of pressure drop along the channel (Da Costa *et al.*, 1994), thus reducing the effective driving force for filtration and introducing a local TMP and a local flux along the membrane channel.

2.1.5. Constant flux vs. constant transmembrane pressure operation

Typically, RO systems can be operated under fixed flux or fixed TMP. However, in practical situations, RO plants tend to be operated at fixed production rate, which requires fixed flux. In fixed flux operation, when the membrane is fouled, higher TMP is required to compensate for fouling via adjusting the pump rate to supply higher feed pressure. When the maximum capacity of the pump is reached, then the permeate flux is allowed to decline due to fouling. This is equivalent to fixed TMP operation. The TMP and flux profiles of the above two operation modes are illustrated in Figure 2.4. For operation starting with a fixed pressure, the system tends to have a high initial flux, J_0 , and hence the deposit layer builds up rapidly at the beginning since fouling is a function of flux. Thus fouling causes a drop in the flux, which in turn diminishes fouling until steady state is reached. On the other hand, the system under constant flux operation may experience a continual rise in the TMP due to a continuous build up of the fouling layer. In fact the constant flux mode can lead to self-accelerated fouling. Despite

the differences in the fouling patterns, the majority of experimental studies involving RO fouling have been performed under fixed pressure conditions. It is necessary to compare the fouling process occurring under fixed flux and fixed pressure operation as they may give different fouling dynamics and mechanisms.

Figure 2.4: Illustration of transmembrane pressure and flux profile for (a) constant flux operation, and (b) constant pressure operation

2.2. Membrane fouling

Fouling is defined as the accumulation of unwanted materials on the surface of process equipment (Epstein, 1983), in this case the membrane surface. There are various types of fouling in RO, categorized under crystallization or scaling (formation of insoluble precipitates from dissolved ions), particulate (deposition of particulate matters), biological (adhesion of microorganisms and subsequent biofilm development), and organic (adsorption of organic compounds) fouling. Normally, scaling can be controlled/prevented by using a scale inhibitor or by operating the RO at a low recovery level such that the solubility of salt is not exceeded. However, the use of microfiltration (MF) or even ultrafiltration (UF) as a pretreatment step, may not completely remove the colloidal particles. The colloids when entering the RO system may deposit and form cake layers on the membrane surface depending on the hydrodynamic conditions. In addition, biological and organic fouling usually occur simultaneously, as the organic matter tends to serve as the nutrient source for the growth of biofilm. In this thesis work, the focus of study is on colloidal and biological fouling.

2.2.1. Colloidal fouling

2.2.1.1. Characteristics of colloids

Colloidal fouling is the formation of a colloidal deposit layer on the membrane surface. Examples of colloidal particles include clay, iron oxide, silica, macromolecules (protein, polysaccharides and natural organic matters), bacteria and viruses (bio-colloids). These colloids are usually in the size range of 1 – 1000 nm (or 0.001 – 1 μm), but there is no strict margin (Elimelech *et al.*, 1995; Gregory, 2006). Colloids have a large surface area due to their relatively small diameter, which is important in adsorption processes and hence membrane fouling. When a colloid is in contact with a solution of ions it will lead to a characteristic distribution of ions. The combined system of surface charge of a colloid and the counterions in solution is known as the electrical double layer, EDL (Elimelech *et al.*, 1995; Gregory, 2006). The EDL is made up of the Stern layer and a diffuse layer as illustrated in Figure 2.5 for a negatively charged particle. An important feature of the EDL is the zeta potential, which is the potential at the plane of shear between the charge interface and the adjacent solution when there is relative motion between them (Elimelech *et al.*, 1995; Gregory, 2006). The role of the EDL on membrane fouling will be explained later (Section 2.2.1.3.).

Figure 2.5: Electrical double layer of a negative charged particle in solution

2.2.1.2. Particle transport

The commencement of colloidal fouling is the transport of the foulant from the bulk fluid to the membrane surface and followed by the particle attachment process. In a crossflow RO system, particles transport towards the membrane surface due to the permeation flux (perpendicular to the surface) while the crossflow (tangential to

the surface) induces particles to move away from the membrane surface and back-transport into the bulk solution. These back-transport mechanisms include Brownian diffusion, shear-induced diffusion, and inertial lift forces (Belfort *et al.*, 1994; Huisman and Tragardh, 1999). The transport phenomena in crossflow filtration is a very well studied topic and detailed accounts of the work can be found in several review papers (Belfort *et al.*, 1994; Bowen and Jenner, 1995; Ripperger and Altmann, 2002). Only a brief summary is provided in the next section, and several important parameters in the transport models are highlighted.

2.2.1.2.1. Brownian diffusion

For sub-micron size particles (typically $< 0.1 \mu\text{m}$), molecular or Brownian diffusion is important. Brownian diffusivity, D_{Br} , can be estimated by the Stokes-Einstein equation (Einstein, 1956):

$$D_{\text{Br}} = \frac{k_B T}{6\pi\mu a_p} \quad \text{Eq. (2.15)}$$

where k_B is the Boltzmann's constant, T is the temperature, μ is the viscosity, and a_p is the particle radius. Solving the convection-diffusion equation, the flux based on Brownian diffusion for dilute solution ($\phi_w \gg \phi_b$) is (Trettin and Doshi, 1980):

$$J_{\text{Br}} = 1.31 \left(\frac{\gamma_w D_{\text{Br}}^2 \phi_w}{L \phi_b} \right)^{1/3} \quad \text{Eq. (2.16)}$$

where γ_w is the wall shear rate, L is the channel length, ϕ_w is the particle volume fraction at the membrane wall and ϕ_b is the particle volume fraction in the bulk solution. Note that the flux based on the Brownian diffusion mechanism increases with shear rate to the 1/3 power while it decreases with particle radius to the 2/3 power.

2.2.1.2.2. Shear-induced diffusion

Shear induced diffusion of particles occurs because individual particles undergo random displacements from streamlines in a shear flow as they interact with and tumble over other particles (Zydney and Colton, 1986). For micron-sized particles (typically $> 0.2 \mu\text{m}$), the flux based on shear-inducing diffusion is (Zydney and Colton, 1986):

$$J_{\text{SID}} = 0.078\gamma_w \left(\frac{a_p^4}{L} \right)^{1/3} \ln \left(\frac{\phi_w}{\phi_b} \right) \quad \text{Eq. (2.17)}$$

Note that the flux based on shear induced diffusion mechanism is proportional to the shear rate and increases with particle radius to the 4/3 power.

2.2.1.2.3. Inertial lift

Lateral migration of particles due to inertial lift arises from non-linear interactions of particles with the surrounding flow field under the conditions where the Reynold number based on the particle size is not negligible. The steady state flux is (Drew *et al.*, 1991):

$$J_{\text{IL}} = 0.036 \frac{\rho a_p^3 \gamma_w^2}{\mu} \quad \text{Eq. (2.18)}$$

where ρ is the density of solution. It should be noted that the flux based on inertial lift theory is very sensitive to both particle size (increases to the power of 3) and shear rate (increases to the power of 2). However for particles with size of less than a few microns, such as the nano-sized silica colloids used in this study, the inertial lift force is negligible (Belfort *et al.*, 1994).

2.2.1.3. Particle attachment

When a particle is in the vicinity of the membrane-solution interface, colloid-membrane interactions will determine the attachment of the particle onto the membrane surface. The interactions may be attractive (e.g. van der Waals or hydrophobic attraction) or repulsive (e.g. electrical or steric repulsion). The nature of the interaction is greatly dependent on the nature of the particle and membrane surface as well as the solution chemistry (Elimelech *et al.*, 1995; Gregory, 2006; Hoek *et al.*, 2003).

2.2.1.3.1. DLVO interactions

Classically, the attachment of a colloidal particle is best described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory for colloid stability (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). The net interaction is the sum of two additive forces, van der Waals (VDW) forces, which are always

attractive; and the electrical double layer (EDL) interaction forces, which are attractive if the particle and the wall have zeta potentials of opposite sign, and repulsive if these charges are of the same sign. The two forces are illustrated in Figure 2.6, as a plot of interaction energy as a function of separation distance, for the case of zeta potentials of like signs. It is seen that the summation of the interaction energies involved results in a large energy barrier that must be overcome before a particle can actually get to the wall. The interaction energy is strongly affected by various physicochemical parameters such as particle size, zeta potential, ionic strength of the solution, and surface roughness (Elimelech *et al.*, 1995; Hoek *et al.*, 2003).

Figure 2.6: Illustration of potential energy for the particle-membrane interaction by DLVO theory

2.2.1.3.2. Effect of particle size and zeta potential

The critical roles of particle size and zeta potential on the colloidal interactions and hence particle deposition are clearly depicted in the correlations to estimate the potential energy of van der Waals attraction and the electrical double layer. A simple expression can be used to estimate the van der Waals attractive energy, E_{VDW} , of a spherical particle interacting with an infinite planar surface in terms of the particle radius, a_p , and the interfacial separation distance, d_s , as follows (Gregory, 2006):

$$E_{VDW} = -\frac{A_H}{6} \left\{ \frac{a_p}{d_s} + \frac{a_p}{(d_s + 2a_p)} + \ln \left[\frac{d_s}{(d_s + 2a_p)} \right] \right\} \quad \text{Eq. (2.19)}$$

where A_H is the Hamaker constant (Hamaker, 1937). A detailed calculation of the Hamaker constant can be found elsewhere (Gregory, 2006).

As for the electrical double layer interaction energy, E_{EDL} , the expression based on a constant surface potential boundary condition is (Hogg *et al.*, 1966):

$$E_{EDL} = \pi \epsilon_0 \epsilon_r a_p \left\{ 2\zeta_p \zeta_m \ln \left[\frac{1 + \exp(-\kappa d_s)}{1 - \exp(-\kappa d_s)} \right] + (\zeta_p^2 + \zeta_m^2) \ln [1 - \exp(-2\kappa d_s)] \right\} \quad \text{Eq. (2.20)}$$

where ϵ_0 and ϵ_r are the relative permittivity of water and vacuum, respectively; ζ_p and ζ_m are the zeta potential of particle and membrane, respectively; and κ is the inverse Debye length which is proportional to the ionic strength of solution, I_s ($\kappa \propto I_s^{1/2}$).

2.2.1.3.3. Effect of ionic strength

The effect of ionic strength of solution upon the colloidal interaction energies is well understood (Elimelech *et al.*, 1995; Gregory, 2006). Generally, particle deposition efficiency increases with increasing solution ionic strength. This is attributed to the suppression of the EDL repulsive forces at higher ionic strength (increase in κ) and hence decreases the energy barrier between the particle and membrane surface as illustrated in Figure 2.7. A further increase in the salt concentration will eventually reach the “critical” point where $E_T = 0$, and the system is completely destabilized. In this case, the particle can easily come in contact with the membrane surface without much effort.

Figure 2.7: Illustration of effect of ionic strength on the interaction energy

2.2.1.3.4. Effect of surface roughness

A correlation of the DLVO interaction energy between colloidal particles and the roughness of polymeric membrane surfaces was developed using atomic force microscopy (Hoek *et al.*, 2003). It was established that a rough surface has a higher affinity for particle deposition due to a lower repulsive interaction energy barrier as compared to a smooth surface. Also, the valleys on the rough membrane surface serve as preferential sorption sites for the colloidal particle (Bowen and Doneva, 2000; Hoek *et al.*, 2003).

2.2.1.3.5. Extended-DLVO and non-DLVO interactions

Quite often, the DLVO theory alone cannot satisfactorily describe the fouling behaviour of a membrane. The discrepancy can be attributed to the contribution of short-ranged acid-base (electron donor/electron acceptor) interaction between two surfaces immersed in a polar solvent (Bhattacharjee *et al.*, 1996; Brant and Childress, 2002; 2004). This interaction may be attractive due to hydrophobic attraction or repulsive due to hydrophilic repulsion. Such interaction is important to explain why the hydrophilic particle-hydrophilic membrane system has a lower propensity towards fouling compared to a hydrophobic particle-hydrophilic membrane system (Brant and Childress, 2002).

There is also another non-DLVO force such as steric interaction, which is considered important in the particle attachment process for colloidal particles carrying adsorbed polymers such as a bacteria cell. Some segments of the polymer are adsorbed strongly to the particle, while other parts of the adsorbed polymer extend away from the surface into the dispersion medium; repulsion occurs when two such polymer layers overlap, thus giving rise to enhanced stability against aggregation known as steric stabilization (Elimelech *et al.*, 1995; Gregory, 2006).

2.2.1.4. Critical flux

From the particle transport and attachment process, it is recognised that the accumulation of particles on the membrane is dependent on the total force acting on the particle. The total force is the summation of permeate drag force, back transport forces and surface interaction forces. However, most RO applications are in a high

salinity environment (seawater, brackish water and reclaimed water) where the charge interactions are greatly suppressed. Therefore, the controlling step in membrane fouling is mainly the particle transport step. Since particle transport is a function of convection (permeation drag), this gives rise to the concept of critical flux, which was introduced by Field and co-workers (Field *et al.*, 1995).

Critical flux refers to the flux level below which no fouling occurs and above which a membrane is fouled (Field *et al.*, 1995). In the context of colloidal fouling, when operating the RO beyond the critical flux, the colloids initially present in the polarised layer will transform from the liquid phase into an irreversible cake layer (Bacchin *et al.*, 2002a; Bacchin *et al.*, 2002b; Chen *et al.*, 1997). Therefore, the onset of fouling and the subsequent build up of deposit layer is dependent on the net flux, which is the difference between operating flux, J_v , and critical flux, J_{crit} , or $(J_v - J_{crit})$.

Numerous investigations have been carried out to determine the critical flux of different particles under a wide range of operating conditions by employing various methods (refer to Section 2.3. on fouling monitoring techniques), and the highlights of this topic were summarized in two recent review papers (Bacchin *et al.*, 2006; Howell, 2004). It is obvious that since critical flux is linked to the particle transport phenomena, factors (e.g. particle size and shear rate) that control the particle transport step could also manipulate the critical flux. For example, the critical flux of 5 μm yeast and 6.4, 11.9 μm latex particle in the shear rate range of 100 to 3000 s^{-1} was satisfactorily predicted with a modified version of the shear induced diffusion model, by replacing the constant from 0.078 to 0.0595 in Eq. (2.17) and assuming $\phi_w = 0.2$ (Li *et al.*, 2000).

The critical flux concept has been widely and successfully applied in microfiltration/ultrafiltration, for example in membrane bioreactor operations (Le-Clech *et al.*, 2006). However, its application in the RO process is limited and this warrants a thorough investigation into the critical flux of colloids in the RO process.

2.2.1.5. Fouling resistance

The formation of a colloidal deposit layer on the membrane introduces an additional resistance to permeate flow known as the cake resistance and this increases the overall hydraulic resistance. As a result, Eq. (2.2) is rewritten as

$$J_v = \frac{TMP - \Delta\Pi_w}{\mu(R_m + R_f)} \quad \text{Eq. (2.21)}$$

where R_f is the hydraulic resistance of the fouling layer or commonly known as the cake resistance. The cake resistance is related to its own mass load, m_f (in kg/m^2), and the specific cake resistance, α_f , as follows:

$$R_f = \alpha_f m_f \quad \text{Eq. (2.22)}$$

The specific cake resistance can be estimated from the Carmen-Kozeny equation:

$$\alpha_f = \frac{180(1-\varepsilon)}{\rho_p d_p^2 \varepsilon^3} \quad \text{Eq. (2.23)}$$

where ε is the porosity of the fouling layer and ρ_p and d_p are the density and diameter of particles, respectively. As can be seen, the specific cake resistance is very sensitive to the particle size ($\propto 1/d_p^2$), e.g. 200 nm diameter particles gives a 100 X lower specific resistance and hence cake resistance than 20 nm diameter particles. As evident from Eq. (2.23), the specific cake resistance is also a function of the porosity, which in turn is strongly influenced by the ionic strength of the solution. The inter-particle distance is greatly reduced at high ionic strength, resulting in the formation of a more consolidated cake layer with low porosity, thus increasing the cake resistance (Faibish *et al.*, 1998; McDonogh *et al.*, 1989; McDonogh *et al.*, 1984; Yiantsios and Karabelas, 1998; Zhu and Elimelech, 1997).

2.2.1.6. Cake enhanced osmotic pressure (CEOP)

Apart from introducing an additional hydraulic resistance, the deposit layer could also cause the cake enhanced osmotic pressure (CEOP) phenomenon (Hoek and Elimelech, 2003; Hoek *et al.*, 2002). The CEOP phenomenon arises due to the hindered back diffusion of solutes from the fouled-membrane surface to the bulk solution, where the solutes now need to diffuse through the tortuous paths within the cake layer. In addition, the solutes in this “unstirred” deposit layer are not exposed to the shear by tangential flow as compared to those in a free flow channel.

Since CP is a function of diffusion according to Eq. (2.7), a drop in the effective back diffusion, causes the concentration and the osmotic pressure of solutes at the membrane wall to be greatly enhanced. An elevated osmotic pressure means a loss in the effective transmembrane pressure. Therefore, in reality the CEOP effect coupled with the hydraulic resistance of the cake layer both contribute towards the overall RO membrane performance loss. In fact, the CEOP effect could be more serious especially for cake layers of larger particles than small particles, in which the resistance is comparatively negligible as shown earlier. This trend is examined in detail in Chapter 5.

Unfortunately, despite its substantial role in membrane fouling, there are only a few reports available in the literature that pay attention to the CEOP phenomenon. Molecular simulations on the diffusion of solutes through a solid (formed by rigid spherical particles) and soft cake layer (biofilm structure treated by allowing overlaps among the adjacent particles and taking into account only the void spaces) was carried out in a recent work (Kim and Chen, 2006). Four cake structures of uniform spheres were assumed, namely the simple cubic, body-centered cubic, face-centered cubic, and random colloidal cake structures; and found that for cake layers with high volume fractions (greater than ~ 0.5), different cake constructions gave distinct effects on the diffusive transport of solutes. However, the simulations were restricted to cake layers of single-sized particles. Likewise, other experimental studies on RO colloidal fouling (Hoek and Elimelech, 2003; Hoek *et al.*, 2002; Ng and Elimelech, 2004; Wang and Tarabara, 2007) were also limited to using mono-dispersed silica as a model colloid since the CEOP estimation was dependent on the mathematical model calculations, in which the accuracy fully relied on uniform cake properties. Thus, the possibility of CEOP effect in other complex colloidal systems, such as macromolecule gel layer or biofilm, has not been explored. Therefore, a versatile and robust technique is essential to demonstrate the CEOP effect in fouling of RO. Also, since the CEOP effect is due to the build up of a deposit layer, other factors such as critical flux, imposed flux, crossflow, particle concentration and size, and ionic strength that could possibly influence the membrane fouling and hence the CEOP phenomenon need to be critically assessed.

2.2.2. Biofouling – A problem of biofilm development

Biofouling in RO is often regarded as a problem of formation of a biofilm (Flemming, 1997; Flemming and Schaule, 1988). Biofilm is defined as, “a surface accumulation, which is not necessarily uniform in time or space, which comprises cells immobilized at a substratum and frequently embedded in an organic polymer matrix of microbial origin” (Characklis and Marshall, 1990). From the “autopsies” of biofilm (Baker and Dudley, 1998; Flemming and Wingender, 2001; Sutherland, 2001), the biofilm mainly consists of,

- > 90% moisture content;
- of dried deposit, > 50% organic content;
- of extracellular polymeric substances (EPS), polysaccharides (40 – 90%), proteins (< 1 – 60%), nuclei acids (< 1 – 10%) and lipids (< 1 – 40%);
- high microbiological counts (> 10^6 CFU/cm²);
- inorganic compounds.

The biofilm is held together by EPS, which is the key component that determines the physical-chemical properties of biofilm such as mechanical stability, binding of water and surface hydrophobicity (Flemming *et al.*, 1997; Flemming *et al.*, 2000; Wolfaardt *et al.*, 1999). Due to this nature, EPS plays an important role in the fouling process. EPS provides sorption sites for water, inorganic and organic solutes and particles and therefore could induce other types of fouling such as particulate fouling. In fact, it is postulated that EPS is the main cause of membrane failure (Pollice *et al.*, 2005; Ye *et al.*, 2005).

2.2.2.1. Successive events in microbial fouling

The biofouling process can be divided into five stages: 1) the formation of a conditioning film, 2) bacteria transport and adhesion, 3) biofilm development and accumulation, and 4) biofilm detachment; as illustrated in Figure 2.8.

Figure 2.8: Formation of biofilm (Maier *et al.*, 2000)

2.2.2.1.1. Surface conditioning

The first step in biofilm formation is the adsorption of macromolecules (e.g. humic substances, lipopolysaccharides, or other products of microbial turnover) onto the membrane surface, which is aided by the concentration polarization effect. The thin film organic layer is known as the conditioning film. This phase is completed within seconds to minutes after immersion of a surface into an aqueous system; e.g. there was 0.8 mg/m^2 of organic matter adsorbed to a stainless steel surface after 15 minutes of exposure in seawater (Little and Zsolnay, 1985). These adsorbed macromolecules can mask the original surface properties of the membrane and facilitate the attachment of microorganisms onto the surface. It was demonstrated that there was an increase of water contact angle from 15° for bare glass up to 50° for the glass after incubation for 1 hr in natural seawater (Bakker *et al.*, 2003).

2.2.2.1.2. Bacteria transport and adhesion

Before bacteria adhere to the membrane surface, bacteria have to be transported from the bulk liquid to the membrane-water interface. In natural systems, one of the transport mechanisms is chemotaxis; whereby a cell will move towards the source of chemical attractant, such as nutrients, which are essential components for metabolism and reproduction, but move from a negative chemotaxis (Bryers, 2000). Therefore a membrane surface serves as a favourable spot for bacteria attachment

due to higher availability of substrates under the concentration polarization effect. Other transport mechanisms in RO are from the permeation flux, back-diffusion and crossflow. Since most bacteria have an average size of about 1 μm , bacteria cell transport is often treated equivalent to particle transport (Section 2.2.1.2.). However, it should be noted that actual bacteria cells are semi-solid and some have an overall irregular shape due to the flagella.

Upon arriving at the membrane surface, microorganisms will attach to the surface. The factors affecting the adhesion are dependent on (Characklis, 1990b):

- 1) microorganisms (semi-solid phase), governed by factors such as species compositions of microflora, cell number in the bulk, viability, nutrient status, growth phases, hydrophobicity, surface charge, and EPS;
- 2) fluid (liquid phase), with factors such as temperature, pH, ionic strength, viscosity, and surface tension;
- 3) membrane surface (solid phase), via chemical compositions, hydrophobicity, surface charge, and conditioning film.

Bacteria adhesion is often treated as a physicochemical process where the attachment can be explained in terms of Gibbs energy associated with the interfaces between membrane/bacterium, membrane/liquid, and bacterium/liquid (Absolom *et al.*, 1983; Busscher *et al.*, 1984) as well as the DLVO theory for colloid stability (Azeredo *et al.*, 1999; Hermansson, 1999; van Loosdrecht *et al.*, 1989). In addition, hydrophobic interaction and steric repulsion with the membrane surface may be critical.

Experimental studies that relate the initial stage of bacteria deposition onto the membrane surface with the transport models (shear induced diffusion) and the surface interaction forces (DLVO and acid-base interactions) have been demonstrated using direct observation methods (Kang *et al.*, 2004; Li *et al.*, 2003a; Wang *et al.*, 2005). Despite that, this may have oversimplified the adhesion process, as the main component that comes in contact with the membrane is indeed the EPS that surrounds the outer membrane of the bacteria cell.

2.2.2.1.3. Biofilm development and accumulation

Once attached, bacteria cells may grow and proliferate into micro-colonies, excreting EPS, colonizing free surface areas, and forming a biofilm. The development of a mature biofilm can be considered in three stages (Marshall, 1989). First stage is the multiplications of primary colonizing bacteria as well as further deposition of bacteria from the bulk liquid. The population density in this stage is low. This is followed by a transition stage where the bacteria cells are actively reproducing, excreting EPS and thus forming a matrix of cells embedded in the EPS. As a result, the population density increases. Finally a mature biofilm is formed where the population density is high and with high levels of competition.

2.2.2.1.4. Detachment

Detachment is an interfacial transfer process, which transfers cells from the biofilm back to the bulk liquid. The detachment is dependent on the fluid dynamic conditions. It was observed that biofilm detachment increases with both fluid shear stress and biofilm mass (Characklis *et al.*, 1982). As the fluid velocity increases, the viscous sub-layer thickness decreases. Consequently, the region near the surface subject to relatively low shear forces is reduced. Other factors such as the availability of nutrients can also determine the detachment of biofilm. If the nutrients in the biofilm are consumed, the situation will be unfavourable for the growth of microorganisms. Hence, microbes will tend to swim to a high nutrients environment. However, with the presence of concentration polarisation effects, the nutrient supply may not be a problem in the microenvironment near the membrane surface. In addition, when there is more than one species of microorganisms present in the biofilm matrix, this could either create competition for nutrients, which means weaker species will be rejected from the biofilm or one species could produce toxin waste that kills another species and causes detachment (Brading *et al.*, 1995).

2.2.2.2. Biofouling and flux-mass transfer relationship in a reverse osmosis system

Although biofilm formation is linked to flux and mass transfer, the information available on this topic is very limited. Very often, biofilm formation in reverse osmosis is treated in a similar fashion to that occurring in natural water systems. Nonetheless, the major difference between a RO system and other systems is the presence of permeation flux and having complex hydrodynamic conditions e.g. the presence of feed spacer in the flow channel.

The convective flux and back diffusion (or mass transfer) has been proven to play a major role in the deposition of bacteria cell on the membrane and therefore influences the initial stage of fouling. Previous studies have confirmed that there exists a critical flux and above this value bacteria cells will deposit on the membrane while negligible deposition is observed when operating below the critical flux (Li *et al.*, 2003a). Though negligible accumulation of bacteria cells occurs at the beginning, yet some EPS footprints are left on the membrane surface, as the actual component that comes in contact with the membrane is the EPS. The residue of EPS can promote subsequent bacteria adhesion. Firstly, it could modify the membrane surface properties and facilitate the attachment of bacteria cells. It could also serve as nutrient for the consumption of bacteria. Lastly, it helps the adsorption of bacteria cells due to its sticky nature. Thus, it does not require a high degree of colonisation of bacteria to develop a biofilm on the membrane surface. Moreover, biofilms form in natural systems without imposed flux even though the process may take longer. So, the concept of critical flux that applies at the early stage of deposition may not be the determinant in the long run. However, there is a need to identify the sustainable flux region (Bacchin *et al.*, 2006) where the growth of biofilm is considered acceptable because frequent cleaning of the membrane is not required.

In addition, the influence of flux-mass transfer on the subsequent build-up of the biofilm has not been well explored. Apart from convecting the bacteria cells to the membrane surface, solute concentration polarization exists in a RO system as a function of flux-mass transfer. With higher flux, a higher CP effect is expected (Eq. 2.7). CP increases the nutrient concentration at the wall, and this could result in a

faster development of the biofilm. In natural water systems, the biofilm layer is limited by the balance between diffusion of nutrient in the biofilm matrix and the rate of consumption of nutrient (Gonpot *et al.*, 2000; Stewart, 1998; 2003; Wood and Whitaker, 1998). Once the nutrient supply is discontinued, the biofilm is likely to detach from the surface. However, this situation may be overcome under the effect of CP where the nutrient supply is not restricted. Therefore, it is hypothesized that the impact of flux-mass transfer on RO biofouling is through the control of the nutrient level at the membrane wall, which in turn determines the growth of the biofilm, rather than through the control of the deposition of bacteria cells onto the membrane surface. This hypothesis will be examined in this thesis.

The build up of biofilm on the membrane surface means an additional resistance to solvent flow through the membrane. More importantly, the possibility of enhancing the concentration polarization level by the biofilm as in the case of colloidal fouling has not been well studied. The enhanced CP is important for two reasons. Firstly, similar to colloidal fouling, the elevated concentration of solutes at the membrane wall means an increase in the osmotic pressure and hence a loss in the effective transmembrane pressure. Secondly, not only is the salt concentration increased, but the nutrient level is also enhanced and this will accelerate the growth of the biofilm. So biofouling in RO becomes an interplay between CP and biofilm development. There are numerous studies in the literature that investigate the effective diffusivity of solutes and molecules in the biofilm formed on non-permeable surfaces (de Beer and Schramm, 1999; de Beer *et al.*, 1996; Melo, 2005; Stewart, 1998; 2003; Vogt *et al.*, 2000). However, the outcomes are not conclusive, mainly due to the complex heterogeneous structures of the biofilm. In general, the diffusivity is linked to the tortuosity factor of the biofilm. So it is likely that the back diffusion of solutes in the biofilm on RO is hindered, similar to the colloidal cake layer. This statement needs to be validated, and it should be reminded that permeation drag was not present in previous studies.

2.3. Monitoring of membrane fouling

The failure of membranes is exacerbated by the absence of methods that can detect early stages of fouling and activate necessary countermeasures to minimize fouling. Current methods to monitor fouling are via the decline in flux or rise in transmembrane pressure. This is a measure of the performance of the membrane rather than a direct measurement of the amount of deposit present on the membrane. To relate these data to the foulant, conversion through a series of mathematical models is required. The accuracy of this approach depends on how well the model can describe the fouling process. In addition, the TMP rise or flux decline data only reflects average changes and fails to identify the exact location of the deposits on the membrane. For instance, there are areas on the membrane that are more prone to fouling e.g. fouling due to calcium sulphate scaling was the most severe nearer to the retentate effluent end while there was only a small amount of foulant detected at the feed end of the membrane module (Chai *et al.*, 2001).

Other conventional methods to detect fouling are by membrane autopsy. In membrane autopsy, the membrane element is disassembled and visually inspected for the location of deposit. The visible deposit is then scraped off and quantified and characterised for its physical, chemical and biological properties. Among the methods used include optical microscopy, scanning and transmission electron microscopy, scanning confocal laser microscopy, atomic force microscopy, attenuated total reflection Fourier transform infrared spectrometry, and energy dispersive X-ray microanalysis (Dudley, 1998; Dudley and Darton, 1996; Kuehn *et al.*, 1998; Schmid *et al.*, 2003; Schmitt and Flemming, 1998; Suci *et al.*, 1997; van Hoof *et al.*, 2002; Yang *et al.*, 2000; Zhang and Fang, 2001). Although a large amount of information can be gathered, this is a destructive method and the membrane has to be sacrificed. This leads to the need to seek for non-invasive, in-situ and real-time fouling monitors.

For an efficient monitoring of the fouling process in RO, there are 3 important elements that need to be accounted for: 1) concentration polarisation, 2) critical flux, and 3) build up of the cake layer. These are crucial, as CP is the precursor to fouling, critical flux is a measure of inception of fouling whereas the build up of cake layer represents the extent of fouling. There have been several conventional

and non-invasive fouling measurement techniques developed over the years and are summarised in two review papers (Chen *et al.*, 2004a; Chen *et al.*, 2004b). Some important features of the fouling monitoring techniques/methods are outlined in Table 2.2. Some of these techniques have their limitations and could not establish their practical use in the spiral wound RO module. Therefore, there is a need to develop a more flexible fouling monitor that can achieve the 3 goals mentioned above.

Table 2.2: Fouling monitoring techniques in membrane processes

<i>Concentration Polarization</i>		
Technique	Descriptions	Limitations
Optical shadowgraph (Vilker <i>et al.</i> , 1981)	Deflection of light that passes through a medium of continuously varying refractive index. Refractive index can be calibrated against the concentration of solutes.	Complex procedure to align the laser light. Poor resolution whereby data less than 200 μm above the membrane surface need to be extrapolated. CP layer thickness in RO is less than 200 μm .
Nuclear magnetic resonance imaging (Yao <i>et al.</i> , 1995)	Excitation and relaxation of protons in a specimen under the influence of an external magnetic field. Can obtain flow and concentration profile along membrane module.	Module must fit within the magnetic field. Too expensive.
Radio isotope labeling (McDonogh <i>et al.</i> , 1995)	Accumulation of radio-isotope labeled macromolecules on the membrane surface is detected as an increase in voltage by a scintillation detector. Signal is calibrated against a known mass of macromolecule.	Only applicable for macro-molecules.
Capacitive micro-sensor (Zhang <i>et al.</i> , 2006)	Micro-capacitor stores energy within the electrode when immersed in electrolyte solution. Device capacitance is a function of dielectric constant of the medium, and is calibrated against known salt concentrations. Multiple devices with different vertical positions of electrode are fixed on membrane surface to provide a concentration profile against the vertical distance from membrane surface.	Requires modification of membrane module to integrate the sensors and electrical circuits.

Table 2.2 continued: Fouling monitoring techniques in membrane processes

<i>Critical Flux</i>		
Technique	Descriptions	Limitations
Flux stepping – TMP measurement (Chen <i>et al.</i> , 1997; Kwon <i>et al.</i> , 2000)	Increase the flux level in a step-wise method and monitor the change in TMP. Each step lasts between 10 to 30 minutes. The rate of change of TMP or $\partial \text{TMP} / \partial t > 0$ when the membrane is above critical flux. Can be applied for large scale and lab scale.	Large particle gives cake layer with low resistance and negligible increase in TMP. Depend on time interval of each step. Not suitable for RO application (operational pressure of few MPa) as the TMP change due to fouling in such a short interval is usually only few kPa.
Particle mass balance measurement (Kwon <i>et al.</i> , 2000)	Monitoring the change in particle concentration in the feed solution, where below critical flux no loss of particles is expected.	Not sensitive if only a low amount of deposition of particles (shown in Chapter 3 in this thesis work). Need to reduce the volume of test solution or use larger membrane area. Possible particles attachment in other parts of system and not on membrane. Only for lab scale.
Direct observation through membrane (DOTM) (Li <i>et al.</i> , 1998; 2003a)	Direct visual observation of particle deposition on the membrane surface under light microscope through a transparent membrane. Able to capture the particle-particle and particle-membrane interactions at the vicinity of membrane surface. Can enhance the detection capability to study bacteria adhesion by using stained bacteria and fluorescence microscope	Limited to big particle, small particle ($< 0.5 \mu\text{m}$) is not visible under microscope. Only able to capture the first layer of deposit, no information on subsequent build up of cake layer. Specific design of module is required to allow the use of microscope, as there is a limited in-plane view due to the depth of field of the optics. Not suitable for RO application as the membrane is not transparent. Only for lab scale.

Table 2.2 continued: Fouling monitoring techniques in membrane processes

<i>Fouling Layer</i>		
Technique	Descriptions	Limitations
Laser triangulometry (Altmann and Ripperger, 1997)	Reflection of laser light shone on the membrane surface through a window on the feed side. Light is deflected from the central axis with the build-up of cake layer.	No detail of particle membrane interaction. Poor resolution (5 μm). Specific design of module is required for the penetration of laser light. Only for lab scale.
Electrical impedance spectroscopy (Chilcott <i>et al.</i> , 2002; Gaedt <i>et al.</i> , 2002)	Measure the dispersion of alternating current across a membrane that is sputtered with a metal layer. The dispersion is characterized by the capacitance and conductance, and changes in values are due to fouling.	Requires membrane surface coated with a metal thin film, which may modify the actual surface properties. Complex mathematical formulation required for fouling characterization.
Tracer residence time distribution (RTD) measurement (Hasson <i>et al.</i> , 2006; Roth <i>et al.</i> , 2000; Roth <i>et al.</i> , 1999)	Injection of a tracer into the membrane module and measure the RTD profile on feed and permeate side. Fouling layer alters the dispersion of tracer in the flow channel and changes the RTD. Distinct distribution of tracer for a fouled and clean membrane due to difference in solute permeation.	RTD data provides information on the membrane performance instead of direct information on the cake layer. Membrane channel of small module only occupies a fraction of the total flow path in a RO system, so minute changes are not reflected on the RTD profile (This is shown in detailed in Chapter 3).
Ultrasonic time domain reflectometry (UTDR) (Mairal <i>et al.</i> , 2000; Mairal <i>et al.</i> , 1999)	Reflection of ultrasound wave from fouling layer and membrane surface. Based on changes in the acoustic property of the medium (density changes) and the time of flight of sound wave (thickness measurement of the medium). Transducer is easily assembled on the spiral wound RO module.	Not sensitive for interfaces with poor acoustic contrasts, for example the gel layer and biofilm.

A novel sodium chloride tracer response technique is employed to monitor the transient CP level (CEOP effect) and build up of cake resistance in this study. The technique can also be used to measure the critical flux of particles in the RO process. This technique has some similarities to the tracer RTD measurement (Hasson *et al.*, 2006; Roth *et al.*, 2000; Roth *et al.*, 1999), but it is not based on the RTD analysis of the tracer and provides a different interpretation of data. In addition, the ultrasonic time domain reflectometry (UTDR) technique has been selected in this study as it can be applied to both the lab scale flat plate RO module used in this thesis work (Mairal *et al.*, 2000; Mairal *et al.*, 1999) and large scale spiral wound RO modules (Chai *et al.*, 2001). However the application of UTDR for the detection of the gel layer or biofilms has yet to be verified. Another technique developed in this study for the biofilm detection in membrane process is the fiber optical sensor (FOS). FOS has not been applied in membrane processes for fouling detection. The detection principle is based on the interaction of foulants with the light transmitted along the fiber. In recent years, FOS has been widely used in biosensing of biomolecules and environmental applications (Holst and Mizaikoff, 2002; Kashyap, 1994; Kersey, 1996; Philip-Candy *et al.*, 2000; Rowe-Taitt and Ligler, 2002). For example, the tip type optical fiber, one fiber for light transmission and another one for receiving the reflected signal, was successfully used to monitor biofilm formation in a brewery pipeline (Tamachkiarowa and Flemming, 2003). However, a different evanescent wave sensor is used in this study.

The basic principles associated with the sodium chloride tracer response technique, ultrasonic time domain reflectometry (UTDR) and the fiber optical sensor (FOS) are given in Chapters 3, 6, and Appendix A, respectively, in this thesis.

2.4. Summary

A literature review on the basic principles of the operation of reverse osmosis, the fundamentals of colloidal fouling and biofouling and various tools or techniques to monitor the fouling process are reported in this chapter.

The initial stage of colloidal fouling is linked to critical flux, which is governed by the transport and attachment step. The critical flux concept has been widely

applied in MF/UF operations but not in the RO process. Also, previous methods to measure critical flux in MF/UF are not suitable for the RO process.

The subsequent build up of colloidal cake layer beyond the critical flux can induce an additional hydraulic resistance as well as the cake enhanced osmotic pressure (CEOP) effect, in which both factors contribute to the overall membrane performance loss. Unfortunately, previous studies on the CEOP effect were limited to uniform cake layers due to the lack of a proper tool to detect the CEOP effect. Therefore it is essential to develop a technique that allows CEOP study in other more complex systems like biofilms. Also, the assessment of the roles of parameters such as critical flux, imposed flux, crossflow velocity, particle size and concentration, and salt concentration on the CEOP effect in fixed pressure and fixed flux operation is critical.

Biofilm growth is dependent upon the nutrient availability at the membrane surface, thus it is hypothesized that biofouling can be controlled through flux-mass transfer. Furthermore, the possible existence of CEOP phenomenon in biofouling needs confirmation.

An effective fouling monitor should be able to detect the transient CP, critical flux and build up of cake layer. Most current methods either require modification of the membrane module to fit in the detector or are not user-friendly. It is proposed that the ultrasonic time domain reflectometry (UTDR) technique coupled with a novel sodium chloride tracer response technique is able to achieve the goals mentioned above. In addition, the fiber optical sensor (FOS) has potential to be used as a biofilm monitor in the RO process.

CHAPTER 3

Enhanced Concentration Polarization by Unstirred Fouling Layers in Reverse Osmosis: Detection by Sodium Chloride Tracer Response Technique *

This chapter describes a sodium chloride tracer response technique to determine the effect of fouling on concentration polarization level in a reverse osmosis (RO) system operated in the constant flux mode. Colloidal silica and alginic acid were used as model fouling agents. It was found that the formation of the unstirred fouling layer, either solid cake deposit or gel layer, greatly exacerbated the concentration polarization (CP) level in RO separations, with a more pronounced effect at high flux operation. The results suggested that operation at high flux could significantly reduce the apparent permeability, but that this was through a dramatic increase in CP and consequent loss in driving force via the enhanced osmotic pressure rather than through an additional hydraulic resistance. The study also showed that the sodium chloride tracer response technique is a promising technique that can be applied as a non-invasive tool to detect and monitor fouling development in reverse osmosis.

3.1. Introduction

Reverse osmosis (RO) is widely used to convert seawater or 'used' wastewater to potable quality water. However membrane fouling is still a bottleneck in RO technology, which tends to reduce the permeate flux in constant pressure filtration or increase in transmembrane pressure (TMP) in constant flux filtration. Inevitably, fouling in RO is linked to concentration polarization (CP), a phenomena that arises when the rejected solutes accumulate at the surface of the membrane. CP can be the precursor to fouling events in the RO processes; and therefore various attempts have been made to develop mathematical models for predicting the CP level in a membrane system (Bhattacharjee *et al.*, 2001; Elimelech and Bhattacharjee, 1998; Jain and Gupta, 2004; Kim and Hoek, 2005; Song and Elimelech, 1995). These models are usually for clean membrane systems and only account for CP

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development in the absence of fouling. However, upon formation of a fouling layer, which can be considered as an unstirred layer, the back diffusion of salt ions from the membrane surface to the bulk solution is hindered (Hoek and Elimelech, 2003; Hoek *et al.*, 2002). As a consequence, the concentration at the membrane surface is significantly increased, where $CP(t) \gg CP(0)$ as illustrated in Figure 3.1, and so is the trans-membrane osmotic pressure.

Figure 3.1: Concentration polarization in a reverse osmosis membrane system (a) before membrane is fouled, and (b) after membrane is fouled

The increase in osmotic pressure means a decrease in the effective trans-membrane pressure. This ‘cake enhanced osmotic pressure’ (CEOP) effect, defined by Hoek and Elimelech (Hoek and Elimelech, 2003), is often neglected and any drop in permeate flux is usually attributed solely to the additional hydraulic resistance of the fouling layer. This assumption leads to an over estimation of the actual amount of fouling layer. Conversely, it means that a relatively low load of particles on the membrane can produce a greater impact on performance than anticipated from ‘cake resistance’ considerations alone.

It is essential to characterize accurately the build up of CP as fouling progresses to fully understand the fouling mechanisms in RO processes. Various non-invasive techniques for monitoring the polarization phenomena in a membrane system had been developed over the years; these include the light deflection technique (Vilker *et al.*, 1981), magnetic resonance imaging (Airey *et al.*, 1998; Yao *et al.*, 1995), radio-isotope labeling (McDonogh *et al.*, 1995), and electronic diode array

microscope (McDonogh *et al.*, 1995). The advantages and shortcomings of the above techniques were critically assessed in a review paper by Chen *et al.* (Chen *et al.*, 2004a). In general, these techniques are not practical for routine use in a plant; either a special configuration of the membrane module is required to facilitate the monitoring tools or the techniques are too expensive to be considered economically viable. Therefore, a simple tool that requires the least modifications to an existing membrane system is desired. In previous studies on the CEOP effect in membrane systems (Hoek and Elimelech, 2003; Hoek *et al.*, 2002; Ng, 2005; Ng and Elimelech, 2004), colloidal silica of uniform size was used to form a cake layer on the membrane in the presence of sodium chloride under constant pressure operation. The cake enhanced osmotic pressure was analyzed by a lengthy mathematical iteration process only applicable for particles with known size and a uniform cake layer.

In this current study, a simple sodium chloride tracer response technique has been developed to examine the CEOP effect in an RO system under constant flux operation. This mode of operation was chosen as it reflects large-scale operation; the method can also be used for constant pressure operation as explained later. A tracer is injected into the system of interest as an extended pulse, and the exit concentration profile of the tracer is analyzed to provide valuable information about the fouling in the system. Tracer testing is a well established method, which is commonly used to study the residence time distribution (RTD) of chemical reactors and other vessels (Levenspiel, 1972); and has been recently applied to detect fouling in a membrane module by comparing the arrival time and magnitude of the peak from a pulse-spike of a used membrane against a new membrane (Roth *et al.*, 1999). It is critical to select a tracer with the following properties: (i) sensitive to the retention property of membrane, whereby the system gives immediate signal when subjected to the tracer; (ii) does not react or duly interact with other species or the fouling layer presence in the system that could have altered the form/state of the tracer and hence affect the detection of the tracer; (iii) is easily measured and does not require a complicated detection system; and (iv) is readily available and cheap. Sodium chloride was selected as the tracer in this study as it meets the criteria listed above. When the RO membrane is subjected to sodium chloride solution, the

solutes are rejected by the membrane. As a result, a polarized layer of sodium chloride is formed increasing the osmotic pressure across the membrane. This response is immediate and provides an opportunity to make use of this phenomenon to determine the concentration polarization level of the membrane system.

Colloidal silica and alginic acid were selected as the model foulants in this study to simulate most commonly encountered foulants in water treatment applications. Normally, feed water to an RO system has a turbidity of less than 1 NTU, and this turbidity would be contributed by particles of sub-micron sizes. These particles can gradually deposit and form a compact cake layer on the membrane surface. Meanwhile, bio-fouling is the most prevalent and problematic type of fouling in an RO system; e.g. from the autopsies of 150 membrane samples collected all over the world, it had been identified that more than 50 % of the deposits removed from the membrane surface were biological/organic foulants (van Hoof *et al.*, 2002). Biofouling comes from deposition and colonization of bio-colloids (bacteria). The major fouling component in biofilms is the extracellular polymeric substances, EPS, (Flemming *et al.*, 1997) that fill the voids between bacteria. Alginic acid, in the form of sodium alginate, was used as a surrogate for EPS to simulate biofouling in this study. Alginate has been identified as an extracellular polymeric substances produced by *Pseudomonas* and it can play an important role in the formation of microbial biofilms (Nivens *et al.*, 2001). The formation of the solid (colloidal particles) and macromolecular (alginic acid) gel layers on the RO membrane at constant flux operation and their effect on the subsequent build up of CP level on the RO was elucidated in this study by employing the sodium chloride tracer response technique.

3.2. Theory

The sodium chloride tracer response technique is illustrated in Figure 3.2. The technique makes use of the unique property of an RO membrane to reject sodium chloride salts. Before the sodium chloride pulse, flux, J_v , can be expressed as,

$$J_v = \frac{(TMP - CP \cdot \Delta\Pi_b)}{\mu(R_m + R_f)} \quad \text{Eq. (3.1)}$$

Figure 3.2: Illustration of sodium chloride tracer response technique for determination of concentration polarization modulus of a membrane system

where μ is the viscosity of solvent, R_m is the membrane resistance, R_f is the fouling resistance, TMP is the trans-membrane pressure or the applied pressure across the membrane, $\Delta\Pi_b$ is the osmotic pressure difference between the feed and permeate solutions, and CP is the concentration polarization modulus, $(C_w - C_p)/(C_b - C_p)$. CP is linked to the flux, J_v , and mass transfer, k_m , of the membrane system,

$$CP = \frac{C_w - C_p}{C_b - C_p} = \exp\left(\frac{J_v}{k_m}\right) \quad \text{Eq. (3.2)}$$

When the membrane is un-fouled the value of k_m is the boundary layer mass transfer coefficient. However when there is a cake layer present the back transport is hindered, so

$$CP = \exp\left(\frac{J_v}{k_{\text{eff}}}\right) \quad \text{Eq. (3.2b)}$$

k_{eff} is the effective mass transfer coefficient. As modeled in Chapter 5, k_{eff} decreases as the fouling layer grows, and CP increases. For a linear increase in fouling layer thickness, CP increases exponentially due to the form of Eq. (3.2b).

When a pulse of sodium chloride is injected into the system, this causes an increase in the osmotic pressure. In order to maintain constant flux operation, the TMP of the system has to be raised to TMP_s . Therefore,

$$J_v = \frac{(\text{TMP}_s - \text{CP} \cdot \Delta\Pi_{bs})}{\mu(R_m + R_f)} \quad \text{Eq. (3.3)}$$

where TMP_s is the trans-membrane pressure of the system, and $\Delta\Pi_{bs}$ is the osmotic pressure difference between the feed and permeate solutions during the sodium chloride pulse. Combining the above two equations, yields

$$\text{CP} = \frac{\text{TMP}_s - \text{TMP}}{\Delta\Pi_{bs} - \Delta\Pi_b} \quad \text{Eq. (3.4)}$$

Therefore, by knowing the TMP of the system as well as the conductivities of feed and permeate before and during the sodium chloride pulse, CP can be determined. The measured conductivity, K, can be converted to concentration based on the published data (Omega Engineering Inc., 2001):

$$\text{LOG}(K) = 0.9856 \text{ LOG}(C) + 0.3444 \quad \text{Eq. (3.5)}$$

where C is the concentration of sodium chloride in ppm. The osmotic pressure of the sodium chloride can be estimated by (Robinson and Stokes, 1955):

$$\Pi = 2CR_g T \phi \quad \text{Eq. (3.6)}$$

where R_g is the universal gas constant, T is the temperature, and ϕ is the molar osmotic coefficient, given by (Pan, 1981):

$$\begin{aligned} \text{LOG}(1-\phi) = & -1.0937 - 0.08101 \{\text{LOG}(C)\} - 0.1749 \{\text{LOG}(C)\}^2 \\ & - 0.01785 \{\text{LOG}(C)\}^3 \end{aligned} \quad \text{Eq. (3.7)}$$

which is valid for concentrations ranging from 0.0001 to 0.3 M (5.85 to 17,550 ppm NaCl).

3.3. Material and methods

3.3.1. Membranes and chemicals

A commercial RO membrane (FilmTec, model BW30) was used in all the tests. It is a polyamide thin-film composite membrane. Data provided by the manufacturer indicated that the membrane has a salt retention of >99.0% and permeate flux of 45 L/m²h under standard testing conditions with 2000 ppm NaCl,

15.5 bar, 25 °C, pH 8 and 15 % recovery. Also, the membrane has a wide working pH range from 2 – 11. The membrane came in 1 X 1 m size and was cut to fit the RO cell (see Section 3.3.2.). The membranes were stored dried in a refrigerator at 4 °C and soaked in Milli-Q water (Millipore) for 24 hours before use.

Colloidal silica (Sigma Aldrich, Ludox TMA) and sodium alginate (Hayashi Pure Chemical Industries) were used as model fouling agents. The silica was supplied in the form of 34 wt% in deionised water at pH 7.0. No significant change in the pH was detected upon the addition of silica to the test solution, which remained at $\text{pH } 6.5 \pm 0.3$ throughout the experiment. The colloidal silica has a particle size of 20 nm based on the data provided by the manufacturer. Dynamic light scattering measurement (Brookhaven Instruments Corporation, model ZetaPALS) confirmed the colloidal silica has a mono-dispersed mean particle diameter of 23.8 ± 0.1 nm. Sodium chloride (Sigma Aldrich) was used as background ionic solution and for the tracer test. Milli-Q water was used to prepare the concentrated silica, alginic acid and sodium chloride solutions. Alginic acid and sodium chloride solutions were filtered with a 0.45 μm filter (Millipore, model HAWP04700) before use.

3.3.2. Reverse osmosis system

The set up of the reverse osmosis system is shown in Figure 3.3. The RO cell has parallel plate geometry and a flow channel of 310 X 60 X 1.4 mm with an effective membrane area of 0.0186 m². No feed spacer was used. The test solution was delivered from the 10 L feed tank using a high pressure pump (CAT PUMPS, model 277) to the RO cell. The temperature of the feed water was kept constant at 25 ± 1 °C with cooling water from a chiller (AR Engineering, custom made). An overhead stirrer (IKA, model Eurostar) was installed in the feed tank to ensure the solution was well mixed. System pressure and crossflow rate were controlled by a back pressure regulator (Veriflo Corporation, model ABP 1ST52BP4) and a flow control valve (Cole Parmer, model CP-32505-40) respectively. Pressures of the feed and permeate stream were monitored with pressure transducers (Bourdon Haenni, model E913); while the flow rate of the feed stream was monitored with a turbine flow meter (McMillan, model 114).

Figure 3.3: Schematic diagram of reverse osmosis set-up for colloidal fouling studies

The amount of permeate withdrawn, which fixes the flux, was controlled by a mass flow controller (Brooks Instrument, model 5882), which consisted of a thermal mass flow meter and a micro control valve, located on the permeate side of the RO cell. To achieve constant flux operation, the RO system was first operated at an excess feed pressure so that the mass flow controller self adjusted to the permeate side pressure to meet the set permeate flow rate; i.e. only a transmembrane pressure of 3 bar was required to obtain a flux of $10 \text{ L/m}^2\text{h}$, but instead the applied pressure was set to 20 bar, so the mass flow controller regulated the permeate side pressure to 17 bar. If this was insufficient to maintain the desired constant flux level, then the feed side hydrostatic pressure was increased via adjusting the pump rate.

The quality of feed and permeate were monitored with conductivity meters (Mettler Toledo, model Seven Multi and Rosemount Analytical, model Solu Comp II, respectively). During the tests, concentrate and permeate were recycled back to

the feed tank. For the tracer test, sodium chloride solution was injected into the high pressure feed line of the RO cell via a metering pump (Pulsafeeder, model Pulsatron). During the tracer test, concentrate and permeate samples were discharged to drain and the feed solution was topped up in order to maintain a constant volume. Pressures, crossflow rate, flux, and conductivity readings were recorded with a data acquisition system (National Instrument, model PCI 6014 and LabView).

3.3.3. Experimental procedure

The experimental conditions are summarized and presented in Table 3.1. The experiments were commenced with the compression of the membrane for 2 hours with Milli-Q water at an applied pressure of 20 bar and at the desired crossflow rate. Then, flux was set to the desired value, and the system was left to equilibrate for 12 hours. For test runs with sodium chloride in the background, this protocol was followed by the addition of concentrated sodium chloride solution to achieve a final concentration of 2000 ppm NaCl and the system was left to equilibrate for another 2 hours. Subsequently, the tracer test was carried out and the data were used as reference points for the ‘clean’ membrane i.e. the average CP value determined here was taken as the reading at $t = 0$ for the fouling test. In the tracer test, 200 g/L of NaCl was injected into the high pressure feed line via the metering pump, to give an additional of 500 – 2000 ppm NaCl to the feed solution entering the RO cell. Depending on the operating flux, the pulse length lasted for 10 – 30 minutes. When the tracer pulse was stopped, the system TMP and conductivity readings returned to the previous values and the system was left to equilibrate for 1 hour.

Then the fouling test was initiated by adding the fouling agent to the feed tank. Several tracer tests were carried out during each fouling run. Samples were collected from both the feed tank and the permeate line and analyzed for pH (Mettler Toledo, model SevenMulti), turbidity (Hach, model 2100AN), and total silica content with inductive couple plasma optical emission spectrometer, ICP-OES (Perkin Elmer, model Optima 2000 DV) for silica fouling tests. The total organic carbon (TOC) content was measured with Total Organic Carbon Analyser (Shimadzu, model TOC VHS-C) for alginate fouling tests.

Cleaning tests were carried out on selected runs at the end of the fouling stage. In the cleaning test, the feed tank solution was first replaced with 2000 ppm NaCl solution without the fouling component, and then followed by Milli-Q water for the cleaning stage. After cleaning with Milli-Q water for about 30 min, 2000 ppm of NaCl was added to the solution and the system was left to equilibrate for 30 min. The tracer test was then carried out to determine the CP level in order to evaluate the effectiveness of cleaning.

Table 3.1: Operating conditions for fouling tests

No	Conc. of Silica (ppm) or Alginic Acid (ppm TOC)	Background 2000 ppm NaCl (Y/N)	Cleaning Test (Y/N)	Constant Flux, J_v or Initial Flux, J_0 (L/m ² h)	Crossflow Velocity, v (m/s)
<i>Silica Fouling – Constant Flux Experiments</i>					
1	1000	No	No	30	0.10
2	200	Yes	No	10	0.10
3	200	Yes	No	15	0.10
4	200	Yes	No	20	0.10
5	200	Yes	Yes	25	0.10
6	200	Yes	Yes	30	0.10
7	200	Yes	No	30	0.10
8	200	Yes	No	30	0.10
9	200	Yes	No	10	0.06
10	200	Yes	No	15	0.06
11	200	Yes	No	20	0.06
12	200	Yes	No	25	0.06
13	200	Yes	No	30	0.06
14	200	Yes	No	15	0.15
15	200	Yes	No	30	0.15
16	200	Yes	No	35	0.15
17	200	Yes	No	40	0.15

Table 3.1 continued: Operating conditions for fouling tests

No	Conc. of Silica (ppm) or Alginic Acid (ppm TOC)	Background 2000 ppm NaCl (Y/N)	Cleaning Test (Y/N)	Constant Flux, J_v or Initial Flux, J_0 (L/m ² h)	Crossflow Velocity, v (m/s)
<i>Silica Fouling – Constant Flux Experiments</i>					
18	200	Yes	No	15	0.23
19	200	Yes	No	35	0.23
20	200	Yes	No	40	0.23
21	200	Yes	No	45	0.23
22	200	Yes	No	15	0.40
23	200	Yes	No	35	0.40
24	200	Yes	No	40	0.40
25	200	Yes	No	45	0.40
<i>Alginate Fouling – Constant Flux Experiments</i>					
26	100	No	No	15	0.10
27	100	No	No	25	0.10
28	6	Yes	No	10	0.10
29	6	Yes	No	20	0.10
30	6	Yes	No	25	0.10
31	6	Yes	No	30	0.10
<i>Silica Fouling – Constant Transmembrane Pressure Experiments</i>					
32	200	Yes	No	40	0.10
33	200	Yes	No	40	0.23
34	200	Yes	No	40	0.46

3.4. Results and discussion

3.4.1. Validation of tracer test for concentration polarization detection

3.4.1.1. Selection of tracer injection period and concentrations

First and foremost, it was necessary to determine the response of the system when it was subjected to sodium chloride stimulus. When sodium chloride was injected into the system at the inlet, it took some time to travel through the system before reaching and being detected by the analyzer located at the outlet of the feed

side as well as on the permeate side of the system. For example, since the permeate flow rate (only about 0.0093 L/min at a flux of 30 L/m²h), was much lower than the feed flow rate of 0.5 L/min (or crossflow velocity of 0.10 m/s), there was a time delay before the tracer reached the conductivity detector on the permeate stream. If the corresponding values of TMP, feed, and permeate conductivities during this delay period were taken for calculation of CP based on Eq. (3.4), this would have resulted in a misleading value of CP. To avoid such errors, only the readings after the response had reached a steady value were used in the calculations. Therefore, it was essential to determine the ideal pulse length such that the system had reached steady state before the pulse was stopped. In addition, the responses using different concentrations of tracer were examined to ensure there was no variation in the result. Since the tracer tests were performed at different crossflow flow rates, flux levels, concentrations and pulse lengths, and hence yielded different responses in terms of TMP and conductivity readings due to the intrinsic properties of the membrane; for comparison purposes the signals were converted to the dimensionless form:

$$F_X = \frac{X_t - X_i}{X_{st} - X_i} \quad \text{Eq. (3.8)}$$

where X is the parameter of interest e.g. TMP, feed or permeate conductivity, and X_t , X_i , and X_{st} are the readings at time t , at $t = 0$ and at steady state (steady readings of parameter of interest), respectively.

The tracer responses for different lengths of pulse are shown in Figure 3.4. As shown in Figure 3.4 (a), the system only took about 50 s to reach a steady reading of TMP, whereas it was slightly longer time, about 60 s as shown in Figure 3.4 (b), for the feed conductivity reading since the conductivity analyzer was located further down stream in the RO set-up. However, it was clearly demonstrated that a 1 minute pulse time was not sufficient for the system to reached a steady reading of permeate conductivity even at a high flux of 30 L/m²h as shown in Figure 3.4 (c). Therefore, the tracer was introduced as a step input rather than as a short pulse in this study.

When comparing the responses at fluxes of 30 and 10 L/m²h, it can be seen that flux had no effect on the response time in TMP and feed conductivity as shown in Figures 3.5(a) and (b), respectively. However, the permeate conductivity time lag at

(a)

(b)

(c)

Figure 3.4: Tracer response for different lengths of pulse at $J_v = 30 \text{ L/m}^2\text{h}$ and 2000 ppm NaCl pulsed solution: (a) F_{TMP} , (b) $F_{f,cond}$, and (c) $F_{p,cond}$

(a)

(b)

(c)

Figure 3.5: Tracer response for different flux levels at 30 mins pulse length and 2000 ppm NaCl pulsed solution: (a) F_{TMP} , (b) $F_{f,cond}$, and (c) $F_{p,cond}$

a flux of $10 \text{ L/m}^2\text{h}$ ($\sim 750 \text{ s}$) was roughly 3 times larger than at a flux of $30 \text{ L/m}^2\text{h}$ ($\sim 250 \text{ s}$) since the permeate flow rate was 3 times slower as shown in Figure 3.5 (c). Based on the above results, the pulse length was chosen to be 30 minute for a flux of $10 \text{ L/m}^2\text{h}$ so that the response of the system had reached a steady value; while a 10 minute pulse for a flux of $30 \text{ L/m}^2\text{h}$ was adequate to allow sufficient data points to be taken for the calculations of CP values; i.e. only data points after 300 and 900 s of pulse duration were taken for calculation of CP value for fluxes of 30 and $10 \text{ L/m}^2\text{h}$, respectively.

The results using different concentrations of tracer, 1000 and 2000 ppm of NaCl, are shown in Figure 3.6. Even though the actual values of TMP, feed, and permeate conductivities were different for both cases, at the same flux level and pulse duration, there was no difference in the arrival time of the response. More importantly, the CP values calculated from both tests were similar as shown in Figure 3.6 (d). Therefore, the concentrations of tracer did not affect the CP calculation. However, it should be noted that the magnitude of tracer injected into the system is directly related to the osmotic pressure, which means a higher TMP is required for a higher tracer concentration in order to maintain constant flux operation mode. Considering this restriction, the tracer concentration applied in this study was limited to 2000 ppm of NaCl.

Figure 3.6: Tracer response for different concentrations of pulsed solution at $J_v = 30 \text{ L/m}^2\text{h}$ and 30 mins pulse length: (a) F_{TMP} , (b) $F_{\text{f, cond}}$, (c) $F_{\text{p, cond}}$, and (d) CP profile

(b)

(c)

(d)

Figure 3.6 continued: Tracer response for different concentrations of pulsed solution at $J_v = 30 \text{ L/m}^2\text{h}$ and 30 mins pulse length: (a) F_{TMP} , (b) $F_{f, cond}$, (c) $F_{p, cond}$, and (d) CP profile

3.4.1.2. Application of tracer test for CP detection in a clean membrane system

The CP values extracted from the experimental data at $t = 0$ in the fouling tests can be compared against the theoretical CP values calculated from Eq. (3.2) and using the mass transfer correlation, k_m , for laminar flow in a clean membrane system based on the Graetz-Lvque equation is given by (Hoek *et al.*, 2002):

$$k_m = 1.62 \left[\frac{QD^2}{2W(H)^2 L} \right]^{1/3} \quad \text{Eq. (3.9)}$$

where Q is the crossflow rate; D is the diffusion coefficient; and W , H and L is the channel's width, height and length, respectively. A good correlation between the experimental and theoretical CP values was obtained as shown in Figure 3.7, which supported the applicability of the tracer test for CP estimation. In addition, the calculated average value of membrane resistance, R_m , based on Eq. (3.1) was $(1.0 \pm 0.1) \times 10^{14} \text{ m}^{-1}$, similar to the value from pure water permeability tests.

Figure 3.7: Comparison of experimental and theoretical CP values at different crossflow velocities and flux levels

3.4.1.3. Application of tracer test in fouling experiments

The tracer response during one of the silica fouling tests was compared to the response in a clean membrane system as shown in Figure 3.8. No significant difference in the response time profile was observed in the F function of TMP, feed or permeate conductivity, even though there was an obvious increase in the CP level (the CP value increased from 1.9 to 2.5). This was because the CP

calculations using Eq. (3.4) were based on the actual values of TMP and conductivities, rather than the F function. Compared to the previous tracer test studies using RTD data in an industrial type membrane module (Drak *et al.*, 2005; Roth *et al.*, 1999), the flow channel of our membrane test cell had a small working volume of only about 26 mL, and based on a crossflow rate of 0.5 L/min (or 0.10 m/s), the residence time of the tracer in the channel was only about 3 s which was only about 7.5 % of the total time taken for the tracer to reach the detector. Therefore, the fouling layer on the membrane surface did not substantially alter the flow path, and cause any measurable delay in the arrival time of the tracer. The results suggested that the feed-side RTD data from the tracer testing were not suitable for the characterization of fouling events in our system; however the TMP, feed, and permeate conductivity profiles could be used to determine the CP development and this warranted its application as a diagnostic tool for fouling in reverse osmosis systems.

(a)

Figure 3.8: Comparison of tracer response for membrane system without and with fouling: (a) F_{TMP} , (b) $F_{f, cond}$, and (c) $F_{p, cond}$. Fouling test conditions: silica concentration = 200 ppm, $J_v = 25 \text{ L/m}^2\text{h}$; pulse performed at run time = 483 min

Figure 3.8 continued: Comparison of tracer response for membrane system without and with fouling: (a) F_{TMP} , (b) $F_{f, cond}$, and (c) $F_{p, cond}$. Fouling test conditions: silica concentration = 200 ppm, $J_v = 25 \text{ L/m}^2\text{h}$; pulse performed at run time = 483 min

3.4.2. Effect of fouling on concentration polarization level - the CEOP effect

3.4.2.1. Silica fouling

3.4.2.1.1. Silica fouling without background sodium chloride solution

Colloidal silica fouling test was initially conducted without sodium chloride in the background. An example of TMP, feed and permeate conductivity profiles, as well as the calculated CP values during one of the sodium chloride pulses is shown in Figure 3.9. As shown in the figures, even though the feed concentration was constant throughout the pulse, instead of quickly reaching a steady value, the TMP values continued to increase during the pulse.

Figure 3.9: (a) TMP and flux, (b) feed and permeate conductivity, and (c) CP profile during one of the NaCl pulses in silica fouling without background salt ions. Test conditions: silica concentration = 1000 ppm, $J_v = 30$ L/m²h and $v = 0.10$ m/s

Similarly, the calculated CP values also increased with time and appeared to be very high and the data suggested that there were significant fouling occurring during the tracer test. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and Landau, 1941; Vervey and Overbeek, 1948), colloidal particles are stably suspended in water through Van der Waals attractions and electrostatic double layer repulsion, and the addition of sodium chloride causes a screening of the double layer repulsion so that the silica stability is disturbed causing an exaggerated fouling. After 30 min duration, the pulse was terminated and the TMP returned to the original value. This suggested that colloidal silica fouling was reversible.

3.4.2.1.2. Silica fouling with background sodium chloride solution

The experiment was repeated with 2000 ppm of NaCl in the background. This would be a more typical condition for brackish RO. An example of TMP, feed and permeate conductivity profiles, as well as the calculated CP and resistance, R_f , values during one of the NaCl pulses performed after 80 mins of run time in the silica fouling test at a flux of 30 L/m²h and $v = 0.10$ m/s are shown in Figures 3.10 (a), (b) and (c), respectively. Unlike the previous silica fouling test without background sodium chloride, where the system experienced a continual increase in TMP, in this test the TMP rapidly increased and reached a steady value when sodium chloride was pulsed into the system. Therefore the assumption of negligible fouling during the pulse was valid. The calculated CP was about 2.6, an increase of 18 % as compared to the original CP value of 2.2. At the same time, there was only about 3% increase in the total resistance (the sum of R_m and R_f). A very low cake resistance implied that only a minute amount of silica had deposited on the membrane surface, and this was confirmed by the measurement of the silica content in the feed tank via turbidity as well as ICP-OES where the total content remained almost unchanged throughout the experiment as shown in Figure 3.10 (d).

Figure 3.10: Silica fouling test with background salt ions (a) TMP and flux, (b) feed and permeate conductivity, (c) CP and R_f profile during one of the NaCl pulses; and (d) profile of total silica concentration of feed solution

Figure 3.10 continued: Silica fouling test with background salt ions (a) TMP and flux, (b) feed and permeate conductivity, (c) CP and R_f profile during one of the NaCl pulses; and (d) profile of total silica concentration of feed solution

3.4.2.1.3. Reproducibility tests

Three test runs were conducted at the same test conditions in order to validate the CP measurements and to check the reproducibility of the fouling tests. From Figure 3.11 (a), it was observed that all tests showed an equal increase in the TMP when the membrane was fouled with the same amount of colloidal silica under similar hydrodynamic conditions. The corresponding CP and R_f values, presented in Figure 3.11 (b) and (c), respectively, as determined from the tracer response technique also showed an identical profile, whereby both sets of data could be linearly fitted with an R^2 of 0.95 and 0.94, respectively. The results demonstrated that the experimental protocol was highly reproducible.

3.4.2.1.4. Cleaning tests

To further confirm the CEOP effect, two cleaning tests were conducted following the silica fouling at fluxes of 25 and 30 L/m²h and $v = 0.10$ m/s. As shown in Figure 3.12 (a), marked with region II, the pulse results indicated that the silica layer was not removed by the sodium chloride solution i.e. the resistance remained unchanged although there was a slight drop in the CP level. However, cleaning with Milli-Q water (as indicated by region III) at both flux levels of 25 and

Figure 3.11: Reproducibility check. (a) TMP profile, (b) CP profile, and (c) R_f profile of 3 silica fouling runs at similar test conditions of $J_v = 30$ L/m^2h and $v = 0.10$ m/s

Figure 3.12: (a) TMP profile, (b) CP profile, (c) R_f profile during different stages in silica fouling and cleaning tests; (I) silica fouling, (II) NaCl cleaning, (III) Milli-Q water cleaning

30 L/m²h successfully removed the deposit and restored the membrane resistance to the original value of $\sim 1 \times 10^{14} \text{ m}^{-1}$. These results were in good agreement with the previous work (Zhu and Elimelech, 1997), which suggested that silica colloids did not bind irreversibly to the membrane surface. The outcome also supported the earlier work (Section 3.4.2.1.1.) on silica fouling without the background salt ions whereby there was a dramatic increase in TMP during the tracer test, while the TMP returned to the original value when the pulse was terminated. Moreover, the tracer test also showed that the CP level returned to the initial value (Figure 3.12 (b)) confirming that the dramatic increase in CP level was solely caused by the presence of the unstirred deposit layer on the membrane surface.

3.4.2.1.5. Effect of flux on CEOP

The effect of flux on the TMP, CP, and R_f development in the silica fouling test at $v = 0.10 \text{ m/s}$ was investigated and presented in Figure 3.13 (a), (b), and (c), respectively. The rate of change of CP, $\partial \text{CP} / \partial t$, and the rate of change of R_f , $\partial R_f / \partial t$, at different flux levels were calculated from the slope of CP and R_f plots and summarised in Figure 3.13 (d). At low flux levels of 10 and 15 L/m²h, there were no silica fouling detected; i.e. no increase in CP or R_f value.

Figure 3.13: Effect of flux on silica fouling (a) TMP profile, (b) CP profile, (c) R_f profile, and (d) $\partial \text{CP} / \partial t$ and $\partial R_f / \partial t$ vs. J_v at $v = 0.10 \text{ m/s}$

Figure 3.13 continued: Effect of flux on silica fouling (a) TMP profile, (b) CP profile, (c) R_f profile, and (d) $\partial CP/\partial t$ and $\partial R_f/\partial t$ vs. J_v at $v = 0.10 \text{ m/s}$

However, silica fouling exhibited a drastic increase in CP level, at a rate of 0.4 h^{-1} as shown in Figure 3.13 (d), even in the presence of a small amount of deposit layer on the membrane surface at a flux of $30 \text{ L/m}^2\text{h}$. These results are in good agreement with previous work where a silica cake deposit with a thickness of about $20 \mu\text{m}$ was sufficient to increase the osmotic pressure by a factor of 2 (Hoek and Elimelech, 2003). The results for silica-fouled membranes using the sodium chloride tracer response technique confirmed the importance of the ‘cake enhanced osmotic pressure’ (CEOP) effect proposed by Hoek and Elimelech (Hoek and Elimelech, 2003; Hoek *et al.*, 2002). The results also showed that the CEOP effect was strongly influenced by flux. At low flux, the CEOP was barely evident, presumably because the ‘cake’ deposition was negligible. Once fluxes were moderate to high, the CP showed a steady increase, and this signified an increasing CEOP effect. The contribution of CEOP to apparent loss of permeability could be much greater than the hydraulic fouling resistance, R_f . For example, based on data in Figure 3.13 (d), at a flux of $25 \text{ L/m}^2\text{h}$ at $t = 60 \text{ min}$, the hydraulic resistance was slightly dominant, at 54% as compared to the contribution of CEOP at 46 % to the overall TMP increase. However, at a higher operating flux of $30 \text{ L/m}^2\text{h}$ at $t = 60 \text{ min}$, CEOP contributed 68 % to apparent loss and R_f contributed only 32 %.

3.4.2.1.6. Effect of crossflow velocity on CEOP

Figure 3.14: Effect of crossflow velocity on silica fouling (a) TMP, (b) CP, (c) R_f profile, and (d) $\partial\text{CP}/\partial t$ and $\partial R_f/\partial t$ vs. v at $J_v = 30 \text{ L/m}^2\text{h}$

Figure 3.14 continued: Effect of crossflow velocity on silica fouling (a) TMP profile, (b) CP profile, (c) R_f profile, and (d) $\partial CP/\partial t$ and $\partial R_f/\partial t$ vs. v at $J_v = 30 L/m^2h$

The effect of crossflow velocity on the CEOP effect was extensively studied. Generally, improving the hydrodynamic conditions of a RO system could lower the CP level. Based on Eq. (3.2), CP is inversely proportional to the exponential of k_m while the mass transfer is a function of crossflow velocity. Apart from that, colloidal fouling could be reduced with higher imposed crossflow velocity due to higher shear rate at the membrane wall (Hoek *et al.*, 2002). A reduction in the total amount of deposit would diminish the CEOP effect. This is supported by the data shown in Figure 3.14.

Figure 3.15: (a) $\partial CP/\partial t$ and (b) $\partial R_f/\partial t$ vs. J_v at various crossflow velocities

At a fixed operating flux of 30 L/m²h, when the crossflow velocity was increased from 0.06 to 0.15 m/s, the cake layer hydraulic resistance build up rate

was reduced approximately by 10 times, from 0.06 to $0.006 \times 10^{14} \text{ m}^{-1}\text{h}^{-1}$. This was accompanied by a drop in the rate of change of CP, $\partial\text{CP}/\partial t$, from 0.53 to 0.024 h^{-1} .

In addition, the advantage of increasing the crossflow could minimize the occurrence of a drastic increase in the CEOP effect at higher imposed flux. As shown in Figure 3.15 (a), $\partial\text{CP}/\partial t$ at high crossflow velocity increased almost linearly against the imposed flux instead of an exponential increase when operating at low crossflow and high flux. This was due to only a very thin layer of cake was formed on the membrane at high crossflow even at a high operating flux. For example, at $J_v = 45 \text{ L/m}^2$ and $v = 0.40 \text{ m/s}$, R_f increased at a very low rate of $0.0036 \times 10^{14} \text{ m}^{-1}\text{h}^{-1}$ as shown in Figure 3.15 (b).

3.4.2.2. Alginate fouling

3.4.2.2.1. Alginate fouling without background sodium chloride solution

Alginate fouling tests were also initially conducted without sodium chloride in the background solution. An example of the TMP, feed conductivity, and permeate conductivity profiles during one of the sodium chloride pulses is shown in Figures 3.16 (a), (b), and (c), respectively. The CP values determined based on the TMP and conductivity profiles over a period of steady alginate fouling are shown in Figure 3.16 (d). Only a slight change in the CP value was observed for a relatively low flux of $15 \text{ L/m}^2\text{h}$ whereas the polarization effect at a higher flux of $25 \text{ L/m}^2\text{h}$ was greatly enhanced by the presence of the alginate layer on the membrane surface. Interestingly, instead of quickly reaching a steady value as shown in the data at a flux of $15 \text{ L/m}^2\text{h}$, the CP values continued to rise during the pulse. A possible reason for this transient response was interaction between the Na^+ ions and the alginate layer on the membrane surface. Two models had been suggested: (i) mannuronate and isolated guluronate may complex with Na^+ ; (ii) Na^+ induced association between polyguluronate chain sequences occurs, which can be described in terms of an “egg-box” model with regular packing and coordination of the cations in the interstices of associated and, extended segments of the polymer chains (Zhang *et al.*, 1998a). According to these models, the Na^+ ions would be slowly accumulated and “entrapped” in the vicinity of the alginate layer and therefore cause a steady increase in osmotic pressure.

(a)

(b)

(c)

Figure 3.16: (a) TMP, (b) feed conductivity, (c) permeate conductivity, and (d) CP profile during one of the tracer tests in alginate fouling without background salt ions at alginic acid concentration of 100 ppm TOC

Figure 3.16 continued: (a) TMP, (b) feed conductivity, (c) permeate conductivity, and (d) CP profile during one of the tracer tests in alginate fouling without background salt ions at alginic acid concentration of 100 ppm TOC

3.4.2.2.2. Alginate fouling with background sodium chloride solution

The experiment was repeated with 2000 ppm of NaCl in the background solution. An example of the TMP, feed and permeate conductivity profiles during one of the sodium chloride pulses for alginate fouling is shown in Figures 3.17 (a) and (b), respectively. Before the pulse, the TMP was 10.3 bar at a flux of 20 L/m²h. When sodium chloride was pulsed into the system, the conductivity of the feed increased from 4310 to 7800 $\mu\text{S}/\text{cm}$. Due to the increase in osmotic pressure, in order to maintain constant flux operation, a higher TMP was required; therefore the transmembrane pressure was increased to 13.1 bar. Meanwhile, the conductivity of the permeate increased due to higher salt passage. The CP values estimated from the TMP and conductivity profiles using Eq. (3.4) over a period of steady alginate fouling are shown in Figure 3.17 (c). It should be noted that the CP values quickly reached a steady reading during the pulse, and did not continue to rise as in the test without sodium chloride in the background. After estimating the CP values, the fouling resistances of the alginate layer, R_f , were obtained from Eq. (3.3) and are shown in Figure 3.17 (c).

Figure 3.17: (a) TMP and flux, (b) feed and permeate conductivity, and (c) CP and R_f profile during one of the NaCl pulses in alginate fouling with background salt ions and alginic acid conc. of 6 ppm TOC and $J_v = 20 L/m^2 h$

Experiments at different flux levels were conducted to investigate the effect of fouling on concentration polarization. The TMP profiles are presented in Figure 3.18 (a). The average CP and R_f values determined from the TMP and conductivity data due to alginate fouling at different flux levels are shown in Figure 3.18 (b) and (c), respectively. The CP values increased with time at all flux levels, except at a flux of 10 L/m²h, where the CP values remained constant throughout the test since insignificant fouling was occurring, i.e. no change in R_f . It appeared that alginate fouling and silica fouling behaved in a similar pattern, i.e. the change in CP was more pronounced at high flux levels as shown in the plot of $\partial CP/\partial t$ vs. J_v (Figure 3.18 (d)).

Figure 3.18: Effect of flux on alginate fouling (a) TMP profile, (b) CP profile, (c) R_f profile, and (d) $\partial CP/\partial t$ and $\partial R_f/\partial t$ vs. J_v

Figure 3.18 continued: Effect of flux on alginate fouling (a) TMP profile, (b) CP profile, (c) R_f profile, and (d) $\partial CP/\partial t$ and $\partial R_f/\partial t$ vs. J_v

When comparing the change in R_f as plotted in Figure 3.18 (c), the R_f values also increased linearly with time at all flux levels, except at the flux of 10 L/m²h. However, unlike the change in CP, there was negligible change in R_f when the flux was increased from 25 to 30 L/m²h. The results suggested that for the ‘model’ bio-foulant, alginate, operation at high flux could significantly reduce apparent permeability, but that this was through a dramatic increase in CP and consequent loss in driving force rather than through an additional hydraulic resistance.

3.4.2.3. Discussion

It should be noted that the sodium chloride tracer response technique could also be applied at constant TMP. In this case the pulse would also cause a rise in $\Delta\Pi_{bs}$, but this would result in a drop in flux from J_{v1} to J_{v2} , as well as a change in CP from CP_1 to CP_2 due to the change in flux, which can be written as Eq. (3.10) and Eq. (3.11) for before and during sodium chloride pulse, respectively,

$$J_{v1} = \frac{(TMP - CP_1 \cdot \Delta\Pi_b)}{\mu(R_m + R_f)} \quad \text{Eq. (3.10)}$$

$$J_{v2} = \frac{(TMP - CP_2 \cdot \Delta\Pi_{bs})}{\mu(R_m + R_f)} \quad \text{Eq. (3.11)}$$

Combining the above two equations yields

$$J_{v1}CP_2\Delta\Pi_{bs} - J_{v2}CP_1\Delta\Pi_b = TMP(J_{v1} - J_{v2}) \quad \text{Eq. (3.12)}$$

or

$$J_{v1} \exp(J_{v2}/k_{eff}) \Delta\Pi_{bs} - J_{v2} \exp(J_{v1}/k_{eff}) \Delta\Pi_b = TMP(J_{v1} - J_{v2}) \quad \text{Eq. (3.13)}$$

which can be solved for k_{eff} and subsequently CP can be calculated if the transmembrane pressure, fluxes and conductivities are known.

Silica fouling tests at various crossflow velocities were conducted in constant pressure mode and the results are summarized in Figure 3.19. At high initial operating flux and low crossflow velocity of 0.10 m/s, the colloidal silica initially deposited rapidly on the membrane, but slowed down and reached a steady value. This was supported by the flux decline data where there was a drastic drop in the flux during the first 1000 mins of run. At the same time, both CP and R_f also increased. However, at higher crossflow velocity of 0.46 m/s, the cake slowly built up on the membrane surface as indicated by a slow increase in R_f . Hence, the decline in flux was not so steep as compared to the previous case. The CP increased initially, but then remained constant throughout the fouling process. This was probably due to the balance between a drop in both flux and mass transfer (due to hindered back diffusion).

Figure 3.19: (a) J_v profile, (b) CP profile, and (c) R_f profile of silica fouling tests at different crossflow velocities (in m/s) in constant pressure filtration mode

Thus, in the constant pressure mode the flux declines and the rate of fouling also declines eventually reaching a 'steady state' where $\partial CP/\partial t \rightarrow 0$ and $\partial R_f/\partial t \rightarrow 0$. This can be compared with constant flux operation where the net rate of foulant deposit remains constant, so that $\partial R_f/\partial t$ is effectively constant and $\partial CP/\partial t$ should be a slowly increasing function as CEOP become more dominant. In practice constant flux operation is the target, at least until the limit of the pump is reached.

3.5. Concluding remarks

The cake enhanced osmotic pressure effect was investigated using two model foulants, colloidal silica and alginic acid, by a simple sodium chloride tracer response technique. These results confirmed that typical fouling layers in RO, whether it was a solid cake layer or a gel like layer, could significantly reduce apparent permeability, but that this was predominantly through a dramatic increase in concentration polarization and consequent loss in driving force through the enhanced osmotic pressure rather than through an additional hydraulic resistance. The CEOP effect was more pronounced at higher flux operation. It is suggested that the sodium chloride tracer response technique could be used as a diagnostic tool for assessment of fouling development as it gives a clearer picture of the incipient nature of fouling. The TMP transients, following salt pulse, give details of the osmotic effect of fouling which could be significantly more important. Also the method could be modified to apply to a multistage system to detect fouling in a particular stage of the system, which is not readily done with conventional data.

CHAPTER 4

Critical Flux of Colloids in Reverse Osmosis

This chapter describes the determination of critical flux of colloids in reverse osmosis using the sodium chloride tracer response technique. The tracer technique gave the transient values of concentration polarization (CP) and cake resistance (R_f) as presented in Chapter 3. From these values, the rate of accumulation of deposit, $\partial m_f / \partial t$, could be readily determined. The critical flux was defined as based on the rate of deposition of colloidal silica on the membrane, where below critical flux no deposition or zero deposition rate, $\partial m_f / \partial t = 0$, was observed. It was found that the critical flux concept was applicable to colloidal silica fouling in reverse osmosis (RO) process. The critical flux was strongly influenced by the crossflow velocity, such that $J_{crit} \sim v^{0.4}$. In addition, the critical Peclet number, $(J_v/k_m)_{crit}$, which is a measure of the convective to diffusive force, to trigger silica fouling was approximately 0.52.

4.1. Introduction

Reverse osmosis (RO) is widely used to convert seawater or 'used' wastewater to potable quality water. However, the major drawback that limits the application of RO is the decrease in permeate flux due to membrane fouling. One of the tactics to overcome the decline in flux is to operate the membrane process below critical flux. The concept of critical flux was introduced by Field and co-workers (Field *et al.*, 1995), who stated, "The critical flux hypothesis for microfiltration (MF) is that on start-up there exists a flux below which a decline of flux with time does not occur; above it fouling is observed. This flux is the critical flux and its value depends on the hydrodynamics and probably other variables." Therefore it is desirable to operate the membrane system below critical flux for the sustainability of the process. Large amounts of work have been carried out by various researchers to determine the critical flux for micro/ultra-filtration (MF/UF) operations. Critical flux was found to be influenced by hydrodynamic conditions, particle size, ionic strength, zeta potential, membrane morphology and membrane pore size (Huisman *et al.*, 1999; Kim and Park, 2002; Kwon *et al.*, 2000; Neal *et al.*, 2003). However,

application of the critical flux concept in the RO process has been limited. Only one recent work was carried out in an attempt to investigate the critical flux of silica scaling/fouling in an RO system under constant pressure filtration mode (Lisitsin *et al.*, 2005). A series of tests were performed with different initial operating flux, but keeping the ratio of J_v/k_m constant, or in other words the concentration polarization (CP) modulus was constant, by varying the crossflow velocity. As such, all tests were started with a fixed supersaturation level of 2.1 – 2.2 at the membrane surface. From the critical flux concept, it was expected that the production rate remained unchanged when operating below the critical flux, which indicated no fouling. In their study, it was found that the rate of flux drop (or rate of fouling) was constant regardless of the initial operating flux. The authors then concluded that there was no evidence of critical flux. However, the “critical concentration” which relates to the solubility limit (Howell, 2004) of the silica was more appropriate to describe such a system. The imposed flux was simply controlling the CP level, which caused the silica concentration at the membrane surface to exceed the critical concentration or solubility limit and subsequently triggered the silica fouling. So, for the above case, the critical flux referred to the flux that gave a wall concentration below the supersaturation level.

There are 3 common methods to determine the critical flux: (i) flux – transmembrane pressure (TMP) measurement via flux stepping (Chen *et al.*, 1997); (ii) particle mass balances (Kwon *et al.*, 2000); and (iii) direct observation through the membrane (DOTM) (Li *et al.*, 1998). In the flux stepping method, flux is stepped up while monitoring the changes in TMP; each step usually lasts for 15 to 30 minutes interval. Such a short time interval is not sufficient to demonstrate a noticeable increase in the TMP reading (~ few kPa) relative to the operational pressure in RO processes (normally > 1 MPa) as compared to MF or UF filtration (normally ~ 100 kPa). The mass balance approach could not be applied here as shown in the results presented in an earlier chapter where only a small amount of colloidal silica was deposited on the membrane. The relative changes in the bulk concentration were below the detection limit. Finally, the DOTM technique is limited by the need to use a transparent membrane. In this chapter, a novel sodium chloride tracer response technique was applied to elucidate the critical flux of

colloids in the RO process. A detailed description of the tracer technique was given in Chapter 3; where it was used to characterize the cake enhanced osmotic pressure (CEOP) effect, a phenomenon that arises due to the hindered back diffusion of solutes in the unstirred fouling layer on the RO membrane surface (Hoek and Elimelech, 2003).

4.2. Theory

In the tracer response test, a pulse of sodium chloride is injected into the RO system operated at constant flux mode, thus to overcome the increase in osmotic pressure, the TMP of the system has to be increased to maintain the flux. The method allows the calculations of concentration polarization, CP, and cake resistance, R_f , from the TMP transients and concentrations profiles as presented in Chapter 3. The mass of the deposit, m_f , can be deduced from R_f , since

$$R_f = \alpha_f m_f \quad \text{Eq. (4.1)}$$

where α_f is the specific cake resistance. α_f is a function of ionic strength of the solution (Singh and Song, 2006), which means it is strongly dependent on the salt concentration at the membrane wall, C_w . This is important, as the CEOP effect will further enhance the specific cake resistance. The transient C_w value can be readily calculated from the CP value, where

$$CP = \frac{C_w - C_p}{C_b - C_p} \quad \text{Eq. (4.2)}$$

or rearranging

$$C_w = CP(C_b - C_p) + C_p \quad \text{Eq. (4.3)}$$

The critical flux can be determined from the relationship that accounts for the rate of fouling (Schwinge *et al.*, 2002a):

$$\frac{\partial m_f}{\partial t} = C_{b, \text{SiO}_2} (J_v - J_{\text{crit}}) \quad \text{Eq. (4.4)}$$

where J_v and J_{crit} are the operating and critical fluxes, respectively; and C_{b, SiO_2} is the concentration of silica particles in the bulk solution. J_{crit} can be estimated by extrapolating the plot of $\partial m_f / \partial t$ vs. J_v to where the accumulation rate of deposit is zero or $\partial m_f / \partial t = 0$.

Firstly, it was necessary to determine the relationship between specific cake resistance, α_f , of the silica deposit and the ionic strength effect. The simplest way was to carry out ultra-filtration of silica suspension with a known concentration in an unstirred dead end mode at constant pressure. α_f can be determined from the filtration data according to the complete cake filtration model (Chudacek and Fane, 1984):

$$\frac{1}{J_v^2} = \left(\frac{R_m \mu}{\text{TMP}} \right)^2 + \left(\frac{2\mu C_{b, \text{SiO}_2} \alpha_f}{\text{TMP}} \right) t \quad \text{Eq. (4.5)}$$

where R_m is the intrinsic membrane resistance, and μ is the viscosity of permeate solution. Thus a plot of $1/J_v^2$ vs. t will give α_f from the slope.

4.3. Materials and methods

4.3.1. Experimental set up for specific cake resistance measurements

Measurement of specific cake resistance of silica deposit was performed in a dead end filtration test unit as shown in Figure 4.1. The filtration dead end cell (AR Engineering, custom made) has a working volume of about 200 mL and an active membrane area of 0.00126 m². The intrinsic membrane resistance, R_m , was determined from the filtration with Milli-Q water. Milli-Q water was delivered from a 2 L water reservoir (AR Engineering, custom made) to the dead end cell with compressed air from a gas cylinder. In the measurement of specific cake resistance of silica deposit, α_f , 50 mL of silica test solution was directly put in the dead end cell for filtration. The required trans-membrane pressure for the filtration was set by regulating the compressed air. The pressure of the system was monitored with a pressure transmitter (Cole Parmer, model 68074-08) located on the dead end cell. Permeate was collected and measured with a weighing balance (Mettler Toledo, model PB3002-L). TMP and weight data were recorded with a data acquisition system (National Instrument, model PCI 6014 and LabView).

A polyether-sulfone ultra-filtration membrane with a nominal molecular weight of 50 kDa (Millipore, model PBQK) was used in the experiment to ensure complete retention of the silica particles but not the sodium chloride solution. The membrane was wetted and soaked in Milli-Q water for 24 hours before use. Colloidal silica

and sodium chloride salts used in the experiment were similar to those described in Chapter 3.

Figure 4.1: Schematic diagram of dead end filtration test unit

4.3.2. Experimental procedure for specific cake resistance measurements

The experiment was commenced with filtering Milli-Q water for 1 hour to determine the clean membrane resistance, R_m . Then particle-free salt solution at an ionic strength similar to the silica test solution was used to equilibrate the system for 1 hour. This would minimize the change in membrane surface properties when the test solution was introduced. After the equilibration step, 50 mL of the test solution with 200 ppm of silica at the desired ionic strength (varied from 0 to 10,000 ppm NaCl), was directly introduced into the dead end cell. Filtration was started by applying the required transmembrane pressure (TMP of 100 kPa was used in all experiments) and permeate was collected and measured. Upon the completion of the experiment, i.e. after 50 mL of the permeate solution was collected, the collected permeate was analyzed for the total silica content and conductivity to check for the retention properties.

4.3.3. Experimental set up and procedure for critical flux measurements

The experimental set up and procedure for determining the critical flux of silica fouling was similar to the set up as described in Chapter 3.

4.4. Results and discussion

4.4.1. Specific cake resistance of silica deposit

The retention data showed that the UF membrane fully rejected the silica particles, as no silica was detected in the permeate solution. No retention of sodium chloride by the UF membrane was observed as the conductivity of permeate remained unchanged as compared to the feed solution. So the silica deposit layer was formed at the ionic strength equal to the bulk concentration without the presence of a salt polarized layer effect as those encountered in the RO process.

$$(i) \quad y = 0.0013x + 0.063; R^2 = 0.998$$

$$(ii) \quad y = 0.0037x + 0.088; R^2 = 0.993$$

$$(iii) \quad y = 0.0048x + 0.040; R^2 = 0.987$$

$$(iv) \quad y = 0.0061x + 0.048; R^2 = 0.991$$

$$(v) \quad y = 0.0063x + 0.095; R^2 = 0.983$$

Figure 4.2: Constant pressure dead end filtration of 200 ppm silica solution at various NaCl concentrations (a) flux decline data, and (b) plot of $1/J_v^2$ vs. t

Also, the complete retention of silica particles by the UF membrane allowed the use of Eq. (4.5) to estimate the specific cake resistance. The data from dead end filtration tests is plotted in Figure 4.2 (a). It was shown that at zero salt concentrations, the flux decline rate was the slowest and quickly approached zero when all the filtrate was collected, signaling that the hydraulic resistance of the deposit was low. Whereas as the sodium chloride concentration was increased, the flux dropped rapidly at the initial stage and it took longer to filter all the silica test solution. In order to calculate the specific cake resistance, α_f , based on Eq. (4.5), $1/J_v^2$ was plotted against t as shown in Figure 4.2 (b).

Figure 4.3: Specific cake resistance and porosity of silica deposit as a function of NaCl concentrations

The calculated α_f value as a function of sodium chloride concentrations is summarized in Figure 4.3 and the correlation obtained from the plot is:

$$\alpha_f = 0.0713 \times 10^{15} (C_{\text{NaCl}})^{0.338} \quad \text{Eq. (4.6)}$$

From the α_f data, the cake porosity, ϵ , can be estimated using the Carmen-Kozeny equation (Carman, 1937):

$$\alpha_f = \frac{180(1-\epsilon)}{\rho_p d_p^2 \epsilon^3} \quad \text{Eq. (4.7)}$$

where ρ_p and d_p is silica density and particle size, respectively. As seen from Figure 4.3, the porosity of cake decreased as the ionic strength was increased, ranging from 0.6 to 0.4 at zero to 10,000 ppm NaCl, respectively. This agrees well with previous reported values typically in the range of 0.3 to 0.7 (Faibish *et al.*, 1998; Yiantsios and Karabelas, 1998). The decrease in the porosity was due to the

suppression of the electrostatic double layer repulsion under high ionic strength causing the formation of a more compact deposit (McDonogh *et al.*, 1984).

4.4.2. Critical flux in silica fouling

The transient values of CP and R_f due to silica fouling could be determined from the sodium chloride tracer response technique as reported in the previous chapter. From these CP values (refer to Figure 3.13 (b) in Chapter 3), an example of the estimated build up of solute concentration at the wall, C_w , calculated based on Eq. (4.3), is shown in Figure 4.4 (a).

Figure 4.4: Estimation of (a) C_w and α_f , and (b) m_f and ε , from the CP and R_f data. Test conditions: 200 pm silica and 2000 ppm NaCl, $J_v = 30$ L/m²h and $v = 0.10$ m/s

The estimated specific cake resistance, using Eq. (4.6), under the influence of increasing ionic strength is also plotted in Figure 4.4 (a). Knowing the values of α_f and R_f (from Figure 3.13 (c) in Chapter 3), the accumulation of silica deposit over time could be readily determined using Eq. (4.1) and is presented in Figure 4.4 (b). As can be seen, when the cake mass built up, the estimated porosity of cake decreased over time due to the elevated salt concentration at the membrane wall provoked by the CEOP effect.

The rate of accumulation of silica deposit at various flux levels and crossflow velocities is plotted in Figure 4.5. According to the definition of critical flux, its flux value corresponds to the highest flux for zero accumulation; thus the x-intercept of the $\partial m_f / \partial t$ vs. J_v plot gives the value of critical flux. As shown, under the same crossflow velocity, silica deposition on the membrane was driven by the net difference in operating flux and critical flux, $(J_v - J_{crit})$; i.e. $\partial m_f / \partial t$ increased with increasing J_v when the system was operated above the critical flux. The critical flux values found in this work for silica colloids ($d_p = 20$ nm) ranged from 15 to 30 L/m²h depending on the hydrodynamic conditions. These values coincide with the operational fluxes normally encountered in the RO process, which suggested that most of the RO plants have a high tendency of fouling.

(i) $y = 0.253x - 0.0040$; $R^2 = 0.944$

(iv) $y = 0.0166x - 0.00047$; $R^2 = 0.942$

(ii) $y = 0.269x - 0.0053$; $R^2 = 0.999$

(v) $y = 0.0195x - 0.00060$; $R^2 = 0.957$

(iii) $y = 0.145x - 0.00037$; $R^2 = 0.989$

Figure 4.5: $\partial m_f / \partial t$ vs. J_v for the determination of critical flux at $\partial m_f / \partial t = 0$

Figure 4.6 (a) shows the critical flux of silica colloidal particles as a function of crossflow velocity. The trend of critical flux versus the crossflow velocities agrees well with previously reported studies (Kim and Park, 2002; Li *et al.*, 1998; 2000), where critical flux increased with increasing crossflow velocity. However, the correlation found here, $J_{\text{crit}} \sim v^{0.4}$, was different from previous results where a linear correlation was observed. This is not uncommon, as in another report by Li and co-worker (Li *et al.*, 2003a), the critical flux for sub-micron bacteria *Pseudomonas* SW8 was proportional to $v^{0.656}$. Such an issue was pointed out in a review paper on the critical flux concept (Bacchin *et al.*, 2006) where no common exponent for the power law could be deduced from the large amount of work dealing with the effect of crossflow velocity on critical flux.

Figure 4.6: (a) Critical flux as a function of crossflow velocity, and (b) Critical Peclet number for silica fouling

As suggested (Bacchin *et al.*, 2006; Howell, 2004), a critical ratio linking the permeate flux and the mass transfer coefficient or boundary layer thickness, known as the Peclet number, would be a better term to describe the hydrodynamic effect on critical flux. This could be written as (Bacchin, 2004; Bacchin and Aimar, 2005; Bacchin *et al.*, 1995):

$$(Pe)_{crit} = \left(\frac{J_v \delta}{D} \right)_{crit} = \left(\frac{J_v}{k_m} \right)_{crit} \quad \text{Eq. (4.8)}$$

As shown in Figure 4.6 (b), the critical Peclet number for colloidal silica fouling in our RO test cell was 0.52. A linear relationship between J_{crit} and mass transfer coefficient confirmed that the colloidal fouling of silica particles was controlled by the forces acting on the particles; in this case the balance between the convective drag force due to permeation flux and the back-transport due to Brownian diffusion.

4.4.3. Discussion

It should be noted that, according to Eq. (4.4), under the same particle loading, C_{b, SiO_2} , and net flux, $(J_v - J_{crit})$, one would expect to obtain equal accumulation of deposits, $\partial m_f / \partial t$, regardless of the crossflow velocity. However, it is clearly evident in Figure 4.5, at the same net flux $(J_v - J_{crit})$, at high velocities of 0.23 and 0.40 m/s, the accumulation rates were only about 10% of those at the lower velocities of 0.06 and 0.10 m/s. It seems that not all, but only a fraction of the particles convected to the membrane surface were successfully deposited even above critical flux; as such Eq. (4.4) should be rewritten as:

$$\frac{\partial m_f}{\partial t} = \Phi C_{b, SiO_2} (J_v - J_{crit}) \quad \text{Eq. (4.9)}$$

where Φ is the fractional deposition constant, which can vary between $0 \ll \Phi \leq 1$. When Φ is greater than zero above critical flux, there will definitely be accumulation of mass; and a value of 1 means all particles are depositing. The values of Φ found in this study varied between ~ 0.1 at high crossflow velocity to ~ 1 at low crossflow velocity as shown in Figure 4.7.

Figure 4.7: Fractional deposition of particles as a function of crossflow velocity

Such observations could be attributed to the particle-rolling phenomenon due to viscous shear flow (Knutsen and Davis, 2006). There are a few forms of motions of a particle along the rough surface of a membrane due to the crossflow, after it has been convected to the membrane surface; as following (Knutsen and Davis, 2006):

- 1) “the particle rolls over the membrane at steady velocity, eventually stopping and depositing when it encounters a large asperity on the surface or another previously deposited particle;
- 2) particle decelerates steadily as it approaches the membrane and moves through slower moving streamlines just prior to come in contact with the membrane surface;
- 3) collisions with previously deposited particle may dislodge that particle and cause it to roll away.”

The events of particle rolling over the membrane surface in crossflow filtration have been visualized under the microscope (Kang *et al.*, 2004; Knutsen and Davis, 2006; Li *et al.*, 1998). Mathematical models have been developed to account for the particle-rolling phenomenon upon the subsequent build up of a deposit beyond the critical flux or the net deposition of particles (Knutsen and Davis, 2006). However, the validation of the models was performed with large particles (4.5 to 20 μm) using visual observation techniques. Its direct application to sub-micron size particles, such as the 20 nm colloidal silica particle used in this study, could not be confirmed. However, it is postulated that the particle-rolling phenomenon could

explain the observations in this study. Detailed investigation of this topic was beyond the scope of this thesis but is worthy of further study.

4.4.4. Critical flux in a spacer-filled channel

The critical flux of silica colloids in the presence of a spacer was investigated using a commercial diamond spacer and its characteristics are summarised in Table 4.1. Comparison was made against a slit channel with equivalent channel height.

Table 4.1: Characteristics of slit channel and diamond spacer-filled channel

	<i>Slit</i>	<i>Spacer</i>
Channel height, H (mm)	0.71	0.71
Spacer Height, h_{sp} (mm)	-	0.71
Mesh length, $l_{M, sp}$ (mm)	-	2.5
Filament diameter, $d_{F, sp}$ (mm)	-	0.40
Internal angle, θ_{sp} ($^{\circ}$)	-	90
Voidage, ε_{sp}	1.00	0.83
Hydraulic diameter, d_h (mm)	1.42	0.76

However, it should be noted that the method used to determine the critical flux as outlined in Section 4.4.2. was not suitable to be applied here. The deposit layer in a spacer-filled channel tends to be non-uniform, distributed according to the fluid flow patterns (Neal *et al.*, 2003), and therefore the specific cake resistance, α_f , was not likely to be consistent. To avoid such error, the TMP data was used instead, where J_{crit} was estimated by extrapolating the plot of $\partial \text{TMP} / \partial t$ vs. J_v to $\partial \text{TMP} / \partial t = 0$. It should be noted that the J_{crit} values estimated from the plot of $\partial \text{TMP} / \partial t$ vs. J_v were similar to the values estimated from the plot of $\partial m_f / \partial t$ vs. J_v for the slit channel. The advantage of using the $\partial m_f / \partial t$ method was that this method allowed the estimation of the amount of deposition whereas the $\partial \text{TMP} / \partial t$ method reflected the contributions of both the hydraulic resistance of the deposit and the CEOP effect, which in reality could not be distinguished based on the TMP data alone.

The estimated J_{crit} for the diamond spacer-filled channel was $\sim 33.4 \text{ L/m}^2\text{h}$ (from Figure 4.8). When compared to the value of $\sim 25.1 \text{ L/m}^2\text{h}$ in a slit channel at the same crossflow rate of $Q = 0.5 \text{ L/min}$, which was deduced from Figure 4.6 (a), there was an improvement of $\sim 30 \%$ in J_{crit} . It should be noted that the degree of improvement in the critical flux was a function of crossflow velocity (or represented by Reynolds number) and spacer orientations (Neal *et al.*, 2003). Such enhancement in J_{crit} ($\sim 30 \%$) was much lower than the value reported in previous work, where J_{crit} was approximately doubled (Neal *et al.*, 2003). The difference in the results was possibly due to the different sizes of particle, where $6.4 \mu\text{m}$ latex particles were used in the previous study. The transport mechanism for such large particles was mainly shear-induced diffusion and inertial lift whereas Brownian motion was dominant for the nano-sized silica particle. Also, the effect of electrostatic interactions was important in this study. Such factors might limit the enhancement in the critical flux in a spacer-filled channel.

Figure 4.8: Critical flux determination in spacer filled-channel via $\partial\text{TMP}/\partial T$ vs. J_v at $Q = 0.5 \text{ L/min}$

4.5. Concluding remarks

A sodium chloride tracer response technique has been developed to determine the critical flux of colloidal silica in a reverse osmosis process. Below the critical flux, no accumulation of silica particles was observed. It was found that the critical flux was proportional to the crossflow velocity, $J_{\text{crit}} \sim v^{0.4}$. Moreover, the critical

flux for colloidal deposition was best described in terms of a Peclet number, defined as the ratio of the convective drag force to the back diffusive force. It was also found that the proportion of particles convected to the membrane that deposited was a function of crossflow velocity; at low crossflow the proportion was 100 % but at high crossflow the proportion was only about 10%. In addition, it was observed that the use of a spacer could enhance the critical flux by about 30 % compared to a slit channel.

CHAPTER 5

Modeling of Colloidal Fouling in Reverse Osmosis: Implications of Critical Flux (J_{crit}) and Cake Enhanced Osmotic Pressure (CEOP)

This chapter describes a predictive model to account for the performance of a reverse osmosis (RO) system under the influence of colloidal fouling in terms of transmembrane pressure increase (ΔTMP) in constant flux operation or flux drop (ΔJ_v) in constant pressure operation. The predictive model considers the implications of both the critical flux (J_{crit}) and cake enhanced osmotic pressure (CEOP) phenomenon and is based on the membrane retention, concentration polarization, mass transfer, resistance in series and osmotic pressure model, cake resistance, and critical flux concept.

5.1. Introduction

Conventionally, fouling models of RO have not considered the simultaneous effects of critical flux (J_{crit}) and cake enhanced osmotic pressure (CEOP) and therefore suffered from a few disadvantages. Firstly, it is not able to identify the initiation and intensity of fouling. Operating a reverse osmosis (RO) system below the critical flux will prevent the deposition of colloidal particles on the membrane. On the other hand, if operated above the critical flux, the particles will start to deposit and form a cake layer. Hence, the accumulation of deposit on the membrane is controlled by the net flux, which is the difference between the operating flux, J_v , and the critical flux, J_{crit} , or $(J_v - J_{crit})$. Subsequently, the build up of this ‘unstirred’ deposit layer on the membrane surface will result in the CEOP phenomenon, through the hindered back diffusion of solutes (Hoek and Elimelech, 2003). In most of the previous studies, an increase in the TMP or decline in flux was attributed solely to the induced hydraulic resistance by the deposit layer. However, the CEOP effect suggests a loss in the available effective driving force, rather than an additional hydraulic resistance, R_f , as demonstrated in Chapter 3. Neglecting the CEOP effect over-estimates the contribution of the cake resistance,

or in other words it does not require a thick layer of cake to cause a significant increase in TMP or decline in flux. Therefore, a fouling model that incorporates both the critical flux and CEOP effects is essential to predict the long-term performance of an RO membrane.

The focus of this modeling work is on the membrane performance at constant flux and constant pressure operation. To date, most of the work reported in literature considers the fouling process under fixed pressure condition. However, both situations are important as in practice RO plants tend to be operated at fixed production rate, which requires fixed flux, so typically TMP is adjusted to compensate for fouling. If this leads to operating at the pump maximum, it may be necessary to then allow the flux to decline. Therefore it is essential to understand the fouling mechanism and the controlling parameters in both cases. The membrane performance loss can be evaluated in terms of transmembrane pressure increase (ΔTMP) for constant flux operation or flux decline (ΔJ_v) in fixed pressure operation. In the following analysis, a comparison of the relative contribution of CEOP and R_f on the performance loss is carried out. Colloidal silica particles are selected as the model compound in the simulation as the data can be readily obtained from the results presented in Chapter 3 and 4 as well as in the literature.

5.2. Model development

The simple predictive model for colloidal fouling in RO developed in this study combines the equations for membrane retention, concentration polarization, mass transfer, resistance in series and osmotic pressure, cake resistance, and critical flux. The system considered in the model is illustrated in Figure 5.1. The assumptions made in the model are:

- 1) Non-compressible cake e.g. specific cake resistance is independent of the pressure change. Colloidal silica cake was reported to be compressible (Singh and Song, 2006). However under the high pressure of the RO process, the effect of time-dependent cake compressibility can be ignored.
- 2) Physical properties (viscosity, density and particle size) of solution and cake remain constant.
- 3) Membrane properties (resistance and real retention) remain constant.

4) The cake layer does not reject the solutes.

The model is presented in the following section.

Figure 5.1: Illustration of concentration profile and boundary layer in RO membrane at steady state (a) before fouling or $t = 0$, and (b) after fouling or $t = t$

5.2.1. Membrane retention

Membrane real retention, R_{real} , is an intrinsic property of a membrane and is assumed to remain constant; unlike the observed retention which is affected by the degree of concentration polarization and fouling, so:

Before fouling:

$$R_{\text{real}} = \frac{C_w(0) - C_p(0)}{C_w(0)} \quad \text{Eq. (5.1)}$$

where C_w and C_p is the solute concentration at membrane wall and in permeate, respectively. After fouling:

$$R_{\text{real}} = \frac{C_w(t) - C_p(t)}{C_w(t)} \quad \text{Eq. (5.2)}$$

5.2.2. Concentration polarization

Concentration polarization, CP, is due to the accumulation of the rejected solutes at the membrane surface. The solutes diffuse back into the bulk solution

due to the gradient in the concentration. For a clean membrane system, the mass balance of solutes in the polarized layer is:

$$J_v(0)C - D \frac{\partial C}{\partial x} = J_v(0)C_p(0) \quad \text{Eq. (5.3)}$$

with the boundary conditions:

$$x = 0; \quad C = C_b$$

$$x = \delta_p(0); \quad C = C_w(0)$$

solving yields:

$$CP(0) = \exp\left(\frac{J_v(0)}{D/\delta_p(0)}\right) = \exp\left(\frac{J_v(0)}{k_m(0)}\right) = \frac{C_w(0) - C_p(0)}{C_b - C_p(0)} \quad \text{Eq. (5.4)}$$

where J_v is the flux, D is the diffusivity of solute, δ_p is the polarized layer thickness, k_m is boundary layer the mass transfer coefficient, and C_b is the bulk concentration. Meanwhile, for a fouled membrane, the concentration at the wall builds up due to the CEOP effect. The mass balance of solutes in the polarized layer is:

$$J_v(t)C - D \frac{\partial C}{\partial x} = J_v(t)C_p(t) \quad \text{Eq. (5.5)}$$

with boundary conditions:

$$x = 0; \quad C = C_b$$

$$x = \delta_p(t); \quad C = C_c(t)$$

solving yields:

$$\exp\left(\frac{J_v(t)}{D/\delta_p(t)}\right) = \exp\left(\frac{J_v(t)}{k_p(t)}\right) = \frac{C_c(t) - C_p(t)}{C_b - C_p(t)} \quad \text{Eq. (5.6)}$$

where C_c is the solute concentration at the solution/cake interface and k_p is the mass transfer in the polarized layer. The mass balance of solutes in the cake layer is:

$$J_v(t)C - D_c(t) \frac{\partial C}{\partial x} = J_v(t)C_p(t) \quad \text{Eq. (5.7)}$$

with boundary conditions:

$$x = \delta_p(t); \quad C = C_c(t)$$

$$x = \delta_p(t) + \delta_c(t); \quad C = C_w(t)$$

solving yields:

$$\exp\left(\frac{J_v(t)}{D_c(t)/\delta_c(t)}\right) = \exp\left(\frac{J_v(t)}{k_c(t)}\right) = \frac{C_w(t) - C_p(t)}{C_c(t) - C_p(t)} \quad \text{Eq. (5.8)}$$

where D_c is the effective solute diffusivity in the cake layer, k_c is the mass transfer in the cake layer, δ_c is the cake layer thickness. By combining Eq. (5.6) and (5.8):

$$\exp\left(\frac{J_v(t)}{k_p(t)}\right) \exp\left(\frac{J_v(t)}{k_c(t)}\right) = \left(\frac{C_c(t) - C_p(t)}{C_b - C_p(t)}\right) \left(\frac{C_w(t) - C_p(t)}{C_c(t) - C_p(t)}\right) \text{ or}$$

$$CP(t) = \exp\left(\frac{J_v(t)}{k_p(t)} + \frac{J_v(t)}{k_c(t)}\right) = \exp\left(\frac{J_v(t)}{k_m(t)}\right) = \frac{C_w(t) - C_p(t)}{C_b - C_p(t)} \quad \text{Eq. (5.9)}$$

$k_m(t)$ is the effective mass transfer coefficient in a fouled channel, equivalent to k_{eff} in Eq. (3.2b) in Chapter 3.

5.2.3. Mass transfer

For a clean membrane system with a thin rectangular channel, the mass transfer coefficient for laminar flow from the Graetz-Lvque correlation is (Hoek *et al.*, 2002):

$$k_m(0) = 1.62 \left(\frac{QD^2}{2W(H)^2 L} \right)^{1/3} = 1.62 \left(\frac{vD^2}{2HL} \right)^{1/3} \quad \text{Eq. (5.10)}$$

where Q is the crossflow rate, W is the channel width, H is the channel height, L is the channel length, and v is the crossflow velocity. Meanwhile for a fouled system, the effective mass transfer comprises two parts; the mass transfer in the un-fouled section and the mass transfer in the cake layer. For the un-fouled section:

$$k_p(t) = \frac{D}{\delta_p(t)} \quad \text{Eq. (5.11)}$$

Assuming $\delta_c(t)$ is small as compared to the channel height, e.g. $\delta_c(t) \ll H$. This is a reasonable assumption as shown in Chapter 3, only a minute amount of cake was formed even at high flux and low crossflow and hence the channel height was not noticeably altered by the cake deposit. Therefore:

$$k_p(t) \approx \frac{D}{\delta_p(0)} = k_m(0) \quad \text{Eq. (5.12)}$$

The mass transfer in a cake layer is:

$$k_c(t) = \frac{D_c(t)}{\delta_c(t)} \quad \text{Eq. (5.13)}$$

where $D_c(t)$ is the diffusion of solute in the cake layer through the porosity with a tortuous path, and can be estimated by (Boudreau, 1996):

$$D_c(t) = D \left(\frac{\varepsilon(t)}{1 - \ln \varepsilon(t)^2} \right) \quad \text{Eq. (5.14)}$$

where ε is the porosity of cake layer. So:

$$k_c(t) = \frac{D}{\delta_c(t)} \left(\frac{\varepsilon(t)}{1 - \ln \varepsilon(t)^2} \right) \quad \text{Eq. (5.15)}$$

Therefore, the overall mass transfer in a fouled channel is:

$$\frac{1}{k_m(t)} = \frac{1}{k_p(t)} + \frac{1}{k_c(t)} = \frac{1}{k_m(0)} + \frac{\delta_c(t)}{D} \left(\frac{1 - \ln \varepsilon(t)^2}{\varepsilon(t)} \right) \quad \text{Eq. (5.16)}$$

For constant flux filtration, multiplying Eq. (5.16) by J_v and taking exponential, yields:

$$\frac{CP(t)}{CP(0)} = \exp \left\{ \left(\frac{J_v}{k_m(t)} \right) - \left(\frac{J_v}{k_m(0)} \right) \right\} = \exp \left\{ \frac{J_v \delta_c(t)}{D} \left(\frac{1 - \ln \varepsilon(t)^2}{\varepsilon(t)} \right) \right\} \quad \text{Eq. (5.17)}$$

Eq. (5.17) shows that the CP level in a fouled membrane system is strongly affected by the operating flux, cake layer thickness and porosity as $CP(t)$ is an exponential function of these parameters.

5.2.4. Resistance in series and osmotic pressure filtration equation

5.2.4.1. Constant flux filtration

Before fouling, the flux can be calculated from the filtration model:

$$J_v = \frac{TMP(0) - CP(0)\Delta\Pi_b(0)}{\mu R_m} \quad \text{Eq. (5.18)}$$

where μ is the viscosity of the permeate, R_m is the intrinsic membrane resistance, and $\Delta\Pi_b$ is the osmotic pressure difference between the feed and permeate solutions. The osmotic pressure of sodium chloride can be estimated by combining Eq. (3.6) and Eq. (3.7) in Chapter 3, which yields:

$$\log(\Pi_{NaCl}) = 0.9937 \log(C_{NaCl}) - 3.0797 \quad \text{Eq. (5.19)}$$

where C_{NaCl} is concentration of NaCl in ppm. For a fouled membrane, where there is an increase in TMP, CP and build up of cake resistance, R_f , the filtration equation can be written as:

$$J_v = \frac{TMP(t) - CP(t)\Delta\Pi_b(t)}{\mu(R_m + R_f(t))} \quad \text{Eq. (5.20)}$$

Combining Eq. (5.18) and (5.20), yields:

$$\left\{ \frac{CP(t)\Delta\Pi_b(t) - CP(0)\Delta\Pi_b(0)}{TMP(t) - TMP(0)} \right\} + \left\{ \frac{J_v\mu R_f(t)}{TMP(t) - TMP(0)} \right\} = 1 \quad \text{Eq. (5.21)}$$

The first and second terms on the left indicate the relative contribution of CEOP and R_f on the overall increase in the trans-membrane pressure, respectively.

5.2.4.2. Constant pressure filtration

Before fouling, the TMP required for filtration is:

$$TMP = J_v(0)\mu R_m + CP(0)\Delta\Pi_b(0) \quad \text{Eq. (5.22)}$$

Fouling causes a drop in the flux, a build up in the cake resistance and a change in the CP, hence:

$$TMP = J_v(t)\mu(R_m + R_f(t)) + CP(t)\Delta\Pi_b(t) \quad \text{Eq. (5.23)}$$

Combining Eq. (5.22) and (5.23), yield:

$$\left\{ \frac{CP(t)\Delta\Pi_b(t) - CP(0)\Delta\Pi_b(0)}{(J_v(0) - J_v(t))\mu R_m} \right\} + \left\{ \frac{J_v(t)\mu R_f(t)}{(J_v(0) - J_v(t))\mu R_m} \right\} = 1 \quad \text{Eq. (5.24)}$$

The first and second terms on the left indicate the relative contribution of CEOP and R_f on the flux decline, respectively.

5.2.5. Cake resistance and thickness

The hydraulic resistance of the cake, R_f , can be estimated by:

$$R_f(t) = \alpha_f(t)m_f(t) \quad \text{Eq. (5.25)}$$

where α_f is the specific cake resistance and m_f is the mass of deposit per unit area. The specific cake resistance, $\alpha_f(t)$ can be estimated from the Carmen-Kozeny equation (Carman, 1937):

$$\alpha_f(t) = \frac{180(1 - \varepsilon(t))}{\rho_p d_p^2 \varepsilon(t)^3} \quad \text{Eq. (5.26)}$$

where ρ_p and d_p are the particle density and diameter, respectively. As seen from Eq. (5.26), α_f is $\propto 1/d_p^2$, so a 10-fold increase in the particle size (e.g. from 20 nm to 200 nm) will cause a 100-fold decrease in the specific cake resistance. Also, $\alpha_f(t)$ is a function of ionic strength of the solution and is given by (from experimental data in Chapter 4):

$$\alpha_f(t) = 0.07127 \times 10^{15} (C_{\text{NaCl}})^{0.3384} \quad \text{Eq. (5.27)}$$

The cake layer thickness can be estimated from the mass load:

$$\delta_c(t) = \frac{m_f(t)}{\rho_p (1 - \varepsilon(t))} \quad \text{Eq. (5.28)}$$

5.2.6. Critical flux

The accumulation of the deposit layer on the membrane is related to the critical flux, J_{crit} :

$$\begin{aligned} \frac{\partial m_f}{\partial t} &= \Phi C_{b, \text{SiO}_2} (J_v(t) - J_{\text{crit}}) \quad \text{or} \\ m_f(t) &= \Phi C_{b, \text{SiO}_2} (J_v(t) - J_{\text{crit}}) t \end{aligned} \quad \text{Eq. (5.29)}$$

where C_{b, SiO_2} is the bulk concentration of silica. For simplicity, all particles convected to the membrane surface due to permeation drag beyond the critical flux are assumed to fully deposit on the surface, and hence the fractional deposition constant, Φ , is assumed to be 1.0 in the above equation. However this assumption is only correct at lower crossflow velocities as discussed in Chapter 4. Experimental data in Chapter 4 show that J_{crit} is a function of the crossflow velocity and is given by:

$$J_{\text{crit}} = 46.2 v^{0.36} \quad (\text{for } d_p = 20 \text{ nm silica}) \quad \text{Eq. (5.30)}$$

In addition the critical flux is a function of the particle size, d_p , according to the particle transport mechanisms outlined in Chapter 2. Two types of particle back-transport mechanism are considered here, Brownian and shear-induced diffusion. The solute flux estimated based on the above mechanisms is quite different from each other, since the Brownian model predicts a decrease in flux with increasing particle size ($J_v \propto 1/d_p^{2/3}$) while the shear-induced model predicts an increase in flux

with increasing particle size ($J_v \propto d_p^{4/3}$). To include the particle size effect in the critical flux estimation, and using $d_p = 100$ nm as the reference point, for the transition from Brownian to shear-induced diffusion controlled (Harmant and Aimar, 1998), gives

$$\text{Brownian diffusion: } d_p \leq 100 \text{ nm, } \frac{J_{\text{crit}, d_{p2}}}{J_{\text{crit}, d_{p1}}} = \left(\frac{d_{p1}}{d_{p2}} \right)^{2/3} \quad \text{Eq. (5.31)}$$

$$\text{Shear-induced diffusion: } d_p > 100 \text{ nm, } \frac{J_{\text{crit}, d_{p2}}}{J_{\text{crit}, d_{p1}}} = \left(\frac{d_{p2}}{d_{p1}} \right)^{4/3} \quad \text{Eq. (5.32)}$$

The critical flux is plotted as a function of particle size and crossflow velocities in Figure 5.2. A summary of the model is presented in Table 5.1.

Figure 5.2: Critical flux as a function of d_p at different crossflow velocities (in m/s)

Table 5.1: Equations governing the critical flux and CEOP effects

	Before Fouling	After Fouling
Membrane Retention	$R_{\text{real}} = \frac{C_w(0) - C_p(0)}{C_w(0)}$ Eq. (5.1)	$R_{\text{real}} = \frac{C_w(t) - C_p(t)}{C_w(t)}$ Eq. (5.2)
Concentration Polarization	$CP(0) = \exp\left(\frac{J_v(0)}{k_m(0)}\right)$ $= \frac{C_w(0) - C_p(0)}{C_b - C_p(0)}$ Eq. (5.4)	$CP(t) = \exp\left(\frac{J_v(t)}{k_m(t)}\right)$ $= \frac{C_w(t) - C_p(t)}{C_b - C_p(t)}$ Eq. (5.9)
Mass Transfer	$k_m(0) = 1.62 \left(\frac{vD^2}{2HL} \right)^{1/3}$ Eq. (5.10)	$\frac{1}{k_m(t)} = \frac{1}{k_m(0)} + \frac{\delta_c(t)}{D} \left(\frac{1 - \ln \varepsilon(t)^2}{\varepsilon(t)} \right)$ Eq. (5.16)
Resistance in Series and Osmotic Pressure Filtration Model	Constant flux: $J_v = \frac{TMP(0) - CP(0)\Delta\Pi_b(0)}{\mu R_m}$ Eq. (5.18) $\log(\Pi_{\text{NaCl}}) = 0.993 \log(C_{\text{NaCl}}) - 3.079$ Eq. (5.19)	Constant flux: $J_v = \frac{TMP(t) - CP(t)\Delta\Pi_b(t)}{\mu(R_m + R_f(t))}$ Eq. (5.20) $\left\{ \frac{CP(t)\Delta\Pi_b(t) - CP(0)\Delta\Pi_b(0)}{TMP(t) - TMP(0)} \right\} + \left\{ \frac{J_v \mu R_f(t)}{TMP(t) - TMP(0)} \right\} = 1$ Eq. (5.21) Constant pressure: $TMP = J_v(0)\mu R_m + CP(0)\Delta\Pi_b(0)$ Eq. (5.22)
		Constant pressure: $TMP = J_v(t)\mu(R_m + R_f(t)) + CP(t)\Delta\Pi_b(t)$ Eq. (5.23) $\left\{ \frac{CP(t)\Delta\Pi_b(t) - CP(0)\Delta\Pi_b(0)}{(J_v(0) - J_v(t))\mu R_m} \right\} + \left\{ \frac{J_v \mu R_f(t)}{(J_v(0) - J_v(t))\mu R_m} \right\} = 1$ Eq. (5.24)

Table 5.1 Continued: Equations governing the critical flux and CEOP effects

<i>Before Fouling</i>	<i>After Fouling</i>	
Cake	$R_f(t) = \alpha_f(t)m_f(t)$	Eq. (5.25)
Resistance	$\alpha_f(t) = \frac{180(1-\varepsilon(t))}{\rho_p d_p^2 \varepsilon(t)^3}$	Eq. (5.26)
and Thickness	$\alpha_f(t) = 0.07127 \times 10^{15} (C_{NaCl})^{0.3384}$	Eq. (5.27)
	$\delta_c(t) = \frac{m_f(t)}{\rho_p (1-\varepsilon(t))}$	Eq. (5.28)
Critical Flux	$m_f(t) = \Phi C_{b, SiO_2} (J_v(t) - J_{crit})t$	Eq. (5.29)
	$J_{crit} = 46.2 v^{0.36}$	
	(for $d_p = 20$ nm silica)	Eq. (5.30)
	For Brownian diffusion:	
	$d_p \leq 100$ nm, $\frac{J_{crit, d_{p2}}}{J_{crit, d_{p1}}} = \left(\frac{d_{p1}}{d_{p2}}\right)^{\frac{2}{3}}$	Eq. (5.31)
	For shear-induced diffusion:	
	$d_p > 100$ nm, $\frac{J_{crit, d_{p2}}}{J_{crit, d_{p1}}} = \left(\frac{d_{p2}}{d_{p1}}\right)^{\frac{4}{3}}$	Eq. (5.32)

5.3. Methodology

It is relevant to compare the relative impact of the fouling resistance, R_f , and the CEOP effect (reduces the driving force) on the performance loss in RO. The performance loss involves an increase in transmembrane pressure ($\Delta TMP = TMP(t) - TMP(0)$) for constant flux operation, or a decrease in flux ($\Delta J_v = J_v(t) - J_v(0)$) for constant pressure operation. The procedures to estimate the value of $TMP(t)$ or $J_v(t)$ based on the model presented in Table 5.1, are as follow:

a) To estimate the transmembrane pressure, TMP(t), for constant flux operation:

Input: $W, L, H, \mu, D, \rho_p, d_p, C_b, C_{b, SiO_2}, J_v, v, R_{real}, R_m$, and t

Step 1: Compute $k_m(0)$, $CP(0)$, and $TMP(0)$ from Eq. (5.1), (5.4), (5.10), (5.18) and (5.19)

Step 2: Compute $m_f(t)$ from Eq. (5.29) – (5.32)

Step 3: Estimate $\varepsilon(t)$ and compute $\alpha_f(t)$ from Eq. (5.26) and $\delta_c(t)$ from Eq. (5.28)

Step 4: Compute $CP(t)$ from Eq. (5.16) and J_v

Step 5: Compute $C_w(t)$ from Eq. (5.2) and (5.9)

Step 6: Compute $\alpha_f(t)$ from Eq. (5.27)

Step 7: Solve for $\varepsilon(t)$ as such $\alpha_f(t)_{Step\ 3} - \alpha_f(t)_{Step\ 6} = 0$

Recalculate $\alpha_f(t)$, $\delta_c(t)$, $CP(t)$ and $C_w(t)$ with the new value of $\varepsilon(t)$

Step 8: Compute $R_f(t)$ from Eq. (5.25)

Step 9: Compute $TMP(t)$ from Eq. (5.20)

Step 10: Calculate the contribution of CEOP and R_f from Eq. (5.21)

b) To estimate the operating flux, $J_v(t)$, for constant pressure operation:

Input: $W, L, H, \mu, D, \rho_p, d_p, C_b, C_{b, SiO_2}, J_v(0), v, R_{real}, R_m$, and t

Step 1: Compute $k_m(0)$, $CP(0)$, and TMP from Eq. (5.1), (5.4), (5.10), (5.19) and (5.22)

Step 2: Estimate $J_v(t)$ and compute $m_f(t)$ from Eq. (5.29) – (5.32)

Step 3: Estimate $\varepsilon(t)$ and compute $\alpha_f(t)$ from Eq. (5.26) and $\delta_c(t)$ from Eq. (5.28)

Step 4: Compute $CP(t)$ from Eq. (5.16) and $J_v(t)$ from Step 2

Step 5: Compute $C_w(t)$ from Eq. (5.2) and (5.9)

Step 6: Compute $\alpha_f(t)$ from Eq. (5.27)

Step 7: Compute $R_f(t)$ from Eq. (5.25)

Step 8: Compute $J_v(t)$ from Eq. (5.23)

Step 9: Solve for $\varepsilon(t)$ as such $\alpha_f(t)_{Step\ 3} - \alpha_f(t)_{Step\ 6} = 0$ and $J_v(t)_{Step\ 2} - J_v(t)_{Step\ 8} = 0$

Recalculate $\alpha_f(t)$, $\delta_c(t)$, $CP(t)$ and $C_w(t)$, $R_f(t)$ and $J_v(t)$ with the new value of $\varepsilon(t)$

Step 10: Calculate the contribution of CEOP and R_f from Eq. (5.24)

The calculations can be easily solved with Microsoft Excel. The input parameters for the simulations are summarized in Table 5.2.

Table 5.2: Input parameters for simulations

Fixed Input Parameters for All Sections				
$W = 0.06 \text{ m}$	$H = 1.4 \times 10^{-3} \text{ m}$	$\mu = 1.0 \times 10^{-3} \text{ Pa.s}$	$R_m = 1.0 \times 10^{14} \text{ m}^{-1}$	
$L = 0.31 \text{ m}$	$\rho_p = 2410 \text{ kg/m}^3$	$D = 1.5 \times 10^{-9} \text{ m}^2/\text{s}$	$R_{\text{real}} = 0.99$	
Section	Variables	Input Parameters		
5.4.1.	$C_b, d_p, J_v \text{ or } J_0$	$d_p = 20 \text{ nm}$	$C_{b, \text{SiO}_2} = 0.2 \text{ kg/m}^3$	$CP(0) = 1.2$
5.4.2.1.	J_{crit}	$d_p = 20 \text{ nm}$	$C_{b, \text{SiO}_2} = 0.2 \text{ kg/m}^3$	$C_b = 2 \text{ kg/m}^3$
		$v = 0.1 \text{ m/s}$	$J_v \text{ or } J_0 = 40 \text{ L/m}^2\text{h}$	
5.4.2.2.	V	$d_p = 20 \text{ nm}$	$C_{b, \text{SiO}_2} = 0.2 \text{ kg/m}^3$	
		$C_b = 2 \text{ kg/m}^3$	$J_v \text{ or } J_0 = 40 \text{ L/m}^2\text{h}$	
5.4.2.3.	$J_v \text{ or } J_0$	$d_p = 20 \text{ nm}$	$C_{b, \text{SiO}_2} = 0.2 \text{ kg/m}^3$	
		$C_b = 2 \text{ kg/m}^3$	$v = 0.1 \text{ m/s}$	
5.4.2.4.	C_{b, SiO_2}	$d_p = 20 \text{ nm}$	$C_b = 2 \text{ kg/m}^3$	
		$v = 0.1 \text{ m/s}$	$J_v \text{ or } J_0 = 30 \text{ L/m}^2\text{h}$	
5.4.2.5.	C_b	$d_p = 20 \text{ nm}$	$C_{b, \text{SiO}_2} = 0.2 \text{ kg/m}^3$	
		$v = 0.1 \text{ m/s}$	$J_v \text{ or } J_0 = 30 \text{ L/m}^2\text{h}$	
5.4.2.6.	d_p	$v = 0.1 \text{ m/s}$	$C_{b, \text{SiO}_2} = 0.2 \text{ kg/m}^3$	
		$C_b = 2 \text{ kg/m}^3$	$J_v \text{ or } J_0 = 30 \text{ L/m}^2\text{h}$	

5.4. Results and discussion

5.4.1. Simulations for fixed cake thickness

The first scenario considered assumes a membrane channel fouled by a cake layer with thickness of 10 and 50 μm . The initial CP (un-fouled) is assumed to be 1.2, which is commonly found in the RO systems in practice.

5.4.1.1. Cake thickness of 10 μm

Figure 5.3 presents the results of calculations for a cake thickness of 10 μm for constant flux of 30 and 10 $\text{L}/\text{m}^2\text{h}$, respectively. The figures on the top show the responses as the required transmembrane pressure increase, ΔTMP , or the reduction in flux, ΔJ_v . The figures on the bottom show the CEOP contributions.

Figure 5.3: ΔTMP and relative contribution of CEOP for fixed cake thickness of 10 μm at constant flux operation (a) $J_v = 30$ $\text{L}/\text{m}^2\text{h}$, and (b) $J_v = 10$ $\text{L}/\text{m}^2\text{h}$

Figure 5.3 continued: ΔTMP and relative contribution of CEOP for fixed cake thickness of $10 \mu\text{m}$ at constant flux operation (a) $J_v = 30 \text{ L/m}^2\text{h}$, and (b) $J_v = 10 \text{ L/m}^2\text{h}$

At constant flux operation, the contribution of CEOP upon ΔTMP is strongly affected by the particle size, d_p . For instance, when $d_p > 100 \text{ nm}$, more than 90% of the TMP rise is due to the CEOP effect regardless of the operating flux, J_v , or salt concentration, C_b . The role of R_f is barely the reason for TMP increase. Whereas for $d_p < 100 \text{ nm}$, ΔTMP increases exponentially with decrease in the particle size and the CEOP effect decreases. Also, the TMP increase due to the CEOP effect is influenced by C_b . For example, at $d_p = 20 \text{ nm}$ and $J_v = 30 \text{ L/m}^2\text{h}$, the contribution by CEOP upon ΔTMP is 25, 55, and 85 % at C_b of 1000, 5000, and 35000 ppm, respectively. However, the contribution by CEOP due to flux increase; e.g. increasing the J_v from 10 to $30 \text{ L/m}^2\text{h}$, is less than 5 % only for the same d_p and C_b .

The trends at constant pressure operation (as shown in Figure 5.4 for $J_0 = 30$ and $10 \text{ L/m}^2\text{h}$) have a similar pattern to those at constant flux operation. When a particle is greater than 100 nm , ΔJ_v is solely due to CEOP. For $d_p < 100 \text{ nm}$, a greater CEOP component is observed as particle size increases, as salt concentration increases and for the higher flux condition. But the % contribution of CEOP upon ΔJ_v is less than in the constant flux operation upon ΔTMP . This observation is more obvious when operating at lower J_0 . This is because the concentration polarization modulus, CP , is driven by flux and as flux is allowed to decline due to fouling in the constant pressure mode, then CP also drops. Hence the contribution of R_f is more significant in this case.

Figure 5.4: ΔJ_v and relative contribution of CEOP for fixed cake thickness of $10 \mu\text{m}$ at constant pressure operation (a) $J_0 = 30 \text{ L/m}^2\text{h}$, and (b) $J_0 = 10 \text{ L/m}^2\text{h}$

Figure 5.4 continued: ΔJ_v and relative contribution of CEOP for fixed cake thickness of 10 μm at constant pressure operation (a) $J_0 = 30 \text{ L/m}^2\text{h}$, and (b) $J_0 = 10 \text{ L/m}^2\text{h}$

5.4.1.2. Cake thickness of 50 μm

As shown in Figure 5.5 (a) and (b), at constant flux operation of 30 and 10 $\text{L/m}^2\text{h}$, respectively, a thicker cake layer leads to a greater contribution by CEOP upon the overall TMP increase when $d_p < 100 \text{ nm}$. For example, the contribution by CEOP is 35 %, as compared to only 25 % at the cake thickness of 10 μm when $d_p = 20 \text{ nm}$, $C_b = 1000 \text{ ppm}$, and $J_v = 30 \text{ L/m}^2\text{h}$. Moreover, the CEOP effect also increases with increasing d_p , C_b and J_v . Again, when the particle is greater than 100 nm, the contribution of R_f can be ignored.

Generally, in the constant pressure mode, similar trends are observed as those for the cake thickness of 10 μm (Figure 5.5 (c) and (d)). However, only a minute change in the % contribution by CEOP upon ΔJ_v is observed even though the cake

is getting thicker, e.g. at $d_p = 20$ nm, $C_b = 1000$ nm and $J_0 = 30$ L/m²h, the contribution by CEOP is ~ 25 % at both cake thicknesses.

Figure 5.5: Relative contribution of CEOP for fixed cake thickness of 50 μm at (a) $J_v = 30$ L/m²h (constant flux), (b) $J_v = 10$ L/m²h (constant flux), (c) $J_0 = 30$ L/m²h (constant pressure), and (d) $J_0 = 10$ L/m²h (constant pressure)

5.4.1.3. Discussion

Overall, for particles of 100 nm and larger the major fouling effect appears to be CEOP, rather than a fouling resistance. The CEOP effect is less for feed with a low salt content; in the extreme where there are no ‘osmotic solutes’ then there is no need to compensate for the osmotic effect. The above calculations have been based on cakes of colloidal silica particles. However biofilms also provide an unstirred

layer analogous to cakes. Biofilms develop from deposited bacteria that adhere and accumulate by growth on the membrane surface. The major fouling component of a biofilm is due to extracellular polymeric substances (EPS), which has a measured specific resistances of the order of 0.5×10^{16} m/kg (Ye *et al.*, 2005), equivalent to a 20 nm sized fine colloid (assuming $\varepsilon \sim 0.3$). The deposited layers of EPS could also cause CEOP. As shown in Chapter 3, a model EPS, alginate acid, can create a higher loss in the driving force due to the CEOP effect than the hydraulic resistance when above a flux of about 20 L/m²h.

Figure 5.5 continued: Relative contribution of CEOP for fixed cake thickness of 50 μm at (a) $J_v = 30$ L/m²h (constant flux), (b) $J_v = 10$ L/m²h (constant flux), (c) $J_0 = 30$ L/m²h (constant pressure), and (d) $J_0 = 10$ L/m²h (constant pressure)

5.4.2. Kinetics of TMP increase or flux drop and relative contributions of CEOP

The results presented in the previous section are based on fixed cake thickness. This section will look into the dynamics of the build up of the cake and development of CEOP under the effect of critical flux, crossflow velocity, operating flux, particle concentrations, salts concentration, and particle size and their impacts on the membrane performance.

Figure 5.6 (a): Varying J_{crit} at constant flux operation

Figure 5.6 (a) continued: Varying J_{crit} at constant flux operation

5.4.2.1. Varying critical flux, J_{crit}

The first case to consider is the effect of improving the critical flux upon fouling. J_{crit} due to particulate fouling can be improved by various methods such as coagulation forming bigger particles (Genkin *et al.*, 2006; Guo *et al.*, 2005), and the use of electrical fields (Huotari *et al.*, 1999). Undeniably the use of such techniques will modify either the solution physical and chemical properties or hydrodynamic conditions, but only the change in the critical flux value is considered here and

other parameters are assumed unchanged in the calculations. As shown in Figure 5.6 (a), at constant flux operation, as J_{crit} increases then $(J_v - J_{crit})$ decreases, so the net deposition rate decreases i.e. the cake layer formed is thinner. This results in a slower build up in the cake resistance, R_f , and CP level. In this example, a 50 % increase in J_{crit} , from 20 to 30 L/m^2h , reduces ΔTMP rise by ~ 53 %. In addition, the contribution of CEOP to ΔTMP is the lowest for the highest J_{crit} . The CEOP effect increases over time and becomes the controlling fouling mechanism.

Figure 5.6 (b): Varying J_{crit} at constant pressure operation

Figure 5.6 (b) continued: Varying J_{crit} at constant pressure operation

It should be noted that the fouling in terms of the cake build up rate, $\partial\delta_c/\partial t$, is a steady rise but the effect, observed as $\partial\text{TMP}/\partial t$, tends to be accelerating due to the non-linear contribution of CP according to Eq. (5.17). This is more obvious at higher net flux than at lower net flux where the TMP and CP rise can be treated as near-linear (straight lines in the plot). This supports the earlier work presented in Chapter 3 where the CP and TMP profile seemed to increase linearly with time due to the low net flux used in the tests.

Meanwhile in the fixed pressure mode, δ_c increases initially then slows down and eventually reaches an asymptotic value, unlike in the fixed flux mode where there is a continuous accumulation with time. As J_{crit} increases, the rate of flux drop also decreases due to less foulants deposited over time (Figure 5.6 (b)). Since the flux decline rate is at the minimum for the highest level of J_{crit} , in other words, the transient flux level is the highest, so the contribution of CEOP is the highest. However, the CEOP effect remains relatively steady over time as fouling progresses, i.e. at $J_{crit} = 30 \text{ L/m}^2\text{h}$, only less than 0.2 % change in the CEOP contribution is observed after 500 mins of operation. Moreover, the contribution of CEOP in constant pressure mode ($\sim 28 \%$) is notably less than in constant flux operation ($> 50 \%$). This can be explained since J_v drops due to fouling in the fixed pressure operation, and therefore a lower J_v gives a lower CP value according to Eq. (5.17).

5.4.2.2. Varying crossflow velocity, v

Increasing the crossflow velocity results in an increase in the critical flux level due to better back transport of particles induced by the shear (see Eq. (5.30)). This can have significant impact on the rate of fouling.

In constant flux operation, from Figure 5.7 (a), as v increases, the rate of change of TMP and CP is reduced drastically, from an exponential rise to a near-linear increase. For example, at $t = 500$ mins, ΔTMP is only ~ 1.6 bar at $v = 0.50$ m/s as compared to at a lower crossflow of 0.10 m/s where the TMP has doubled, increased from 15.7 to 33.2 bar. At higher crossflow, the CP value is lower, so the CEOP contribution is less than the R_f . Also, it should be noted that the improvement in membrane performance in this case, increasing the crossflow, is better than in the previous case, increasing the critical flux. For example, in the previous simulation when increasing the critical flux from 20 $\text{L/m}^2\text{h}$ to 30 $\text{L/m}^2\text{h}$ at $v = 0.10$ m/s, the ΔTMP is reduced from 17.7 bar to 6.5 bar at $t = 500$ mins (refer to Figure 5.6 (a)). A similar improvement in J_{crit} , from 20 to 30 $\text{L/m}^2\text{h}$, can also be achieved by increasing the crossflow velocity from 0.10 to 0.30 m/s, but this results in a further reduction in ΔTMP , down to 5.2 bar. This is because apart from improving J_{crit} , the CP level is also lowered by higher crossflow velocity since $\text{CP} = \exp(J_v/k_m)$, whereby k_m is a function of crossflow velocity. Therefore the relative

CEOP effect appears to be lower, $\sim 45\%$ as compared to the previous case where CEOP is $> 50\%$. This suggests that other benefits, rather than an improvement in the critical flux level alone, should be considered when selecting an appropriate technique/treatment to reduce fouling.

Figure 5.7 (a): Varying v at constant flux operation

Figure 5.7 (a) continued: Varying v at constant flux operation

In general, in the constant pressure mode, the rate of flux drop, CP and R_f build up rate decreases with increasing crossflow velocity as shown in Figure 5.7 (b). Since the transient value of J_v is higher at high crossflow velocity of 0.50 m/s due to less fouling as compared to a low crossflow of 0.10 m/s, the contribution of CEOP is also the highest. Again, as in the first scenario, the CEOP effect in the fixed pressure operation is much lower than that in the constant flux mode.

It should also be noted that the fractional deposition constant, Φ , in Eq. (5.29) may be less than 1.0 for high crossflow velocities (see Chapter 4). The effect of this is to slow down the rate of deposition. For example if Φ is 0.5, the simulated rates of change are halved, and so on.

Figure 5.7 (b): Varying v at constant pressure operation

Figure 5.7 (b) continued: Varying v at constant pressure operation

5.4.2.3. Varying operating flux, J_v

In constant flux operation, increasing J_v gives a larger net flux, $(J_v - J_{crit})$, when J_{crit} is fixed. This results in an increase in the TMP rise and CEOP effects due to higher deposition rate as depicted in Figure 5.8 (a). It should be highlighted that increasing the J_v only yields a linear increase in the cake accumulation since $m_f \propto (J_v - J_{crit})$. R_f increases near-linearly as well since $R_f \propto m_f$, but there is a slight deviation from linearity due to the effect of NaCl concentrations on the specific

cake resistance, α_f , according to Eq. (5.27). In contrast, the consequence of increasing J_v is an exponential increase in the CP level since $CP = \exp(J_v/k_m)$. Thus, there is a tremendous increase in the CEOP effect, from 50 to 60 %, in 500 mins when operating at a high J_v of 40 L/m²h.

Figure 5.8 (a): Varying J_v at constant flux operation

Figure 5.8 (a) continued: Varying J_v at constant flux operation

Similarly, this principle applies when the net flux, $(J_v - J_{\text{crit}})$, is identical but with different combinations of J_v and J_{crit} . For example, when $J_v = 30 \text{ L/m}^2\text{h}$, $J_{\text{crit}} = 20 \text{ L/m}^2\text{h}$ (Figure 5.8 (a)) and $J_v = 40 \text{ L/m}^2\text{h}$, $J_{\text{crit}} = 30 \text{ L/m}^2\text{h}$ (Figure 5.6 (a)), where both give an equal net flux of $10 \text{ L/m}^2\text{h}$. So the $\partial\delta_c/\partial t$ is same, $\sim 13 \mu\text{m}$ in 500 mins. However, there is an increase of 60 % and 81 % in the CP value in the first and second situation, respectively. This is simply due to higher J_v in the latter situation. This suggests that even if the critical flux is successfully raised, it does not warrant

the system to be pushed beyond that limit. It should be remembered that this outcome is only valid when the CEOP effect occurs, as R_f alone only produces a near-equal increase in TMP in both cases. Therefore without taking into account the effect of CEOP the intensity of the effects of fouling would be underestimated.

Figure 5.8 (b): Varying J_0 at constant pressure operation

Figure 5.8 (b) continued: Varying J_0 at constant pressure operation

Similarly, operating at a higher initial flux, J_0 , results in a greater flux decline rate and thicker cake (Figure 5.8 (b)), although the $J_v(t)$ value is still higher at higher J_0 as compared to lower J_0 , e.g. at $t = 500$ mins, $J_v(t)$ is 22.5 and 30 $\text{L}/\text{m}^2\text{h}$ seen as a drop of 10 and 25 % in the flux for J_0 of 25 and 40 $\text{L}/\text{m}^2\text{h}$, respectively. Hence, the relative CEOP effect is higher for high J_0 .

5.4.2.4. Varying particle concentration, C_{b, SiO_2}

Figure 5.9 (a): Varying C_{b, SiO_2} at constant flux operation

The particle concentrations in the feed solution can be controlled and reduced by micro/ultra-filtration pretreatment processes. As expected, reducing C_{b, SiO_2} will slow down the cake formation rate and TMP increase rate as shown in Figure 5.9 (a). Similar to the situation presented above, R_f increases near-linearly while CP

increases exponentially with increasing C_{b, SiO_2} . This can be reasoned with a linear increase in m_f and hence δ_c , but an exponential trend in CP value with δ_c .

Likewise, operation at fixed pressure, as C_{b, SiO_2} increases, ΔJ_v , δ_c and R_f also increase as shown in Figure 5.9 (b). The contribution by the CEOP upon ΔJ_v is lower at higher particle concentration, but the rate of change is less than 1% in 500 mins. Again, the contribution by R_f in ΔJ_v is dominant.

Figure 5.9 (a) continued: Varying C_{b, SiO_2} at constant flux operation

Figure 5.9 (b): Varying C_{b, SiO_2} at constant pressure operation

Figure 5.9 (b) continued: Varying C_{b, SiO_2} at constant pressure operation

5.4.2.5. Varying salt concentration, C_b

Figure 5.10 (a) presents the membrane performance data at various salt concentrations in constant flux operation. Theoretically, according to Eq. (5.29), the rate of accumulation of deposits at various salt concentrations is identical as m_f is only a function of C_{b, SiO_2} , J_v and J_{crit} . The m_f vs. time plot is not shown here but the plot of cake thickness vs. time is presented instead. As seen, the thickness of cake decreases with increasing C_b (but the difference is not large) due to lower

porosity, ε , at higher ionic strength and thus forming a more compact cake layer (this is a consequence of Eq. (5.26) and Eq. (5.27)). At such a low porosity, the specific cake resistance is high and so is R_f .

Figure 5.10 (a): Varying C_b at constant flux operation

Since CP is also a function of ε (δ_c plays a less significant role here as the difference is small when C_b is increased), CP increases with increasing C_b and this ends up with a huge increase in the CEOP effect. The contribution of CEOP shoots

up from $\sim 30\%$ at 1000 ppm NaCl to $\sim 90\%$ at 35,000 ppm NaCl. This results in an exponential increase in ΔT_{MP} at high ionic strength solution equivalent to seawater.

Figure 5.10 (a) continued: Varying C_b at constant flux operation

Figure 5.10 (b): Varying C_b at constant pressure operation

On the other hand, for constant pressure operation, increasing C_b results in a greater drop in flux as shown in Figure 5.10 (b). As expected, δ_c decreases with increasing C_b due to lower ε . R_f is still relatively high since α_f is high. However, unlike in the fixed flux situation, the CP decreases as C_b increases since there is a greater flux drop due to lower cake porosity and not due to thicker cake formation. Hence, the contribution by R_f is dominant. These results agree with a recent study on colloidal silica fouling at different ionic strengths where more particle deposition

was found at 10^{-2} M than at 10^{-1} M, but the latter has a larger hydraulic resistance because of the smaller effective porosity (Wang and Tarabara, 2007).

Figure 5.10 (b) continued: Varying C_b at constant pressure operation

5.4.2.6. Varying particle size, d_p

5.4.2.6.1. Brownian diffusion

Figure 5.11 (a) shows the effect of particle size upon membrane performance at constant flux operation. For Brownian diffusion, increasing the particle size (up to

100 nm) decreases the J_{crit} . As a result, the net flux of foulant is higher and thus δ_c is higher with increasing d_p . This gives a greater development of CP. However, increasing the particle size greatly reduces the R_f since $\alpha_f \propto 1/d_p^2$. Therefore the contribution of CEOP increases dramatically from $\sim 45\%$ to over 90% when d_p is increased from 20 to 100 nm.

Figure 5.11 (a): Varying d_p for Brownian diffusion at constant flux operation

Figure 5.11 (a) continued: Varying d_p for Brownian diffusion at constant flux operation

Similarly, at fixed pressure, as d_p increases, the flux decline rate increases due to more deposition, which gives a higher CP level as shown in Figure 5.11 (b). Again, the CEOP effect becomes evident as R_f contribution is fading when d_p approaches 100 nm. When the particle is small, e.g. at 20 nm, the R_f is the main fouling mechanism and the effect is more significant ($\sim 75\%$) than in the constant flux operation ($\sim 55\%$).

Figure 5.11 (b): Varying d_p for Brownian diffusion at constant pressure operation

Figure 5.11 (b) continued: Varying d_p for Brownian diffusion at constant pressure operation

5.4.2.6.2. Shear induced diffusion

The shear induced diffusion mechanism is applicable to sub-micron sized particles with $d_p > 100$ nm. As opposed to Brownian diffusion, increasing the size for particles in the shear induced diffusion region results in an increase in J_{crit} since $J_{\text{crit}} \propto d_p^{4/3}$. Hence, for both fixed flux (Figure 5.11 (c)) and fixed pressure operation (Figure 5.11 (d)), bigger particles give a lower rate of change of TMP in

the former or less ΔJ_v in the latter due to less deposition, lower CP and R_f . The contribution by CEOP in both cases is greater than 90% for all the particle sizes.

Figure 5.11 (c): Varying d_p for shear induced diffusion at constant flux operation

The above results are supported by various studies of the colloidal silica fouling in RO at fixed pressure using 300 nm-sized particles where the trans-cake pressure ($\Delta P_c = J_v \mu R_f$) role was less than 2 % of the overall loss in the membrane

performance (Hoek and Elimelech, 2003; Hoek *et al.*, 2002; Ng and Elimelech, 2004).

Figure 5.11 (c) continued: Varying d_p for shear induced diffusion at constant flux operation

Figure 5.11 (d): Varying d_p for shear induced diffusion at constant pressure operation

Figure 5.11 (d) continued: Varying d_p for shear induced diffusion at constant pressure operation

5.4.3. Model validation and sensitivity analysis

The model developed above was checked against the experimental data obtained in Chapter 3 for silica fouling tests. An example of the TMP profiles is presented in Figure 5.12 for silica fouling at 3 different flux levels and at $v = 0.10$ m/s. As can be seen, the regressions of the model predictions and experimental data show a good fit with $R^2 > 0.99$.

Figure 5.12: TMP profile via model predictions and experimental data at $v = 0.10$ m/s

(a)

(b)

Figure 5.13: Sensitivity analysis of specific cake resistance on CEOP contributions to the overall membrane performance for $d_p = 20$ nm in (a) constant flux, and (b) constant pressure operation

For the sensitivity analysis of the model, the changes in the critical flux, J_{crit} , and specific cake resistance, α_c , upon the CEOP contributions to the overall membrane performance are examined. These two parameters are of interest as both values are estimated based on the experimental data reported in previous chapters. However, it should be noted that for the sensitivity analysis involves the critical flux, the approach and results are similar to those reported in Section 5.4.2.1., which accounts for variation in J_{crit} . Hence the analysis is not repeated here.

Figure 5.14: Sensitivity analysis of specific cake resistance on CEOP contributions to the overall membrane performance for $d_p = 200$ nm in (a) constant flux, and (b) constant pressure operation

As shown in Figure 5.13 (a), for the Brownian diffusion type particles, a $\pm 25\%$ change in α_c will only cause 5 % difference in the contribution of CEOP upon the overall membrane performance under constant flux operation. For constant pressure operation, the effects are slightly greater, but remain less than 10 % difference. A bigger difference observed here is due to the increasing contribution of R_f upon the flux decline. On the other hand, when the particle size is greater than 100 nm as shown in Figure 5.14, a $\pm 25\%$ change in α_c has negligible impact on the CEOP contribution in both operation modes since R_f has relatively insignificant role in the membrane performance.

5.5. Concluding remarks

A simple model has been developed to predict the membrane performance under the effect of critical flux (J_{crit}) and cake enhanced osmotic pressure (CEOP). In summary, for conventional constant flux operation the fouling in terms of rate of deposition, $\partial m_f / \partial t$, is a steady rise but the effect, observed as $\partial TMP / \partial t$, tends to be accelerating due to the non-linear contribution of CEOP. This happens at high net flux, low crossflow, high particle loading and high salt content. Also, it is found that the fouling mechanism is greatly controlled by the particle size. When $d_p > 100$ nm, regardless of the operating flux, crossflow velocity, critical flux, salt concentration and particle concentration, the loss in membrane performance is predominantly due to the CEOP effect. When d_p is significantly less than 100 nm, other factors then play a part in the overall loss in performance. In constant flux operation, it is found that the transition from R_f controlled to CEOP controlled occurs when J_v , C_b and C_{b, SiO_2} is high as well as when v and J_{crit} is low. It is also evident that the CEOP effect is greater at fixed flux operation than at fixed pressure operation simply due to the decline in flux, hence CP, in the latter situation.

CHAPTER 6

Fouling Detection by Ultrasonic Measurement

This chapter describes a non-invasive ultrasonic technique to detect and monitor the fouling process in reverse osmosis. It is based on the approach initially developed by the Greenberg and Krantz (Bond *et al.*, 2000; Mairal *et al.*, 2000; Mairal *et al.*, 1999). The ultrasonic measurement is based on changes in the acoustic properties of the target medium, in this case the fouling layer. The data were correlated well with data obtained from the sodium chloride tracer response technique (presented in Chapters 3 and 4) for colloidal silica fouling and cleaning tests. Although the responses in the time domain for alginic acid as a model foulant were comparatively weak due to the similarity in its acoustic properties to the feed solution, the ultrasonic responses in the frequency domain were able to provide promising results for the detection of an alginate gel layer on a RO membrane. The ultrasonic measurement is valuable in the study of fouling and can be applied as early warning system to provide critical information such as the extent of the fouling layer.

6.1. Introduction

The successful combat against fouling events in reverse osmosis (RO) relies on an early warning system to activate an appropriate countermeasure to be implemented in the initial stages of fouling, before the fouling phenomenon causes detrimental effects on the membrane performance. Conventional methods based on TMP changes or flux decline data are not very satisfactory as the changes are usually unnoticed in the early stage of fouling. In addition, the data are average values reflecting the overall drop in membrane performance; it does not identify the nature and the location of the foulants. As shown by the results from direct observations of fouling processes and membrane autopsies (Beatson and Fane, 1999; Chai *et al.*, 2001; Neal *et al.*, 2003) as well as computer simulation data (Schwinge *et al.*, 2002a), there is a tendency to uneven distribution of fouling layers along the membrane channel due to the complex hydrodynamics and local flux effects. Therefore to have an effective control against fouling, it is important to target the weakest point on the membrane that is more susceptible to fouling. However, many

common practices such as physical, biological, chemical, and image analysis techniques used to gain insights into the foulants present on the membrane, require sacrifice of the membrane and cannot be performed online. Therefore, there have been several non-invasive online techniques developed to investigate the fouling process as summarized in two recent review papers (Chen *et al.*, 2004a; Chen *et al.*, 2004b). Among the methods, in terms of ease of use, adaptability, complexity of analysis protocol, labour intensiveness, and costs, the ultrasonic non-destructive technique is an attractive and well-established method.

The ultrasonic measurement technique, commonly known as the ultrasonic time domain reflectometry (UTDR), was pioneered by Greenberg and Krantz (Bond *et al.*, 2000; Mairal *et al.*, 2000; Mairal *et al.*, 1999) for application to fouling detection in membrane systems. The initial studies were focused on the characterization of formation and removal of membrane fouling by calcium sulfate deposits in a flat sheet RO module, which was similar to the one used in this thesis. The technique was later extended to more challenging spiral wound geometry (Chai *et al.*, 2001; Zhang *et al.*, 2003). Since then, the ultrasonic technique has been employed to monitor the progress of fouling by various compounds such as paper mill effluent (Li *et al.*, 2002a; Li *et al.*, 2003b; Li *et al.*, 2002b; Li *et al.*, 2002c; Sanderson *et al.*, 2005), natural brown water (Sikder *et al.*, 2006), proteins (Li *et al.*, 2006; Li *et al.*, 2005b), inorganic calcium sulfate and carbonate (Li *et al.*, 2005a; Sanderson *et al.*, 2002; Zhang *et al.*, 2006), kaolin (Li and Sanderson, 2002) and oily water (Liu *et al.*, 2006). Recently, the major advance in the technology was the application to detect the early stages of biofilm growth on polymeric surfaces (Kujundzic *et al.*, 2007). In addition, the UTDR has been successfully used for membrane characterization such as pore size and thickness measurement and membrane compaction phenomenon (Aerts *et al.*, 2001; Gomez Alvarez-Arenas, 2003; Kools *et al.*, 1998; Laux *et al.*, 2005; Ramaswamy *et al.*, 2004).

The objective of this research was to explore the application of the ultrasonic technique to colloidal fouling in RO by nano-sized silica and gel-liked alginic acid. The challenge was the relatively thin cake layer formed by the silica colloids (as shown in Chapter 3); unlike most of the previous work which selected foulants that are relatively large in size, e.g. the average diameter of kaolin was $\sim 2 \mu\text{m}$ (Li and

Sanderson, 2002), thus forming a thick cake layer that was easily measurable. Apart from that, the detection of the gel-like alginate layer was restricted by the similarity in the acoustic properties to the feed solution. In addition, the ultrasonic measurement was used as an independent measurement to cross check and to establish a correlation with the results obtained from transmembrane pressure profiles and the sodium chloride tracer response technique (presented in Chapter 3 and 4 for concentration polarization and critical flux studies).

6.2. Background

Ultrasonic measurement uses the velocity of a sound wave and its attenuation (due to reflection, refraction, diffraction, and scattering) as well as dispersive losses (due to internal friction, heat conduction and molecular relaxations) that occur as it propagates through a medium to characterise the properties of that medium (Krautkramer and Krautkramer, 1990). The ultrasonic signal is reflected by a change in acoustic impedance when it reaches a layer with different acoustic impedance from the medium it is travelling through. The acoustic impedance, Z , is the product of the sound velocity in the medium, ω_m and the medium density, ρ_m (Krautkramer and Krautkramer, 1990):

$$Z = \omega_m \rho_m \quad \text{Eq. (6.1)}$$

The amplitude of the reflected wave depends on the acoustic impedance difference between the mediums. The amplitude, A , of the reflected wave relative to the incident wave is given by (Krautkramer and Krautkramer, 1990):

$$A_{\text{Reflected}} = \frac{Z_2 - Z_1}{Z_1 + Z_2} \quad \text{Eq. (6.2)}$$

Subscripts 1 and 2 refer to medium 1 and 2, respectively. Part of the energy is also transmitted across the medium and its amplitude is given by (Krautkramer and Krautkramer, 1990):

$$A_{\text{Transmitted}} = \frac{2Z_2}{Z_1 + Z_2} \quad \text{Eq. (6.3)}$$

In addition, the medium thickness, h_m , can be calculated based on the time required for the wave to travel through the medium, t_m , (Krautkramer and Krautkramer, 1990):

$$h_m = 0.5 \omega_m t_m \quad \text{Eq. (6.4)}$$

Hence, the application of UTDR in fouling detection is based on, (i) the change in amplitude of the reflected ultrasonic signal from the fouling layer/membrane interface, and (ii) the time of flight or the amount of time for the sound to travel through the fouling layer (Mairal *et al.*, 2000; Mairal *et al.*, 1999). The principle of UTDR measurement for a simple RO module similar to the one used in this thesis is illustrated in Figure 6.1.

Note: In reality the incident and reflected acoustic waves (A, C and B/B') are perpendicular to the transducer and membrane surface. The angles are used in the diagram for ease of explanation purpose only.

Figure 6.1: Principle of ultrasonic detection of fouling layer

A high frequency transducer is fixed on the external wall of a flat sheet membrane module. A pulser/receiver is used to send and receive the ultrasonic signals. When incident waves hit the top plate surface/feed solution interface and feed solution/membrane interface, reflected echoes (labelled as A and B, respectively) are generated from these surfaces. Other surfaces such as the bottom plate may or may not be detected depending on the penetration depth of the pulse. The signals, A and B, will remain unchanged as long as no fouling occurs. Once fouling is initiated on the membrane surface, the acoustic impedance difference of the membrane changes, resulting in a change in the amplitude of B, and this is labelled as echo B'. Furthermore, if the fouling layer has reached the detectable limit of the UTDR, a new echo C will appear, as there is formation of a new feed solution/fouling layer interface. Fouling progress can be measured by monitoring

the change in the amplitude of signal B/B' and C. Also, the thickness of the fouling layer can be calculated from the difference between the arrival time of echo B and C, Δt_p , provided the sound velocity in the fouling layer, ω_f , is known.

6.3. Materials and methods

6.3.1. Chemicals and experimental set up

All chemicals used in the fouling tests were similar to those described in Chapter 3. The reverse osmosis unit for the fouling tests was similar to the set up as described in Chapter 3, except that the RO test cell was equipped with an ultrasonic measurement facility, as shown in Figure 6.2.

Figure 6.2: Schematic diagram of RO system with ultrasonic measurement facility

The ultrasonic measurement hardware comprised a pulser-receiver (GE Panametrics, model 5800); a digital oscilloscope (Tektronix, model TDS5082) that enabled a 4 ns sampling rate and recorded a generation of 2500 data points per

ultrasonic waveform (each waveform recorded was an average of 32 waveforms); and a 5 MHz ultrasonic transducer (Shantou Ultrasonic Instrument Corporation, model 5P14) coupled to the top plate of the RO cell. The top plate of the RO cell was made from stainless steel and had a glass-viewing window. The transducer was mounted to the glass with a plastic block screwed tightly to the stainless steel plate, near the exit region of the module as shown in Figure 6.3. The position of the ultrasonic transducer corresponded to $1/3$ of the membrane length from the feed exit and $1/2$ the membrane width.

Figure 6.3: Assembly of ultrasonic transducer on the RO cell, (a) top view (b) side view

6.3.2. Experimental procedure

The ultrasonic measurement was performed simultaneously with the sodium chloride tracer response test during the fouling experiment. The detailed experimental procedure and conditions for the silica and alginate fouling and cleaning tests have been outlined in Chapter 3 (Section 3.3.3.). The ultrasonic waveform was captured periodically during the experiment and stored on the oscilloscope. Analysis of the waveforms was carried out after the experiment.

6.4. Results and discussion

6.4.1. Ultrasonic measurement in silica fouling tests

6.4.1.1. Ultrasonic waveforms

Sequential ultrasonic response waveforms recorded during the silica fouling and cleaning experiment at $J_v = 30 \text{ L/m}^2\text{h}$ and $v = 0.10 \text{ m/s}$ are presented in Figure 6.4. The plots show the signal amplitude in volts (V) vs. the peak arrival time in microseconds (μs). Peaks labeled as M/M' and F corresponds to the peaks generated from the feed solution/membrane, fouling layer/membrane, and feed solution/fouling layer interfaces, respectively.

Figure 6.4: Ultrasonic response signals during silica fouling and cleaning test. (a) – (h) fouling stage, (i) NaCl cleaning stage, (j) MQ cleaning stage

(c) Run Time = 20 min

(d) Run Time = 30 min

(e) Run Time = 65 min

Figure 6.4 continued: Ultrasonic response signals during silica fouling and cleaning test. (a) – (h) fouling stage, (i) NaCl cleaning stage, (j) MQ cleaning stage

(f) Run Time = 130 min

(g) Run Time = 200 min

(h) Run Time = 270 min

Figure 6.4 continued: Ultrasonic response signals during silica fouling and cleaning test. (a) – (h) fouling stage, (i) NaCl cleaning stage, (j) MQ cleaning stage

Figure 6.4 continued: Ultrasonic response signals during silica fouling and cleaning test. (a) – (h) fouling stage, (i) NaCl cleaning stage, (j) MQ cleaning stage

Other peaks reflected from the glass top plate/feed solution, membrane/permeate support, permeate support/stainless steel bottom plate interfaces are not shown as they are not of interest in this study. The signal for a clean membrane system at run time = 0 min, was used as the reference point for monitoring the development of fouling. As can be seen before fouling, there was no peak F. After 10 minutes upon the addition of colloidal silica to the feed solution, peak F appeared due to the formation of cake layer; and peak M was labeled as M'. The peak arrival time and amplitude of peaks M' and F were closely monitored to study the progress of fouling.

6.4.1.2. Peak arrival time analysis

As shown in Figure 6.4 (b) to (h), peak M', from the initial position of 7.068 μs , shifted to the right on the peak arrival time axis as fouling progressed. The total shift in the peak arrival time of membrane peak, Δt_M , was about 0.032 μs , equivalent to a distance of $\sim 24 \mu\text{m}$ (calculated using Eq. (6.4), based on the assumption that $\omega_f \approx \omega_w = 1500 \text{ m/s}$). The shift in peak M' was due to the compression of membrane, which was the densification of the membrane structure in the skin layer and micro-porous support layer, as well as the permeate support under the increasing hydrostatic pressure effect (Aerts *et al.*, 2001; Li *et al.*, 2003b). In fixed flux mode, pressure was increased (through the self adjustment of the permeate mass flow controller or via increasing the pump rate) to compensate for membrane fouling. This caused the membrane and permeate support to move further away from the ultrasonic transducer, hence increasing the spacing between the top plate and the membrane, or in other word, the feed flow channel became slightly widened. At run time = 360 min (Figure 6.4 (i)), peak M' remained at 7.100 μs , even after the fouling process was stopped and the feed solution was replaced with sodium chloride particle free solution. Since the deposit was hardly removed during the NaCl cleaning stage, the pressure remained unchanged and so was the arrival time of peak M'. Peak M' only returned to the original position after cleaning with MQ water (Figure 6.4 (j)), which removed the silica cake layer and restored the initial pressure, and hence the membrane was relaxed.

At the same time, peak F also shifted to the right on the peak arrival time axis, as the fouling layer moved downward together with the membrane. However the total shift in the peak arrival time of peak F, Δt_F , was only 0.012 μs , from 6.940 to 6.952 μs (Figure 6.4 (h)), which was equivalent to a distance of 9 μm . The total shift in the cake layer peak was less than in the membrane peak. This was due to the competition between the build up in the cake layer thickness, which resulted in a forward peak shift on the peak arrival time axis, and the opposite direction of downward compression by pressure.

6.4.1.2.1. Cake layer thickness

The dynamic build up in the thickness of the silica deposit layer, $\delta_c(t)$, can be estimated using Eq. (6.4), expressed as;

$$\delta_c(t) = 0.5 \omega_f (\Delta t_p(t) - \Delta t_p(0)) \quad \text{Eq. (6.5)}$$

where Δt_p is the difference in the peak arrival time between peak F and M'. The sound velocity of the fouling layer, ω_f , was assumed similar to the sound velocity in water, approximately 1500 m/s. A similar assumption was applied in previous studies, as the actual value was not known; and the calculated thickness agreed well with the results from the scanning electron microscope (Li *et al.*, 2003b; Li *et al.*, 2002b).

Figure 6.5: Build up of cake layer thickness in silica fouling and cleaning test at $J_v = 30 \text{ L/m}^2\text{h}$ and $v = 0.10 \text{ m/s}$. A comparison between ultrasonic method and sodium chloride tracer response test

The cake thickness as function of run time at different stages of silica fouling and cleaning is shown in Figure 6.5. The cake thickness increased with time as fouling progressed, but the cake was not removed in the NaCl cleaning stage. Peak F returned to its original position on the peak arrival time axis during the MQ water cleaning stage, which suggested that the cake layer was no longer on the membrane. However it could see in later section that there was still some residue remained on the membrane even after the MQ water cleaning.

The values obtained from the UTDR measurement were compared with those obtained from the tracer response technique; whereby the thickness of cake was calculated from the mass, m_f , and assumed porosity, ε , of the cake as follows:

$$\delta_c(t) = \frac{m_f(t)}{\rho_p (1 - \varepsilon(t))} \quad \text{Eq. (6.6)}$$

ρ_p is the silica particle density. The transient m_f and ε were calculated from the concentration polarization, CP, and cake resistance, R_f , profile given by the tracer response technique as described in Chapter 4. It was found that the values given by the UTDR method appeared to be higher ($\sim 15 \mu\text{m}$ max.) than the tracer response technique ($\sim 9 \mu\text{m}$ max). There are several possible reasons for this difference. One is that the value given by the tracer response technique based on the TMP profile was actually an average reading where there could be a variation of cake layer thickness along the membrane channel. On the other hand, the UTDR method was location specific; it only detected the thickness of cake formed within the focal point of the ultrasonic transducer. However, a repeat experiment also observed such a difference in the value between the two methods, so this might not be the reason. One uncertainty in the calculation was the assumption that both cake layer and membrane moved downward together at the same distance under the increasing hydrostatic pressure effect. However, both cake layer and membrane have different compressibility and hence the actual shift distance might be different from each other. Another possible explanation was the limitation of the UTDR method for such a low thickness measurement. The smallest scale on the peak arrival time axis was 4 ns, which was equivalent to 3 μm . This could give an error of 3 – 6 μm to the reading since the thickness calculation was based on the peak arrival time of both peaks M' and F. This error was significant considering the thickness of cake was only around 10 μm . The other potential source of error is the value of porosity used in Eq. (6.6). This was obtained by separate 'dead-end' filtration experiments (see Chapter 4), and small errors in this can be magnified via the Carman-Kozeny equation (Eq. (4.7)) used to estimate m_f from R_f . Finally the assumption that sound velocity, ω_f , is similar to water may bring about some errors in the use of Eq. (6.5). Despite such uncertainties in the thickness measurement by the ultrasonic method, the cake thickness data gained from both methods were in the same order of

magnitude, which confirmed that only small amounts of silica particles were depositing on the membrane, and therefore the performance loss at such high flux ($J_v = 30 \text{ L/m}^2\text{h}$) operation was mainly due to the cake enhanced osmotic pressure (CEOP) effect rather than the hydraulic resistance.

6.4.1.3. Peak amplitude analysis

Another way of quantifying the progress of fouling was via monitoring the amplitude profile of peak M' and F. As shown in Figure 6.4, as fouling progressed, the amplitude of both peaks, M' and F, increased due to changes in the acoustic impedances. Both silica deposit layer and the membrane were getting denser and more compacted with the accumulation of cake mass and increasing pressure effect. The peak height remained unaffected in the NaCl cleaning stage but returned to the initial value after cleaning with MQ water. A summary of the change in amplitude, $\Delta A = (A(t) - A(0))$, of both peaks, M' and F is presented in Figure 6.6. The dynamics of the amplitude of the reflected waves were consistent with the TMP profile (Figure 3.12).

Figure 6.6: Change in amplitude of echoes from feed solution/fouling layer (peak F) and fouling layer/membrane (peak M') interfaces in silica fouling and cleaning test at $J_v = 30 \text{ L/m}^2\text{h}$ and $v = 0.10 \text{ m/s}$

6.4.1.4. Ultrasonic frequency domain reflectometry (UFDR)

Although the peak arrival time and amplitude analysis in the time domain (as presented in earlier sections) were satisfactorily applied to characterize the fouling process by colloidal silica, there is a more sensitive approach, the ultrasonic frequency domain reflectometry, UFDR (Kujundzic *et al.*, 2007; Ramaswamy *et al.*, 2004), especially for treating the data where there is a poor acoustic contrast between the fouling layer and the feed solution as in the alginate fouling (presented in Section 6.4.2.). It is important to note that although the transducer is characterized by a single frequency value, the transducer actually generates broadband pulses that combine a band of frequencies ranging between 40 to 160 % of the peak frequency (Ramaswamy, 2002). The shape of the time domain signal is obtained as a result from the positive and negative interferences between all the waves transmitted; it is the combination of all the frequencies observed in the frequency domain signal. Scattering and absorption of energy at specific frequencies can occur and therefore the changes in signals in the time domain may not be significant (Fonseca, 2002). An alternative approach is to convert the data from the time domain to frequency domain by performing Fast Fourier Transform (FFT) of the digitized time domain signal (Kujundzic *et al.*, 2007; Ramaswamy *et al.*, 2004). In the signal processing process, gates or windows can be used to isolate signals of interest or frequency filters to smooth or reject unwanted frequencies. The frequency domain shows the signal's energy that is present as a function of frequency.

In the UFDR analysis reported below, the conversion operation was carried out using commercial mathematical software, Origin 6.1 (OriginLab Corporation). In addition, the energy of the reflected signal, expressed as Total Reflected Power (TRP), was determined from the area under the curve of the amplitude-frequency spectrum. The calculations were also performed with the Origin 6.1 software.

The frequency domain spectrum of the ultrasonic signals reflected from the fouling layer peak F is plotted in Figure 6.7. As can be seen, the peak frequency was around the specified frequency of the transducer (5 MHz), and this was the most sensitive detection frequency for the fouling layer. The magnitude of the spectrum, or amplitude, increased as more deposits built up during the silica fouling

stage, from $t = 0$ to 270 min. The replacement of the feed solution with the silica-free NaCl solution stopped the further growth, but failed to remove the deposit layer. The spectrum collected during the NaCl cleaning stage, at $t = 360$ min, nearly superimposed onto the spectrum at $t = 270$ min. Finally, the cleaning process with MQ water was able to restore the membrane, but not 100 % recovery. The spectrum at $t = 551$ min, was slightly different from the original spectrum, as there could be some residue of silica particles still present on the membrane surface.

(a)

(b)

Note: The spectra at 0 and 270 min are included in this plot for the purpose of comparison of the effectiveness of cleaning method

Figure 6.7: UFDR spectra from the fouling peak F in silica fouling and cleaning test at $J_v = 30 \text{ L/m}^2\text{h}$ and $v = 0.10 \text{ m/s}$. (a) fouling stage from 0 to 270 min (b) NaCl and MQ water cleaning stage at 360 and 510 min, respectively

A better representation of the fouling development would be via monitoring the relative Total Reflected Power, TRP_R , of the spectrum, defined as $TRP_R = [TRP(t) - TRP(0)]/TRP(0)$. This approach was also used in a recent study to monitor early stages of biofilm growth on polymeric surfaces (Kujundzic *et al.*, 2007). Figure 6.8 shows the plot of TRP_R profile and a comparison with results obtained from the TMP profile and sodium chloride tracer response technique. The first plot (Figure 6.8(a)) is the TMP profile, expressed as $TMP_R = [TMP(t) - TMP(0)]/TMP(0)$. The TMP_R data during the pulse injection was excluded from the plot, for the purpose of clarity of the graph.

Figure 6.8: TRP_R profile in silica fouling test at $J_v = 30 \text{ L/m}^2\text{h}$ and $v = 0.10 \text{ m/s}$,

(a) TRP_R and TMP_R vs. t , and (b) TRP_R and m_f vs. t

The TRP_R data resembled the TMP_R data in the fouling and NaCl cleaning stage, but the UFDR method was about 10 times more sensitive than the TMP measurement. It was interesting to note that when the feed solution was replaced with MQ water in the last stage of cleaning, the TMP_R instantaneously dropped to a level below the initial value. This drop was partly due to the removal of the cake layer that regained the membrane performance, but undoubtedly it was mainly caused by a drastic decrease in the osmotic pressure (zero osmotic pressure for MQ water). Therefore based on the TMP_R data alone, it was uncertain whether the membrane was fully cleaned during that period, until a permeability test was carried out to cross check against the original value at $t = 0$. However, the ultrasonic measurement was able to provide valuable information on the cleaning status of the membrane. Unlike its effect upon the TMP, a drop in the osmotic pressure of the solution gave negligible impact on the ultrasonic measurement. In fact, it was observed that the deposit layer was being rather slowly removed, and took about 20 minutes for the whole removal process.

The second plot (Figure 6.8 (b)) shows the UFDR results and the cake accumulation data obtained from the tracer response technique (Chapter 4). Both curves displayed an identical fouling pattern, which supports the claim that a denser cake layer induced greater reflection energy received by the ultrasonic transducer.

6.4.1.5. UFDR analysis under various fouling conditions

6.4.1.5.1. Fouling tests without and with background salt ions

Referring to the results presented in Chapter 3 (Section 3.4.2.1.1.) for silica fouling tests without the background salt ions, it was observed that the TMP profile showed an increasing trend during the NaCl pulse, but returned to the previous TMP value when the pulse was stopped. This suggested that there was a rapid deposition of silica colloids on the membrane during the pulse but the process was reversible. The deposition was probably due to the screening of the electrical double layer by sudden introduction of salts into the feed solution. This result was corroborated by the UFDR measurement, where it was evident that there was a large jump in the TRP_R value during the pulse that returned to the previous value when the pulsed was stopped (Figure 6.9 (a)).

Conversely, with the presence of background 2000 ppm NaCl (Section 3.4.2.1.2.), there was no accelerated deposition of particles onto the membrane surface, as clearly shown by both the TMP and TRP_R profile in Figure 6.9 (b) where both values remained constant during the NaCl pulse. Therefore the UFDR results validated the assumption of negligible fouling during the pulse, provided there was a background salt concentration.

Figure 6.9: TMP and UFDR response during one of the NaCl pulse in silica fouling test (a) without background salt ions (b) with 2000 ppm NaCl background solution

6.4.1.5.2. Fouling tests at different flux levels and crossflow velocities

The UFDR method was employed in the study of the effect of flux on fouling. Figure 6.10 (a) shows the development of TRP_R at various flux levels at $v = 0.06$

m/s. At low flux of $10 \text{ L/m}^2\text{h}$, there was no change in the TRP_R values, which meant the system was below the critical flux and hence zero deposition occurred. Increasing the operating flux resulted in an increase in the accumulation of silica colloids due to the larger net flux, $(J_v - J_{\text{crit}})$, that convected the particles to the membrane surface. In addition, the porosity of the cake was greatly reduced due to the higher ionic strength at higher J_v and this caused the formation of a more compacted deposit. Thus, the rate of change of TRP_R increased with increasing flux.

Figure 6.10: UFDR analysis for silica fouling tests under different test conditions, (a) effect of flux at $v = 0.06 \text{ m/s}$, and (b) effect of crossflow velocities at $J_v = 30 \text{ L/m}^2\text{h}$

The UFDR results (Figure 6.10 (b)) also agreed with the results from the tracer response technique for silica fouling at different crossflow velocities as discussed in

Section 4.4.2. Increasing crossflow velocity enhanced the shear, which improved the critical flux ($J_{\text{crit}} \propto v^{0.4}$) and reduced the fractional deposition of the particles (only 10 % deposition at high crossflow as shown in Figure 4.7), and therefore a thinner cake layer was formed on the membrane. This was evident from the TRP_R values, which showed a reduction in the rate with increasing crossflow velocities.

6.4.1.5.3. Comparison between UFDR measurement and sodium chloride tracer response technique for the determination of critical flux

The critical flux, J_{crit} , of silica colloids was estimated from the UFDR measurement by extrapolating the plot of $\partial \text{TRP}_R / \partial t$ vs. J_v to where the rate of change of TRP_R was zero or $\partial \text{TRP}_R / \partial t = 0$, as depicted in Figure 6.11 for silica fouling test at $J_v = 30 \text{ L/m}^2\text{h}$ and $v = 0.06 \text{ m/s}$. The values of $\partial \text{TRP}_R / \partial t$ at different flux levels were obtained from the slopes of the plots in Figure 6.10 (a).

Figure 6.11: Comparison between UFDR measurement and sodium chloride tracer response technique for the determination of critical flux in silica fouling test at $v = 0.06 \text{ m/s}$

It was found that the estimated J_{crit} value was $\sim 15 \text{ L/m}^2\text{h}$ and this result was comparable to the J_{crit} value estimated from the sodium chloride tracer response technique at $\partial m_f / \partial t = 0$. Also, it should be noted that the exponential trend for the TRP_R data was simply because the ultrasonic measurement reflected the combined

effects of deposit build up and membrane compaction, which were significantly greater at higher flux.

6.4.1.5.4. Correlations between UFDR and TMP measurement and sodium chloride tracer response technique

A correlation between the UFDR and the TMP measurement as well as the tracer response technique could be established by comparing the rate of change of TRP_R vs. TMP_R and TRP_R vs. m_f , respectively, at all fouling conditions as outlined in Table 3.1 (Chapter 3).

Figure 6.12: Correlations between UFDR measurement and TMP profile and sodium chloride tracer response technique, (a) $\log \{ \partial \text{TRP}_R / \partial t \}$ vs. $\log \{ \partial \text{TMP}_R / \partial t \}$, and (b) $\log \{ \partial \text{TRP}_R / \partial t \}$ vs. $\log \{ \partial m_f / \partial t \}$

As shown in Figure 6.12, both plots yield a linear plot in the log-log scale. The UFDR responses by means of a change in the acoustic impedances of the cake layer and membrane were consistent with the mass accumulation and TMP increase under various fouling conditions. This means the UFDR results also agreed with the conclusion from the tracer response technique, in which the performance loss in the RO membrane test was due to the cake enhanced osmotic pressure effect that reduced the effective driving force rather than through an additional hydraulic resistance.

6.4.2. Ultrasonic measurement in alginate fouling tests

The ultrasonic technique was employed to monitor alginate fouling in RO. Representatives of the ultrasonic response waveforms in the time domain recorded at different run times for alginate fouling at $J_v = 30 \text{ L/m}^2\text{h}$ and $v = 0.10 \text{ m/s}$ are shown in Figure 6.13 (a). First, it should be noted that peak M arrived earlier on the x-axis in this case than in the previous results as shown in Figure 6.4. The difference was about $0.05 \mu\text{s}$ and equivalent to $\sim 40 \mu\text{m}$, which meant the flow channel, was slightly narrower than in the former case. This was probably because the wearable O-ring, which was held between the top and bottom RO plates, had lost its elasticity strength over time. However, this small variation in the flow channel height was not expected to cause a major variation to the hydrodynamic conditions of the RO system.

As can be seen from the plot, even though there was severe fouling occurring at such a high flux level (TMP increased at a rate of 0.8 bar/h), no new interface (feed solution/fouling layer interface) was detected. The feed solution/membrane interface, peak M/M', almost superimposed onto each other and it was difficult to distinguish the changes in the amplitude. This was due to a very poor acoustic contrast between the alginate layer and the feed solution. There was a slight shift in the arrival time of peak M/M' solely due to the compression of the membrane under the rising pressure effect.

However, when the time domain data were converted to the frequency domain through the FFT operation, an increase in the magnitude of the spectrum as fouling progressed could be observed as shown in Figure 6.13 (b). The positive response

came from the development of an alginate fouling layer as well as the compaction of the membrane (increase in density). This demonstrates that the UFDR analysis as compared to the time domain method was more sensitive and suitable to be applied in fouling study by alginic acid.

Figure 6.13: Ultrasonic responses recorded at different run time (in minutes) in alginate fouling at $J_v = 30 \text{ L/m}^2\text{h}$ and $v = 0.10 \text{ m/s}$ (a) waveform in time domain, and (b) spectrum in frequency domain

The progress of alginate fouling at various flux levels was monitored with the UFDR technique and the results are shown in Figure 6.14. The TRP_R profile showed an increasing rate with an increase in J_v , or in other words, more severe fouling. These data were well correlated to the data obtained from the TMP and tracer response measurements. The UFDR method was successfully applied to a

more challenging fouling species like alginic acid, but the signal response's strength was much lower than for silica colloids, by about 100 times, making it more prone to error.

Figure 6.14: TRP_R profile of alginate fouling under different flux levels

6.5. Concluding remarks

It has been clearly demonstrated that the ultrasonic technique was able to capture the dynamics of a complete cycle of fouling and cleaning for colloidal silica fouling. The ultrasonic results were in good agreement with the data from TMP measurement as well as the sodium chloride tracer response technique. It was observed that only a very thin layer or minute amount of silica deposit was formed even at a very high flux level, and this finding confirmed the dominant role of the cake enhanced osmotic pressure effect on the overall membrane performance loss. In addition, ultrasonic measurement in the frequency domain was successfully applied to monitor the fouling by alginic acid, which has similar acoustic properties to the feed solution. The outcomes suggest that both the ultrasonic measurement and the sodium chloride tracer response technique are suitable to be used, in parallel or alone, as effective monitoring tools for the fouling process in RO.

CHAPTER 7

Biofouling in Reverse Osmosis

This chapter describes a systematic study of biofouling in reverse osmosis (RO) process using model bacteria of *Pseudomonas fluorescens*. It was found that the subsequent growth of biofilm following the initial bacteria colonization of the membrane surface was a function of concentration polarization (CP). The rationale was that biofilm growth was nutrient dependent, where the nutrient availability at the membrane wall was controlled by the magnitude of CP. Furthermore, the build up in biofilm induced the enhanced osmotic pressure phenomenon; hereby known as the biofilm enhanced osmotic pressure (BEOP) effect (Herzberg and Elimelech, 2007), due to hindered back diffusion of solutes through the tortuous path of the heterogeneous structure of the biofilm as compared to the bulk fluid. The ultrasonic technique was applied to detect the biofouling process. In addition, a novel fiber optic sensor (FOS) was developed to detect biofilm on the membrane as reported in Appendix A.

7.1. Introduction

Biofouling has long been recognized as one of the most problematic types of fouling in the reverse osmosis (RO) process. Even after a 99.9 – 99.99 % removal of bacteria could be achieved with the installation of microfiltration (MF) as the pretreatment step, biofouling in RO could not be eliminated as it only requires a few initial colonies on the membrane surface to form a mature biofilm (Flemming, 2002; Flemming *et al.*, 1997). In fact it has been reported that the majority of the bacterial population involved in the biofilm formation are viable but non culturable (VBNC) and are about 0.2 μm in size (Winters, 2005). In order to survive, these recalcitrant bacteria when entering the RO system, adhere to the membrane surface, resuscitate (convert from non-culturable state to culturable form), multiply and secrete extracellular polymeric substances (EPS), and eventually form a mature biofilm. The situation is aggravated with poor anti-fouling strategies that tend to target only the microorganisms but not the EPS, which is the foundation of a biofilm (Flemming, 1997; 2002). Since it seems virtually impossible to eradicate the

biofouling problem in the RO process, a fundamental understanding of the biofouling development is crucial as such an effective tactic can be implemented to minimize the impact of biofouling on the membrane performance.

Over the years, many studies have been carried out to offer insight into biofouling in membrane processes (MF/UF/NF/RO). Most of the research work has focused on the initial stage of fouling, which is governed by the transport of bacteria cells to the membrane surface and followed by attachment. Commonly, the micron-sized bacteria are treated as colloidal particles, such that the transport of bacteria is analogous to a simple colloidal transport mechanism, e.g. the shear-induced diffusion model (Li *et al.*, 2003a). However, it should be remembered that in reality the bacteria cells are semi-solids and have an overall irregular shape due to the flagella, which can assist in the bacteria movement. However, the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory for colloid stability, which accounts for van der Waals and repulsive electrostatic double layer interaction (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) and Lewis acid-base (AB) interaction (van Oss, 1993), has been applied to explain the bacteria attachment onto a membrane surface (Kang *et al.*, 2004; Wang *et al.*, 2005). The primary role of EPS in the attachment process should not be excluded, as the actual component that comes in contact with the membrane surface is indeed the EPS.

Notwithstanding the complexity in the nature of the bacteria transport and attachment, this step is best described via the concept of critical flux. The critical flux concept was introduced by Field and co-workers for particulate fouling (Field *et al.*, 1995). In the context of biofouling, critical flux refers to the flux level below which negligible cell deposition is observed. However, biofilms are also encountered on surfaces in natural system without imposed flux, so it is rather unrealistic to have a critical flux value under prolonged operation of membrane processes. Instead, a sustainable flux region (Bacchin *et al.*, 2006) is more appropriate, where the growth of the biofilm is considered acceptable; and infrequent cleaning of membrane is required.

Apart from its influence on the transport and attachment step, the concentration polarization (CP) in RO is also a function of flux, J_v as well as the mass transfer coefficient, k_m , via $CP = \exp(J_v/k_m)$. Thus, by varying J_v and k_m , a different

magnitude of CP can be obtained. This will then determine the concentration of solutes and nutrients at the membrane surface. This is important as the attached bacteria multiply at the expense of nutrient. So biofilm growth could be significantly accelerated at high CP level. However, the relationship between biofilm development and flux-mass transfer (or CP) in a RO system is still poorly understood.

The build up of biofilm on the membrane surface induces a hydraulic resistance to the permeation. On top of that, since biofilm is comprised of micron-sized bacteria cells embedded in matrix of EPS (Flemming *et al.*, 2000), where the solutes now need to diffuse through the tortuous path in order to back transport to the bulk fluid. A reduction in the effective diffusion means an increase in the CP and hence an enhanced osmotic pressure. This situation is similar to the colloidal fouling, which was reported in Chapter 3. In this case, the enhanced osmotic pressure phenomenon is known as biofilm enhanced osmotic pressure (BEOP), as reported in a recent work (Herzberg and Elimelech, 2007). The consequence of BEOP effect is an additional membrane performance loss on top of the loss caused by biofilm hydraulic resistance. More importantly, the enhanced CP could induce a higher concentration of nutrient at the membrane surface and this would further exacerbate the biofilm growth.

However, only one work on BEOP phenomenon has been reported in the literature (Herzberg and Elimelech, 2007). In that work, a high cell density of late exponential culture of *Pseudomonas aeruginosa* PA01 was inoculated into the RO system with a supply of synthetic wastewater medium (~ 77 ppm TOC) to accelerate biofouling under low crossflow and high initial flux conditions. There was 80% decline in flux in a 24 hours interval. This accelerated biofouling process occurred under conditions that did not mirror the actual biofilms found in practical RO operation as pointed out by the authors, where biofilms are formed through a series of sequential events such as transport, attachment, cell multiplication, secretion of EPS, biofilm maturation and detachment. Also, in this case it was possible that the build up in the biofilm was mainly contributed by the accumulation of suspended bacteria cells rather than from the steady growth of attached cells on the membrane surface.

In addition, the above reported work did not give a quantitative measurement of the actual CP values. The mathematical model developed for the enhanced osmotic pressure estimation in the author's previous works (Hoek and Elimelech, 2003; Hoek *et al.*, 2002; Ng and Elimelech, 2004), which was based on uniform colloidal cake properties, could not be applied here. The BEOP concept in biofouling was deduced from the flux decline data as well as scanning electron microscopy (SEM) image analysis based on biofouling tests with (a) live cells in 14.6 mM wastewater medium (80 % drop in flux in 24 h), (b) dead cells in 14.6 mM wastewater medium (40 % drop in flux in 24 h), and (c) dead cells in 0.01 mM LaCl_3 (10 % drop in flux in 24 h). The explanation was that the SEM images of biofilms obtained from both tests (b) and (c) appeared to have similar porosity, and so the greater flux drop for the higher ionic strength case was due to the BEOP effect. It was further concluded that the cells (without EPS) contributed to BEOP but the contribution of EPS was mainly through an increase in the hydraulic resistance. This was due to the fact that the biofilm of live cells, in test (a), was very compact as revealed in the SEM image while no increase in observed salt passage (no enhanced wall concentration effect) was shown in the salt retention data, but a sharper drop in flux was observed as compared to the biofilm of dead cells, in test (b). It should be noted that this statement is not in agreement with the results obtained from this thesis work (Chapter 3) whereby EPS (using alginate as surrogate for EPS) could also cause an enhanced osmotic pressure effect. Therefore more work on the BEOP effect in biofouling was required.

In this study, a systematic approach was developed to study biofouling in RO. It is difficult to use natural water, e.g. wastewater, as a feed to simulate biofouling in laboratory studies due to the great variations in culture concentrations and compositions over time. This is non-controlled, and non-controllable, which complicates the study of biofouling. To simplify the study, a representative species and laboratory culture media were used. *Pseudomonas fluorescens* was selected as the model bacteria since *Pseudomonas* was the most common species isolated from real world biofilms on RO membranes (Baker and Dudley, 1998; Pang *et al.*, 2005). A steady and continuous low density of culture from a chemostat was injected into the RO system with background ions of sodium chloride as well as Nutrient Broth

(NB) as the carbon source to allow the deposition of bacteria cells and subsequent growth of biofilm on the membrane surface. The system was subjected to different permeate fluxes and crossflow conditions. Here, mature biofilms were formed through a series of sequential events that reflected the real biofouling process in RO.

The experimental work comprised 2 parts. Firstly, the bacteria growth kinetics were studied in batch tests to determine the growth constants at different nutrient concentrations and salinities. This was important as nutrient and salinity variations can occur at the membrane wall due to the dynamics of concentration polarization effects. The second part was the preparation of a chemostat for delivering a continuous and steady culture supply to the RO unit in the biofouling studies to investigate the effect of CP on biofilm growth and the BEOP phenomenon. The sodium chloride tracer response technique, developed in this thesis work to elucidate the enhanced CP effect in a colloidal cake layer (see Chapter 3), was applied here to demonstrate the BEOP phenomenon in a biofilm. In addition, the possible detection of biofouling with the ultrasonic time domain reflectometry (UTDR) technique described in Chapter 6 was explored in this work. Also, a novel fiber optic sensor (FOS) was developed to detect the biofilm and the preliminary findings are reported in Appendix A.

7.2. Materials and methods

7.2.1. Bacteria batch growth tests

All preparation work was performed in a Class II Bio-safety Cabinet (Esco Micro, model Esco Smart Control) to minimise contamination. All glassware and solutions used in the tests were autoclaved in an autoclave (Hirayama, model HV-110) at 121°C and 1 bar for 20 mins.

The bacteria strain, *Pseudomonas fluorescens* (American Type Culture Collection, ATCC 700830), was supplied by Dr. Zhuang Weiqin from the Environmental Engineering Research Centre at Nanyang Technological University in agar plate (solid medium) form. *Pseudomonas* was transferred and sub-cultured in a newly prepared Nutrient Broth (NB) agar plate made from 1 wt% Agar (Becton Dickinson, Bacto) and 8 g/L of Nutrient Broth (Becton Dickinson, Difco) to ensure

healthy and uncontaminated cells. This was done on a weekly basis throughout the whole experimental period.

For the preparation of bacteria stock solution (in liquid medium) for test runs, *Pseudomonas* was first transferred from the agar plate to a 50 mL centrifuge tube of NB and NaCl solution at concentrations similar to the test solutions and cultivated in a shaker incubator (Daiki, model KBLee 1001) at 25°C and 200 rpm for 24 hrs.

Subsequently, 1 mL of bacteria suspension from the tube was transferred to a 250 mL baffled conical flask (Schott, Duran) filled with NB and NaCl test solutions, and incubated at 25°C and 200 rpm until steady state was reached. Samples were withdrawn periodically for analysis of the biomass content during the growth tests. The concentrations of test solutions were 100, 200, 500, 1000, and 2000 ppm NB and 2000, 4000, 8000, and 10,000 ppm NaCl.

7.2.2. Preparation of chemostat

Figure 7.1: Set up of chemostat for biofouling studies in reverse osmosis

The set up of the chemostat is shown in Figure 7.1. It consisted of a 3 L capacity reactor tank fitted with an aerator (AR Engineering, custom made). Aeration was required to provide adequate mixing as well as for the biological activities oxygen demand. Filtered compressed air for aeration was supplied and monitored with an air flow meter (Cole Parmer, model CZ-03217-20). The reactor

top cover contained an air inlet and outlet for purging the waste gas produced from the biological reaction, a nutrient inlet and outlet to a waste container (this port was also used as a sampling point), and an outlet to the bacteria injection pump. The sterile nutrient from a 5 L container (Schott, model Duran) was delivered to the chemostat by a multi-channel peristaltic pump (Cole Parmer, model Masterflex L/S) through a 0.45 μm filter (Millipore, model HAW04700). To ensure a constant volume reactor, an equivalent amount of bacteria solution was withdrawn and discarded into a waste container. However, during the biofouling tests, no solution was discarded, but instead the bacteria solution was injected into the RO system through the bacteria injection pump.

The chemostat was started as a batch reactor. The preparation of *Pseudomonas* stock solution was similar to the growth tests as described above, and at a concentration of 200 ppm NB and 2000 ppm NaCl. After reaching a mid-exponential growth phase, corresponding to an optical density of ~ 0.08 at $\lambda = 660$ nm, the bacteria stock solution was transferred from the centrifuge tube to the chemostat, and filled with 2 L of 200 ppm NB and 2000 ppm NaCl. The bacteria were allowed to grow in the chemostat as a batch system for 24 hrs with aeration rate set at 1 L/min. After 24 hrs of incubation, a continuous supply of nutrient was pumped into the chemostat. The flow rate of nutrient supply was set at 1:500 dilution ratio based on the crossflow requirement in the RO biofouling experiment, e.g. if the crossflow in the fouling test run was set at 500 mL/min, then the nutrient supply was set at 1 mL/min. At the same time, an equal amount of the bacteria solution in the chemostat was either withdrawn and discarded or injected into the RO system for biofouling studies. Samples were withdrawn routinely for the analysis of pH, biomass, EPS, and TOC content. In addition, the content in the chemostat was checked for its bacterial community.

7.2.3. Biofouling experiment in reverse osmosis

7.2.3.1. Experimental set up for RO biofouling

The set up of the biofouling experiment is shown in Figure 7.2. The reverse osmosis test unit was similar to the set up described in Chapter 3 and 6, but with additional items. The chemostat (as described in Section 7.2.2.) and bacteria

injection pump (LMI Milton Roy, model HH925-987) were to provide a continuous supply of bacteria culture for the biofouling tests. There were two units of RO cell used in series, which allowed the experiments at different fluxes to be carried out simultaneously. This was essential for easy comparison of results, as it was often difficult to obtain reproducible biofilms on the membrane. In addition, microfilter cartridges were installed on the bypass line ($0.22\ \mu\text{m}$ filter (Filtrex Technology)) as well as the retentate return line ($5\ \mu\text{m}$ followed by $0.22\ \mu\text{m}$ filter (Filtrex Technology)). The purpose of using the microfilters was to remove the excess bacteria that did not deposit on the membrane from circulating in the system, which prevented the feed tank from turning into an active bioreactor, as the aim was to simulate biofilm growth on the RO membrane surface only.

Figure 7.2: Reverse osmosis set up for biofouling studies

7.2.3.2. Experimental procedure and test conditions for RO biofouling

The biofouling experimental protocol was as follows: 1) membrane compaction, 2) addition of background NaCl solution, 3) addition of NB to feed tank, 4)

continuous injection of bacteria culture to process line, 5) biofouling of RO membrane, and 6) cleaning of system upon completion of fouling test.

The membrane compaction and equilibration with NaCl solution steps were similar to the procedures outlined in Chapter 3. Following the NaCl equilibration step, 20 ppm of NB or equivalent to ~ 6 ppm TOC (this concentration of nutrient was used in all RO biofouling tests) was added to the feed tank and the system was left to equilibrate for 1 h. No change in the TMP was observed during that period.

To initiate the fouling test, bacteria culture from the chemostat was injected continuously into the RO system at a dilution rate of 1:500 based on the feed crossflow rate. Biofilm was allowed to grow on the RO membrane. Samples from the feed tank and permeate were withdrawn routinely for analysis of the pH, biomass, EPS, and TOC content. Several sodium chloride tracer response tests and UTDR measurements were made during the fouling period, and the procedure was similar to those described in Chapter 3 and 6, respectively. During the tracer test, the 20 ppm NB and 2000 ppm NaCl solution was topped up in order to maintain constant volume in the feed tank.

Upon completion of the biofouling test, which lasted between 100 – 150 hours, the RO system was cleaned with: 1) Milli-Q water adjusted to pH 11 with NaOH (Merck) for 5 hrs, 2) Milli-Q water adjusted to pH 2 with HNO₃ (Merck) for 5 hrs, 3) 3 cycles of rinsing with Milli-Q water at unadjusted pH.

In addition, the fouled membrane was removed from the RO cell and the biofilm on the membrane was extracted and analyzed for the biological contents. The membrane coupon was first cut into 14 segments (labelled as No. 1 to 14 from the feed inlet to outlet) with a size of 6 X 2 cm per segment, and each segment was soaked in 50 mL of sterile Milli-Q water in a centrifuge tube. The tubes were sonicated in a sonicator (Elma, model Transsonic T780) for 1 minute to remove the attached biofilm. 1 mL of the solution was removed for plate counts and bacterial community analysis. Then 1 mL of 1.0 N NaOH solution was added to the remaining solution (for EPS extraction purpose) and left in the fridge at 4°C for 24 hours before analyzed for TOC and EPS contents.

Biofouling tests were conducted at constant flux mode, at flux levels of 15, 35, and 40 L/m²h at a crossflow velocity of 0.23 m/s. A second set of experiment was at flux levels of 10, 25, and 30 L/m²h at a crossflow velocity of 0.10 m/s.

7.2.4. Analytical method

7.2.4.1. Total biomass

Bacteria content in the solution was monitored via optical density measurement with a UV/VIS spectrophotometer (Jasco, model V-550) and plate count method. For the optical density method, measurement was made at $\lambda = 660$ nm. In the plate count method, serial dilutions were carried out, and the counting was performed on NB agar plate after 24 hours of incubation time at 25°C in a refrigerated incubator (Velp, model FOC 225I). The optical density data can be expressed in terms of biomass concentration (in units of CFU/mL) through a pre-constructed calibration curve of plate counts on a culture of known optical density as shown in Figure 7.3.

Figure 7.3: Calibration curve for cell density vs. optical density at 660 nm

7.2.4.2. Total organic carbon (TOC) content

The TOC content of the solution was measured with a TOC Analyser (Shimadzu, model TOC VHS-C) after sample treatment; where the sample was first centrifuged (Hettich, model Universal 32R) at 4000 rpm for 10 minutes and then the collected supernatant was filtered with a 0.45 μ m disposable syringe filter (Millipore, model Millex-HA).

7.2.4.3. EPS analysis

Figure 7.4: Calibration curve for (a) glucose concentration vs. absorbance at 490 nm, and (b) BSA concentration vs. absorbance at 562 nm

A modified version of the EPS analysis by Zhang and coworkers (Zhang *et al.*, 1999; Zhang *et al.*, 1998b) was adopted. The bacteria solution consisted of two types of EPS, soluble and bound. The collected bacteria solution (10 mL) was harvested by centrifugation at 4000 rpm at 4 °C for 10 minutes. The supernatant gave the soluble EPS fraction whereas the bound EPS in the pellet was extracted via the chemical method. In this method, 0.6 mL of 8.5 wt% NaCl + 0.22 wt% formaldehyde (Sigma Aldrich) solution and 4.4 mL of Milli-Q water was added to the pellet, and the solution was mixed well and incubated at 4 °C for 1 h. Then, 0.4 mL of 1.0 N NaOH (Merck) and 4.6 mL of Milli-Q water was added to the solution,

and the final solution was mixed well and incubated at 4 °C for 3 hours. After the incubation period, the bound EPS fraction was recovered from the supernatant by centrifugation (Hettich, model Mikro 120) at 13,200 rpm for 20 minutes.

The major component in EPS was made up from polysaccharides and proteins. Polysaccharides were assayed by using the phenol – sulfuric acid method (Dubois *et al.*, 1956), where 1 mL of 5 wt% phenol (Sigma Aldrich) solution and 5 mL of concentrated H₂SO₄ (Merck) were added to 2 mL of sample and mixed thoroughly. The mixed solution was left to stand for 10 minutes at room temperature. Then the polysaccharide concentration was measured against glucose standards (Sigma Aldrich) using absorbance measurement at 490 nm as shown in Figure 7.4 (a).

Proteins were assayed by using commercial Bicinchoninic Acid (BCA) Protein Assay Kit (Pierce, product #23225), where 2 mL of the working reagent (details of the working reagent can be found in the product information sheet by the supplier) was added to 0.1 mL of sample and mixed thoroughly. The mixture was left to stand for 2 hours at room temperature. The protein concentration was measured against bovine serum albumin (BSA) standards using absorbance measurement at 562 nm as shown in Figure 7.4 (b).

7.2.4.4. Bacterial community analysis

The bacterial community analysis via the denaturing gradient gel electrophoresis (DGGE) method was performed with the help of Miss Wu Bing from the School of Civil and Environmental Engineering, Nanyang Technological University. A detailed procedure, which was prepared by Miss Wu Bing, can be found in Appendix B.

7.3. Results and discussion

7.3.1. Bacteria batch growth tests

Figure 7.5 shows the microbial growth in batch tests at various NB concentrations in 2000 ppm NaCl. It was observed that under usual circumstances, the growth of bacteria could be expressed with a lag phase, exponential growth, and stationary phase (Maier *et al.*, 2000). During the lag phase, the bacteria adjusted to the local environment after inoculation into the culture media. This was followed

by an exponential growth phase, whereby the population density increased exponentially with time. This rapid growth phase lasted about 5 to 6 hours, before reaching a stationary state.

Figure 7.5: Growth curve of *Pseudomonas fluorescens* in 2000 ppm background NaCl at different concentrations of Nutrient Broth (NB)

It was evident that the microbial growth rate increased with increasing nutrient supply. The rate of microbial growth was proportional to the amount of biomass in the system, and could be represented by the simple first order rate equation (Characklis, 1990a):

$$\frac{\partial C_{\text{bio}}}{\partial t} = \mu_{\text{bio}} C_{\text{bio}}$$

or

$$C_{\text{bio}} = C_{\text{bio},0} \exp(\mu_{\text{bio}} t) \quad \text{Eq. (7.1)}$$

where μ_{bio} is the specific growth rate; and C_{bio} is the biomass concentration, which in this case is the optical density reading at 660 nm. This equation described the exponential growth and was valid as long as the environmental conditions remained constant and the system was under balanced growth. Therefore by fitting the best-fit curve on the exponential growth phase, μ_{bio} could be determined.

An example of the curve fitting method by using commercial mathematical software, SigmaPlot 8.0 (Systat Software Inc.), is shown in Figure 7.6 (a). In this particular example at 1000 ppm NB, the calculated μ_{bio} was 0.7475 h^{-1} . After

obtaining the specific growth rates at different nutrient levels (denoted as N), a curve of μ_{bio} vs. N was plotted as shown in Figure 7.6 (b) in order to determine the maximum specific growth rate, $\mu_{\text{bio-max}}$, of *Pseudomonas fluorescens* based on the Monod kinetic (Characklis, 1990a):

$$\mu_{\text{bio}} = \frac{\mu_{\text{bio-max}} N}{K_N + N} \quad \text{Eq. (7.2)}$$

where K_N is the saturation constant of NB. The Monod kinetic is important in studying the biofilm as it is the most commonly used expression to represent the generation of bacteria in biofilm modeling (Characklis, 1990a).

Figure 7.6: Growth constants for *Pseudomonas fluorescens* (a) curve fitting of exponential growth phase in 1000 ppm NB and 2000 ppm NaCl, and (b) plot of μ_{bio} vs. N

However, it should be noted that the $\mu_{\text{bio-max}}$ determined in this experiment was specifically for the Nutrient Broth as the limiting nutrient source, as such $\mu_{\text{bio}} = f(\text{N})$. The actual specific growth rate would be influenced by many other environmental and physiological factors such as temperature, pH, ionic strength, dissolved oxygen level and concentration of inhibiting substances. For instance, the $\mu_{\text{bio-max}}$ reported in growth tests on nutrient agar plate at 7 °C and 20 % oxygen level was only 0.132 h⁻¹ (Geysen et al., 2005), about 6 times lower than the value obtained in this study. Therefore its application to describe the biofilm growth in the reverse osmosis system has to be used with care; as such the RO biofouling studies should be conducted at similar conditions as those in the batch tests.

Figure 7.7: Effect of ionic strength (expressed in terms of NaCl concentration in ppm) on growth of *Pseudomonas fluorescens* at 200 ppm NB

The effect of ionic strength, expressed in terms of the concentration of NaCl, on the growth rate of *Pseudomonas* in the batch system was investigated. This was an important factor to account for the salt tolerance of the bacteria as well as the biofilm growth rates at the membrane surface under the dynamics of elevated salt concentrations through the enhanced concentration polarization effect due to membrane biofouling. From Figure 7.7, it was found that the viability of *Pseudomonas* was not significantly affected by a change in the ionic strength of solution for concentrations up to 10,000 ppm NaCl, which covered the range of concentrations of NaCl tested for RO biofouling experiments in this thesis. Thus,

the growth constants determined for bacteria growth in 2000 ppm NaCl was applied in this thesis to describe the bacteria growth rate at other ionic strengths.

7.3.2. Biofouling in reverse osmosis

7.3.2.1. General observations

An example of the variability of content in a chemostat during the biofouling test runs is presented in Figure 7.8.

Figure 7.8: Variability of content in chemostat for biofouling test at $J_v = 35 \text{ L/m}^2\text{h}$ and $v = 0.23 \text{ m/s}$ (a) OD_{660 nm} and TOC, and (b) Total EPS, total polysaccharides and total protein

The average biomass content recorded over a period of 150 hours based on optical density measurement at 660 nm was ~ 0.08 , which was similar to the

reading at steady state in the batch test at 200 ppm NB. In general, the values of TOC, total EPS, polysaccharides and protein remained constant, with less than about 10 % variation throughout the experiment. Such conditions would have ensured that the bacteria culture injected into the RO system for biofouling studies were consistent in their physiological properties. This was critical to obtain a reproducible biofilm on the membrane.

Meanwhile the solution in the feed tank was free from uncontrolled microbial growth with the installation of microfilters on the process streams that removed the excess bacteria, so that the optical density reading was near zero throughout the experiment as indicated in Figure 7.9. This was also supported by the TOC (between 2 – 6 ppm) and Total EPS (non detected) measurements, where the TOC in the feed tank came solely from the NB and not from the microbial products secreted by the microorganisms during metabolism activities. It should be noted that the decrease in TOC content of bulk solution (from 6 to 2 ppm in a duration of 12 hours) was mainly due to consumption of nutrients by bacteria attached on the membrane as well as possible adsorption of nutrient molecules onto the membrane surfaces. The TOC concentration returned to the original level during the sodium chloride tracer response test when fresh feed solution was topped up.

Figure 7.9: Variability of content in feed tank for biofouling test at $J_v = 35 \text{ L/m}^2\text{h}$ and $v = 0.23 \text{ m/s}$

Therefore, the system in this thesis was only exposed to a bulk solution with uniform chemical, physical and biological properties for the formation of a

reproducible biofilm, unlike the previous studies (Herzberg and Elimelech, 2007; Ivnitsky *et al.*, 2005) where the feed tank was allowed to turn into an active bioreactor and thus the solution properties varied with time. Under such conditions, the fouling of membrane was expected to be severe at the beginning and cease when the nutrient supply was exhausted (no fresh solutions were topped up in those studies). Such an approach had a disadvantage, as biofilm formation was uncontrolled.

7.3.2.2. Biofilm enhanced osmotic pressure (BEOP) phenomenon in RO biofouling

Figure 7.10: Profile of (a) CP, and (b) R_f in biofouling tests at $v = 0.23 \text{ m/s}$

With a continuous supply of nutrient and continuous inoculation of bacteria to the RO system, the biofilm slowly built up and consequently caused an increase in the transmembrane pressure (TMP) in fixed flux operation. The variations in CP levels over time were determined quantitatively from the sodium chloride tracer response technique and are presented in Figure 7.10 (a) and Figure 7.11 (a) at $v = 0.23$ and 0.10 m/s, respectively.

Figure 7.11: Profile of (a) CP, and (b) R_f in biofouling tests at $v = 0.10$ m/s

The results directly confirmed the existence of biofilm enhanced osmotic pressure (BEOP) phenomenon in RO biofouling. Similar to the colloidal fouling in RO, the solute back transport was hindered due the presence of an unstirred layer of biofilm on the membrane. As a result, the overall membrane performance loss was contributed predominantly by the BEOP effect (between 50 to 70 %) and partially

by the build up in the hydraulic resistance of biofilm (see Figure 7.10 (b) and Figure 7.11 (b)).

Also, It was found that the BEOP effect was more profound at higher flux operation e.g. $\partial\text{CP}/\partial t$ increased from 0.0014 to 0.0053 h^{-1} when the flux level was increased from 35 to 40 $\text{L}/\text{m}^2\text{h}$ at $v = 0.23$ m/s (see Figure 7.12), due to the formation of a thicker biofilm layer. However, it was interesting to note that increasing the crossflow velocity generally reduced the degree of fouling when operated at the same flux level, but the improvement in the membrane performance was significantly less than for colloidal silica fouling, which was reported in Chapter 3. For example, in colloidal silica fouling, when the crossflow velocity was doubled, from 0.10 to 0.23 m/s , there was a 10-fold reduction in $\partial\text{CP}/\partial t$ (see Figure 3.15). However in the RO biofouling, the $\partial\text{CP}/\partial t$ values were of the same order of magnitude at both crossflow velocities as shown in Figure 7.12.

Figure 7.12: Plot of $\partial\text{CP}/\partial t$ vs. J_v at different crossflow velocities

The explanation is that in colloidal fouling, crossflow velocity or shear played a critical role in the accumulation of deposit through the control of the fractional deposition of the silica colloids onto the membrane, e.g. only 10 % of particle deposition was observed at higher crossflow (see Figure 4.7). Since $\partial\text{CP}/\partial t$ was a function of the amount of deposit, the relative extent of $\partial\text{CP}/\partial t$ was also a function of the crossflow velocity. However, in RO biofouling, it is postulated that the

contribution of direct deposition of suspended bacteria cells to the total accumulation of biofilm on the membrane surface was relatively low, as compared to the contribution from the growth of attached bacteria cells. Even with a low deposition initially, the biofilm could build up to reach a thick layer. Therefore, $\partial CP/\partial t$ in biofouling was not considerably influenced by the crossflow velocity.

7.3.2.3. Role of concentration polarization (CP) on RO biofouling

Figure 7.13: Summary of (a) $\partial R_f/\partial t$, and (b) $\partial CP/\partial t$ vs. $CP(0)$ for biofouling tests

An assessment of the role of CP upon RO biofouling was carried out by comparing the membrane performance at the same initial CP level. Tests for both

sets of experiment at $J_v = 10, 25$ and $30 \text{ L/m}^2\text{h}$ and $v = 0.10 \text{ m/s}$ and $J_v = 15, 35$ and $40 \text{ L/m}^2\text{h}$ and $v = 0.23 \text{ m/s}$ corresponded to the initial CP values of $\sim 1.3, 2.0$, and 2.2 , respectively. It was found that at the same initial CP level, there was a near-equal rate of build up in the biofilm resistance, $\partial R_f / \partial t$, as depicted in Figure 7.13 (a). Presumably, this was because at the same initial CP level, the membrane surface was exposed to same amount of nutrient, and since microorganism proliferation was dependent on the nutrient availability, the biofilm growth rate as well as the hydraulic resistance increase was expected to be the same. The above results suggested that RO biofouling development was a function of CP level, which was controlled by the exponential ratio of flux-mass transfer, or $CP = \exp(J_v/k_m)$. In other words, the effect of crossflow velocity (k_m is a function of v according to Eq. 5.10) upon the biofilm growth was through the interplay of CP and nutrient level rather than through its influence on the direct deposition of bacteria cell on the membrane surface. It should be noted that a slight deviation from a linear increase in $\partial R_f / \partial t$ value with increasing $CP(0)$ value (Figure 7.13 (a)) was simply due to the non-linear increase in growth rate as a function of nutrient concentration as depicted in Figure 7.6.

In addition, it should be noted that the trend displayed by the plot of $\partial CP / \partial t$ vs. $CP(0)$ (Figure 7.13 (b)) was not as expected. At the same initial CP value, for higher crossflow velocity, J_v was also higher. As a result, $\partial CP / \partial t$ should be higher when the amount of biofilms in both cases was similar, according to the fouling model developed in Chapter 5 (results from simulation using silica colloids at $CP(0) \approx 2.2$ are shown in Figure 7.14). However, the experimental results showed negligible differences in the $\partial CP / \partial t$ values at the same initial CP levels under different crossflow conditions. One possible explanation was that apart from the influence of flux and thickness of biofilm, the effective mass transfer of solutes and hence $\partial CP / \partial t$ was also a function of the tortuosity factor of the biofilm (see Eq. 5.17)). The tortuosity of the biofilm was much more complex, unlike the uniform colloidal silica deposit layer where it could be easily predicted via Eq. (5.14). It has been generally recognized that the tortuosity factor of the biofilm is related to its density and porosity (Melo, 2005; Stewart, 2003). However, no simple calculation

was developed to account for its value. Such uncertainties in the tortuosity factor might cause the deviation of experimental data from the simulation results. A second explanation was that the degree of $\partial CP/\partial t$ was very sensitive to the amount of biofilm. As shown in Figure 7.14, at lower deposit thickness, the differences in the CP values at both crossflow conditions were smaller, but the deviations were greater as δ_c increased. So, it was possible that the biofilms in this study were relatively too thin to see an obvious difference in the $\partial CP/\partial t$ value. Furthermore, the mathematical model developed in Chapter 5 was for a uniform cake layer. Hence, deviation in results could be expected, as biofilm was rather patchy and uneven as supported by the membrane autopsies results in Section 7.3.2.5.

Note: A slight difference in the R_f values at equal amount of biofilm was due to the effect of NaCl concentrations upon the specific cake resistance

Figure 7.14: Simulation of silica fouling at initial CP of ~ 2.2 . (a) CP, and (b) R_f profile during deposit build up (expressed in terms of cake thickness)

7.3.2.4. Critical or sustainable flux

Based on the CP and R_f profiles as shown in Figure 7.10 and 7.11, even at a very low flux of 10 L/m²h, minor increases in CP and R_f values were detected. This outcome suggests that it was unlikely to have a critical flux value (no fouling or increase in TMP below this value) under prolong operation of RO in the case of biofouling. However at this low flux level, the fouling rate was low and this region could be considered the sustainable flux region for this feed where the operational life of RO membrane could be extended.

7.3.2.5. Analysis of biofilms on RO membrane

Membrane autopsy was carried out at the end of the fouling tests to characterize the biofilm formed on the membrane. The major component of the biofilm was EPS, which consisted mainly of polysaccharides and proteins. The distribution of EPS along the membrane coupons for biofouling tests at $v = 0.23$ m/s under different flux levels are presented in Figure 7.15 and the average values are summarized in Figure 7.16. At a glance, the EPS was non-uniformly distributed along the membrane surface with no obvious distribution pattern even though under constant flux operation. This could be due to the uneven membrane surface roughness or local permeability that promoted preferential sorption sites for the bacteria deposition and subsequent growth. Despite that, the autopsy results supported the hypothesis that higher operational flux produces greater amounts of biofilm (represented by higher concentrations of EPS) in Figure 7.15 (c) and 7.16.

The data of hydraulic resistance of biofilm, R_f , from Figure 7.10 (b), and the total EPS (TOC) from Figure 7.16 were used to estimate the specific cake resistance of the biofilm, α_f , based on $R_f = \alpha_f m_f$. An average value of $1.3 \pm 0.5 \times 10^{16}$ m/kg was obtained and this value was higher than the reported value of 0.5×10^{16} m/kg for alginate, which was a surrogate for EPS (Ye *et al.*, 2005). The explanations for the difference in values are as following. Firstly, the natural biofilm has a consortium of bacteria cells and EPS with a composite structure, which has a more complex effective particle size and porosity as compared to the alginate gel layer. The second reason may be due to the compressibility of the biofilm layer as a

function of pressure, where the specific cake resistance of the alginate layer was measured at a much lower operating pressure of 1 bar.

(a)

(b)

(c)

Figure 7.15: Distribution of EPS on RO membrane in biofouling tests at $v = 0.23 \text{ m/s}$ and J_v of (a) 15, (b) 35, and (c) 40 $\text{L/m}^2\text{h}$

Figure 7.16: Summary of results from membrane autopsy in biofouling tests at $v = 0.23$ m/s

Figure 7.17: Bacterial population in biofilm extracted from RO membrane and chemostat in biofouling test at $v = 0.23$ m/s

In addition to the EPS analysis, the bacterial population in the biofilm and chemostat was checked using the DGGE method. It was found that more than one species were actually present in the chemostat and biofilm on the membrane. This was not unexpected, as the surrounding environment of the chemostat and the RO test unit was not fully sterilized. Also, contamination could have occurred while

handling the equipment. Despite that, the dominant species identified on the membrane surface were the same as found in the chemostat as shown in Figure 7.17, which was indicated by a darker line.

7.3.2.6. Simple RO biofouling model

A simple model was developed to predict the performance of the membrane in RO biofouling. It was assumed that the net biofilm formation rate, $\partial m_{\text{bio}}/\partial t$, was the summation of the bacteria deposition rate, $\partial m_{\text{D}}/\partial t$, biofilm growth rate, $\partial m_{\text{G}}/\partial t$, and biofilm removal rate, $\partial m_{\text{R}}/\partial t$, as follows:

$$\frac{\partial m_{\text{bio}}}{\partial t} = \frac{\partial m_{\text{D}}}{\partial t} + \frac{\partial m_{\text{G}}}{\partial t} - \frac{\partial m_{\text{R}}}{\partial t} \quad \text{Eq. (7.3)}$$

However, the deposition term was assumed to be only important in the initial stages of fouling, where at a later stage the biofilm growth term was dominant. Also, the actual biofilm density was much higher than the low-concentration culture injected into the system. Thus the contribution of the deposition term upon the overall increase in the biofilm formation rate was negligible and hence was omitted. Meanwhile the biofilm growth term was related to the multiplication of bacteria cells attached to the membrane surface and subsequent production of EPS, which could be estimated by the Monod kinetics (Eq. (7.2)), a factor that has been commonly used in biofilm modeling (Chaudry and Beg, 1998; Eberl and Efendiev, 2003; Horn and Hempel, 1998). In addition, the removal term determines the relative extent of the fouling process. It was a function of fluid shear stress (Stoodley *et al.*, 2001). However, the removal of biofilm would have been relatively insignificant at the beginning as the removal term is proportional to the amount of biofilm on the membrane. Also, it has been reported that nutrient starvation can be a potential trigger for biofilm detachment (Hunt *et al.*, 2004), which was unlikely to occur in the RO process as the nutrient concentration at the membrane wall was indeed enriched under the CP effect. Thus, it was assumed that the biofilm was thin enough and there was a continuous supply of nutrients to allow exclusion of the removal term in the equation.

Therefore, based on the above assumptions, the net biofilm formation only relied on the biofilm growth rate; and as such Eq. (7.3) could be written as:

$$\frac{\partial m_{\text{bio}}}{\partial t} = \frac{\partial m_{\text{G}}}{\partial t} = Y_{\text{bio/NB}} \mu_{\text{bio}} m_{\text{bio}} = Y_{\text{bio/NB}} \left(\frac{\mu_{\text{bio-max}} N_{\text{w}}}{K_{\text{N}} + N_{\text{w}}} \right) m_{\text{bio}} \quad \text{Eq. (7.4)}$$

where $Y_{\text{bio/NB}}$ was the yield coefficient for kg of biomass produced per kg NB, and N_{w} was the concentration of nutrient (in this case NB) at the membrane wall. The growth constants were obtained from the batch growth test as reported in Section 7.3.1., whereas N_{w} was related to the bulk concentration and CP. The CP values determined from the sodium chloride tracer response technique were for NaCl, but the CP values for NB could be deduced from the CP-mass transfer-diffusion relationship based on Eq. (5.4) and Eq. (5.10). Since,

$$\left(\frac{k_{\text{m, NaCl}}}{k_{\text{m, NB}}} \right) = \left(\frac{D_{\text{NaCl}}}{D_{\text{NB}}} \right)^{2/3} \quad \text{Eq. (7.5)}$$

so,

$$\frac{N_{\text{w}}}{N_{\text{b}}} = \text{CP}_{\text{NB}} = \text{CP} \left(\frac{D_{\text{NaCl}}}{D_{\text{NB}}} \right)^{2/3} \quad \text{Eq. (7.6)}$$

for full retention of NB by the RO membrane, which was confirmed by the TOC measurements. The diffusion data of NB was not available, so the diffusion of glucose in water was used as an approximation, which was $6.7 \times 10^{-10} \text{ m}^2/\text{s}$ at 25°C (Stewart, 2003). Based on $D_{\text{NaCl}} = 1.6 \times 10^{-9} \text{ m}^2/\text{s}$ at 25°C (Lide, 2007), so $N_{\text{w}} = N_{\text{b}} \text{CP}^{1.8}$. So, Eq. (7.4) could be re-written as:

$$\frac{\partial m_{\text{bio}}}{\partial t} = Y_{\text{bio/NB}} \left(\frac{\mu_{\text{bio-max}} N_{\text{b}} \text{CP}^{1.8}}{K_{\text{N}} + N_{\text{b}} \text{CP}^{1.8}} \right) m_{\text{bio}}$$

or

$$m_{\text{bio}} = m_{\text{bio, 0}} \exp \left\{ Y_{\text{bio/NB}} \left(\frac{\mu_{\text{bio-max}} N_{\text{b}} \text{CP}^{1.8}}{K_{\text{N}} + N_{\text{b}} \text{CP}^{1.8}} \right) t \right\} \quad \text{Eq. (7.7)}$$

However, based on the above equation, the biofilm formation rate and hence the build up of hydraulic resistance of the biofilm should follow an exponential trend. But the results from the tracer response technique showed a near-linear increase in R_{f} (Figure 7.10 and 7.11). A probable reason was that the experiment was not long enough to observe the exponential increase in the R_{f} values. To check this, a repeated test of 300 hours of run time at $J_{\text{v}} = 35 \text{ L/m}^2\text{h}$ and $v = 0.23 \text{ m/s}$ (Figure 7.18) showed an exponential increase in R_{f} . At the same time, CP values also

increased exponentially due to the enhanced effect under the greater amount of biofilm.

Figure 7.18: CP and R_f profile of repeated run of biofouling test at $J_v = 35 \text{ L/m}^2\text{h}$ and $v = 0.23 \text{ m/s}$

Including the resistance in series model (Eq. (5.20)) and the specific resistance of the biofilm (Eq. (5.25)) into Eq. (7.7), yields:

$$R_f = \left[\frac{\text{TMP} - \text{CP}\Delta\Pi_b}{\mu J_v} \right] - R_m = \alpha_f m_{\text{bio},0} \exp \left\{ Y_{\text{bio/NB}} \left(\frac{\mu_{\text{bio-max}} N_b \text{CP}^{1.8}}{K_N + N_b \text{CP}^{1.8}} \right) t \right\} \quad \text{Eq. (7.7)}$$

The parameters used to fit the model in order to calculate the TMP profile are given in Table 7.1 and the results are compared against the experimental data in Figure 7.19 for $J_v = 35 \text{ L/m}^2\text{h}$ and $v = 0.23 \text{ m/s}$. The model captures the overall trend but shows a steeper exponential rise. There are a number of factors that may have contributed to the discrepancies between the experimental and fitted data. Firstly, the bulk concentration nutrient was assumed to be constant, which in fact was fluctuating due to the adsorption on membrane surface and the consumption by bacteria and it only returned to the original value when the feed solution was topped up during the tracer test. Also, error could come from the assumption that the specific resistance of the biofilm was constant. In reality, α_f (which was a function of biofilm porosity, particle size and density) would change due to the secretion of EPS, which has a wide range of “particle sizes”, and these EPS could fill up the pores within the biofilm matrix. Also, the model might have been over-simplified

by omitting the deposition and removal terms. Nevertheless, the simulations give a total biomass of $\sim 0.030 \text{ mg/cm}^2$ at 150 h, which agrees well with the autopsy result of $\sim 0.027 \text{ mg/cm}^2$ of EPS (assuming the major component of the biofilm was EPS).

Figure 7.19: Comparison of TMP profile between experimental data and fitted model at $J_v = 35 \text{ L/m}^2\text{h}$ and $v = 0.23 \text{ m/s}$

Table 7.1: Input parameters for biofouling model simulations

<i>Input Parameters</i>	
$\mu_{\text{bio-max}} = 0.787 \text{ h}^{-1}$	$N_b = 20 \text{ ppm}$
$K_N = 52.5 \text{ ppm}$	$Y_{\text{bio/NB}} = 0.15 \text{ (assumed)}$
$m_{\text{cell},0} = 5 \times 10^7 \text{ cell/m}^2 \text{ (assumed)}$	$m_{\text{cell}} = 1.0 \times 10^{-13} \text{ g/cell}$
$m_{\text{bio},0} = m_{\text{cell},0} \times m_{\text{cell}} = 5 \times 10^{-6} \text{ g/m}^2$	$\alpha_f = 1.3 \times 10^{16} \text{ m/kg}$
$R_m = 1.0 \times 10^{14} \text{ m}^{-1}$	$\mu = 1 \times 10^{-3} \text{ Pa.s}$

7.3.3. Ultrasonic detection for biofouling

The ultrasonic frequency domain reflectometry (UFDR) method was applied to detect biofilm formation on the RO membrane. The relative total reflected power, TRP_R , data for the biofouling test at $v = 0.23 \text{ m/s}$ is presented in Figure 7.20. In general, the ultrasonic technique did show a positive response when biofilm was built up on the membrane surface. However, the UFDR measurements gave a poor detection of biofilm on the membrane, where the overall changes in the TRP_R signal were below 10 %. This was anticipated since such low sensitivity in the ultrasonic detection was also observed in the alginate fouling as revealed in Chapter 6. Also,

the data points were scattered and the R^2 of the best-fit curve was much less 0.6. In addition, the signals obtained at $J_v = 15 \text{ L/m}^2\text{h}$ appeared to be higher than at $J_v = 35$ and $40 \text{ L/m}^2\text{h}$. A possible explanation was due to the non-homogeneity of the biofilm structure as well as the non-uniform distribution (patchy coverage) of biofilm along the membrane surface (which was supported by the membrane autopsy results shown in Figure 7.15) that resulted in variability in the acoustic responses that were sensitive to the local region of the reflecting surface. An average value from multi-points scanning along the membrane could reduce such error.

Figure 7.20: Ultrasonic detection (expressed in terms of relative total reflected power, TRP_R) of biofilm in RO biofouling tests at $v = 0.23 \text{ m/s}$

In addition, it should be noted that the increasing trend of TRP_R with increasing biofilm accumulation was in agreement with the trend observed in the alginate fouling (Chapter 6). However, this trend was opposite to the decreasing trend of TRP_R observed in biofilm detection on polymeric material surfaces reported in a recent publication (Kujundzic *et al.*, 2007). The major difference in the former study and the current work that could gave the distinctive observation was that the biofilms were grown on coupons in an annular bioreactor without being subjected to permeation flux and high pressure operation. The coupons with mature biofilms were removed from the bioreactor and placed in a water bath, and acoustic monitoring was executed by using an spherically focused 20 MHz immersion

transducer. The low density of biofilms formed on the coupons (introduction of low density new interfaces) attenuated the reflection energies hence lower TRP values were detected (Kujundzic *et al.*, 2007). However in this study, the signals obtained reflected not only the consolidation of the biofilm due to growth on the membrane surface but also the compaction of membrane under increasing TMP effect due to fouling in fixed flux operation, which was not encountered in previous study. Here, the membrane bulk density increased and therefore reflection energy increased due to 'harder' reflection (Greenberg *et al.*, 2006).

7.4. Concluding remarks

A systematic protocol was developed to study RO biofouling. The biofilm enhanced osmotic pressure (BEOP) phenomenon was confirmed with the sodium chloride tracer response technique. BEOP effect was more severe at higher flux operation. In addition, it was found that the growth of biofilm on the membrane surface was controlled by the level of concentration polarization (CP) through the interplay between CP and nutrient concentrations at the membrane wall. The tracer test results were corroborated by membrane autopsy data where greater amounts of EPS were extracted from the membrane operated at higher flux (or CP level). The data obtained from this thesis on UTDR only serves as a preliminary result for the application of the ultrasonic method to biofouling detection in the RO process. The poor statistics in the data obtained were associated with the nature of the variability in biofilm. However, the data did demonstrate a shift in the reflected power with increasing amount of biofilm. More work needs to be done to further explore its application in monitoring biofouling in the RO process.

CHAPTER 8

Summary, Conclusions and Recommendations

8.1. Summary and conclusions

Reverse osmosis (RO) technology is widely used in the desalination and reclamation industry to produce high quality water from seawater, brackish or wastewater. This is especially crucial to a water scarce country like Singapore. In Singapore, RO plays a critical role in NEWater production as well as in the seawater desalination plant. Productivity loss, and therefore an increase in production costs due to membrane fouling is a bottleneck of RO technology. The most common fouling in RO is colloidal and biofouling. Successful fouling minimization or control requires a fundamental understanding of the inter-relationships between the fouling process and parameters such as operational flux, J_v , and mass transfer, k_m , in the RO system, which is represented by the concentration polarization (CP) through the relationship $CP = \exp(J_v/k_m)$. In addition, to be able to take immediate counter measures to prevent or limit fouling, a non-invasive monitoring tool that detects early stages of fouling is crucial.

An extensive literature review on colloidal and biofouling as well as available techniques to monitor fouling process were summarised in Chapter 2.

In Chapter 3, a novel sodium chloride tracer response technique was employed to elucidate the cake enhanced osmotic pressure (CEOP) effect in an unstirred layer of deposit originated from sub-micron sized silica colloids and alginic acid, which was used as a surrogate for extracellular polymeric substances (EPS) in a biofilm. The CEOP effect arises due to the hindered back diffusion of solutes through the tortuous path in the fouling layer. This results in an increase in the accumulation of solutes at the membrane surface, hence increasing the osmotic pressure, which causes a loss in the effective transmembrane pressure. It was revealed that the CEOP effect was most significant at high flux and low crossflow conditions.

In Chapter 4, the sodium chloride tracer response technique was further extended to determine the critical flux of silica colloids in a RO process. It was shown that the critical flux for colloidal deposition was best described in terms of the Peclet number, defined as the ratio of the convective drag force to the back

diffusive force. It was also found that the proportion of particles convected to the membrane that deposited was a function of crossflow velocity, varying from 100 % at low crossflow velocity to about 10 % at high crossflow velocity.

A simple membrane performance predictive model combining the critical flux and CEOP effect in RO was developed and reported in Chapter 5. In summary, for conventional constant flux operation the fouling in terms of rate of deposition, $\partial m_f / \partial t$, was a steady rise but the effect, observed as $\partial \text{TMP} / \partial t$, tended to be accelerating due to the non-linear contribution of CEOP. This happened at high net flux, low crossflow, high particle loading and high salt content. When the particle size was greater than 100 nm, the membrane performance loss due to the CEOP effect was dominant, regardless of other parameters mentioned above. It was also evident that the CEOP effect was greater at fixed flux operation than at fixed pressure operation simply due to the decline in flux, hence dropping the CP level, in the latter situation.

The applicability of the non-invasive ultrasonic technique as a fouling monitor for the development of silica and alginate fouling was validated and discussed in Chapter 6. It was found that the ultrasonic measurement in the frequency domain was sensitive to be used for detecting the alginate fouling layer, which had a poor acoustic contrast as compared to the feed solution. The ultrasonic data was consistent with the data from the TMP measurements as well as the sodium chloride tracer response technique. Both techniques supported the claim that only a small amount of deposit was formed even at high flux operation, and the loss of membrane performance was through the CEOP effect rather than through an additional hydraulic resistance of the fouling layer.

A systematic approach was developed to study the RO biofouling and this reported in Chapter 7. The biofilm enhanced osmotic pressure (BEOP) phenomenon was confirmed with the sodium chloride tracer response technique. The BEOP effect was more severe at higher flux operation due to the greater amount of biofilm formation, which was confirmed by membrane autopsy data. In addition, it was found that the accumulation of biofilm on membrane surface was controlled by the level of concentration polarization (CP) through the interplay between CP and nutrient concentrations at the membrane wall, as the growth factor

was nutrient dependent. Also, preliminary results were obtained for the application of the ultrasonic method in biofouling detection in the RO process. The poor statistics in the data were associated with the nature of the variability and complexity of the biofilm. However, the data did demonstrate a shift in the reflected power with increasing amount of biofilm. Therefore more work need to be done to further explore its application in monitoring biofouling in the RO process.

8.2. Recommendations

Areas of potential and future research are listed below:

- i. The formation of a deposit layer could also cause an enhanced concentration of organics at the membrane surface and hence increase the transmission of organic molecules through the membrane. This poses a threat when the compounds are toxins or priority pollutants. A detailed study on this topic would be of great interest.
- ii. Including the CEOP effect into the spiral wound module (SWM) fouling model developed by Schwinge *et al.* (Schwinge *et al.*, 2002a; Schwinge *et al.*, 2004a) to predict the membrane performance in a RO plant would be useful.
- iii. Further study of critical flux phenomenon is prompted by this study. In particular the supra critical flux deposition factor (the proportion of convected foulant that remains in the deposit layer) appears to vary with surface shear. Study of the effect of operational parameters and particle properties on the deposition factor is called for.
- iv. Improving the ultrasonic technique for fouling detection by performing a multipoint scanning to obtain an average value in order to minimize the error from single point detection.
- v. Characterization of the biofilm structure and morphology with molecular probes to enable estimation of biofilm porosity and tortuosity factor and link these factors to the BEOP effect.
- vi. Developing a 'smart' module combining the sodium chloride tracer response technique and/or the ultrasonic technique and/or a fiber optic fouling sensor in a RO plant to allow online optimization and control of operation and cleaning.

APPENDIX A

Biofilm Detection with Fiber Optic Sensor (FOS)

During the course of this thesis a preliminary attempt was made to develop a fiber optic sensor (FOS) for biofilm detection. This appendix gives the background and preliminary results of this work.

A.1. Background theory

The fiber optic sensor (FOS) can either directly detect the changes of the optical properties or spectral characteristics of an analyte; or use various types of interaction, recognition or reaction process to translate a signal generated by the interaction of analyte with the recognition site into a detectable characteristic optical signal (Holst and Mizaikoff, 2002). Generally, there are two distinct optical configurations for the FOS: tip type and side fiber. In the tip type sensor, the active sensing region is located at the end facet of the fiber, where the fiber acts as a light-guide to and from the analyte or alternatively the fiber provides only excitation light while a second fiber collects the signal (Holst and Mizaikoff, 2002; Rowe-Taitt and Ligler, 2002). The side fiber utilizes the electromagnetic component of light, the evanescent wave, to provide transmission of light to analyte closely associated with, or immobilized onto, a de-clad surface of the fiber core (Rowe-Taitt and Ligler, 2002). The tip type sensor is limited by the surface area of the sensing region and the surface concentration of the analyte; whereas the evanescent wave sensor has a penetration depth of the order of several hundred nanometers, approximately a wavelength, and therefore confines the transducible optical changes to within a discrete distance from the surface of the fiber which limits the interference from the bulk solution (Rowe-Taitt and Ligler, 2002). Because of this uniqueness in sensing method, the evanescent fiber sensor is the preferred choice to be used in biofouling detection.

A.1.1. Evanescent wave

Figure A.1: Evanescent field penetration depth

The basic mechanism behind evanescent wave FOS is total internal reflection. Light propagation in an optical fiber as shown in Figure A.1 and can be described by Snell's law (Rowe-Taitt and Ligler, 2002):

$$n_{\text{core}} \sin \theta_{\text{core}} = n_{\text{clad}} \sin \theta_{\text{clad}} \quad \text{Eq. (A.1)}$$

where n_{core} and n_{clad} are refractive index of the core fiber and cladding, respectively; θ_{core} and θ_{clad} are angle of refraction in the core fiber and cladding, respectively. The critical angle, θ_{crit} , beyond which light is totally reflected, is given by (Rowe-Taitt and Ligler, 2002):

$$\theta_{\text{crit}} = \sin^{-1} (n_{\text{clad}} / n_{\text{core}}) \quad \text{Eq. (A.2)}$$

However light propagation is not confined to the core region but extends into the surrounding cladding as an evanescent wave, which decays exponentially, the $1/e$ distance being called the penetration depth, d_{pen} , and is defined as (Rowe-Taitt and Ligler, 2002):

$$d_{\text{pen}} = \frac{\lambda}{2\pi \sqrt{n_{\text{core}}^2 \sin^2 \theta_{\text{inc}} - n_{\text{clad}}^2}} \quad \text{Eq. (A.3)}$$

where λ is the wavelength of light, and θ_{inc} is the angle of incidence of the reflected light. The value of the penetration depth in a typical cladding is on the order of 100 nm (Lieberman *et al.*, 1993).

When a region of the cladding material is removed from the fiber, that region is exposed and this will allow the deposition of material onto its surface. The deposited material will now act as the cladding material, and hence the signal transmission will be altered due to: 1) the change in refractive index due to different

medium, and 2) the interaction of absorbing species and the evanescent field that leads to the absorption of the evanescent wave by the medium. The application of FOS in detection of a biofilm is based on this change in signal in comparison to the original value.

The power transmitted by an optical fibre, the cladding of which has been replaced locally by an absorbing medium may be written as (Kumar *et al.*, 2002)

$$P_{\text{abs}} = P_0 \exp(-\gamma C_{\text{abs}} L_{\text{unclad}}) \quad \text{Eq. (A.4)}$$

where P_{abs} and P_0 are, respectively, the power transmitted through the fiber with and without an absorbing medium over an unclad portion of length, L_{unclad} ; C_{abs} is the concentration of the absorbing medium; and γ is the evanescent wave absorption coefficient, given by,

$$\gamma = r_f \alpha_m \quad \text{Eq. (A.5)}$$

where r_f is the effective fraction of the total guided power in the sensing region; and α_m is the bulk absorption coefficient of the absorbing species.

In the absence of evanescent wave absorption, the guidance of light through the uncladded region is modulated by changes in the refractive index of the coupling medium. The optical power output through an unclad region of the fiber is (Jose *et al.*, 1998):

$$P_{\text{ref}} = P_0 \left(\frac{n_{\text{core}}^2 - n_{\text{medium}}^2}{n_{\text{core}}^2 - n_{\text{clad}}^2} \right) \quad \text{Eq. (A.6)}$$

A.2. Experimental set up

The first attempt was to test the FOS by forming a layer of biofilm on the unclad section of the fiber without the presence of a membrane. The FOS with 10 cm uncladded section was inserted into a flow chamber (as shown in Figure A.2) through a hole on the sidewall and sealed with epoxy glue to prevent leakage. The flow chamber (AR Engineering, custom made) had a cross section of 0.8 X 0.8 cm.

The schematic diagram of the test unit equipped with FOS for biofilm detection studies is shown in Figure A.2. The chemostat set up was as described in Chapter 7. A peristaltic pump (Cole Parmer, model Masterflex L/S) was used to circulate the test solution in the loop from the chemostat to the flow chamber. The flow rate was

monitored with a flow meter (Gilmont Instrument). The FOS unit consisted of an adjustable 500 mW laser light source with a peak at ~ 660 nm (Intelite, model RS660), a dual channel fiber optic spectrometer (Ocean Optics, model SD2000) and a 1 X 2 Polymethyl methacrylate (PMMA) optical fiber with 1000 μm core diameter (Industrial Fiber Optics, model IF-C-E1000). One fiber was used as reference (denoted as reference fiber) while the other one was for biofilm detection, which was denoted as sample fiber. The intensity of the laser light was recorded with a spectrometer and using the manufacturer's acquisition software.

Figure A.2: Schematic diagram of crossflow test unit with fiber optical sensor (FOS) for biofilm detection

A.3. Experimental procedure and test conditions

The first step was to establish a baseline with Milli-Q water. Milli-Q water was circulated in the loop for about 2 hours before switching over to the test solution from the chemostat. The content in the chemostat was at steady state throughout the experiment with $\text{OD}_{660 \text{ nm}}$ of ~ 0.07 . A biofilm was allowed to grow on the exposed region of the fiber. At the end of the run, the system was thoroughly cleaned with NaOH, HNO_3 and Milli-Q water solutions following a procedure

similar to the RO biofouling test in Chapter 7. Experiments were conducted at crossflow rates of 0.2 and 0.5 L/min.

During initial test, it was found that the stability of the light source and hence the signal's intensity was sensitive to the temperature fluctuations. In order to minimize the fluctuations, the surrounding temperature was controlled at $25 \pm 2^\circ\text{C}$ by air conditioning.

A.4. Results and discussion

Figure A.3: Fiber optic sensor (FOS) for biofilm detection. (a) Intensity profile of reference and sample signal, and (b) Normalized intensity profiles for 3 experimental runs

Typical intensity profiles of the reference and sample signal are shown in Figure A.3 (a). There were fluctuations of about $\pm 3\%$ in the reference signal. To have a better representation, the intensity signal was normalized against the initial value via $(I_{\text{sam}}/I_{\text{sam},0})/(I_{\text{ref}}/I_{\text{ref},0})$, and the data are shown in Figure A.3 (b). Both Run 1 and 2 were at a crossflow of 0.2 L/min while Run 3 was at 0.5 L/min. As seen, at lower crossflow, the shear was lower, thus a thicker biofilm was formed on the fiber. Hence, there was greater interaction between the evanescent wave and the biofilm that resulted in a greater loss of the intensity ($\sim 12\%$ loss). On the other hand, signal loss was relatively lower ($\sim 4\%$ loss) when the crossflow was increased due to lower biofilm formation rate.

To evaluate the method more fully, detailed characterizations of the biofilm formed on the FOS are required and need to be related to the signal loss profile. Further study of the application of the FOS to detect biofouling in a membrane system is recommended.

A.5. Concluding remarks

A preliminary study on the application fiber optic sensor (FOS) for biofilm detection is reported. The results were promising where a thin layer of biofilm was able to cause a significant loss in the intensity of evanescent wave. Further development of the FOS was beyond the scope of this thesis but it warrants more detailed study.

APPENDIX B

Bacterial Community Analysis via Denaturing Gradient Gel Electrophoresis (DGGE)

B.1. Direct lysis PCR conditions

The genomic DNA of the pure culture was extracted by the direct lysis method. Several colonies were picked from the agar plates into a PCR tube and 87 µl lysis buffer was added to the tube. The lysis buffer consisted of 10 mM Tris-HCl, 50 mM KCl, 2 mM MgCl₂ and 0.05% Nonidet P40 (NP40). Then the tube was put in a thermal cycler (Mastercycler, Eppendorf, Germany) for 30 minutes at 98°C. A 5.3 µl mixture including 0.8 µl 200 µM of deoxynucleoside triphosphate (including deoxyadenosine triphosphate, deoxyguanosine triphosphate, deoxythymidine triphosphate, deoxycytidine triphosphate), 2 µl 25 pmol forward primer Eubac27F (5'-AGAGTTTGATCCTGGCTCAG-3'), 2 µl 25 pmol reverse primer Universal 1492R1 (5'-GGTTACCTTGTTACCTT-3') and 0.5 µl 5 U/µl *Taq* DNA polymers was added into the tube. PCR was run in the thermal cycler under the following conditions: 30 cycles consisting of 1 minute and 30 seconds at 94°C, 1 minute and 30 seconds at 62°C, 2 minutes at 72°C (Maszenan *et al.*, 2000). 1.5% (wt/vol) agarose gel in 1×TAE buffer was used to run electrophoresis with ethidium bromide staining to confirm the proper size of the PCR products. These DNA products were purified with Qagen DNA clean kit (Qagen, Germany). Then the 16S rRNA gene was amplified from genomic DNA by the PCR method described as below.

B.2. PCR conditions

Polymerase chain reaction (PCR) primers 357F (5'-GCC CGC CGC GCG CGG CGG GCG GGG CGG GGG CAC GGG GGG CCTCCT ACG GGA GGC AGC AG-3') and 517R (5'-ATT ACC GCG GCT GCT GG-3') were used to amplify the variable V3 region of bacterial 16S rRNA (Muyzer *et al.*, 1993). A 50 µl mixture containing 1.25 U of *Taq* DNA polymers, 5 µl 10× Buffer B, 4 µl 25 mM MgCl₂ was prepared with deoxynucleoside triphosphate (including deoxyadenosine triphosphate, deoxyguanosine triphosphate, deoxythymidine triphosphate,

deoxycytidine triphosphate), at a concentration of 200 μ M (Promega, USA), 25 pmol of each primer and 0.5 μ l of the DNA solution. PCR was performed in a thermal cycler (Eppendorf, Germany) under the following conditions: 10 min of activation of the polymerase at 94°C before two cycles consisting of 1 min at 94°C, 1 min at 65°C and 2 min at 72°C. Then the annealing temperature was decreased by 1°C for every second cycle until it reached 55°C. Subsequently, 20 additional cycles were carried out also at 55°C; finally, a 10 min extension process was performed at 72°C. In order to confirm the proper size of the PCR products, 1.5% (wt/vol) of agarose gel in 1 $\times$ TAE buffer was used to run electrophoresis with ethidium bromide staining (Zhuang *et al.*, 2005).

B.3. DGGE analysis of DNA fragments

A denaturing gradient gel electrophoresis (DGGE) system (BIORAD Decode, USA) was employed to analyze the DNA fragments. A 10 % (w/v) acrylamide solution (40% acrylamide and bisacrylamide, 37.5:1 stock solution, Bio-Rad, USA) in 1 $\times$ TAE buffer (Bio-Rad, USA) was used, with urea-formamide denaturing gradient gel ranging from 30-70%. Electrophoresis was performed at a constant voltage of 90 V for 15 hours. After that, the gel was stained with ethidium bromide for 20 minutes and destained in 1 $\times$ TAE buffer for 1 hour. The gel was viewed and photographed by a Gel Imaging System (Kodak, USA) (Watanabe *et al.*, 1998). GelCompar II (Applied Maths, Kortrijk, Belgium) was used to obtain the Similarity Index, which was employed to evaluate the differences and similarities of the bands observed in two lanes of the DGGE profile. The Similarity Index was automatically calculated with the Dice coefficient, without band weighting (band density) by the unweighted pair group method with arithmetic mean algorithms (UPGMA).

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