Development of techniques to characterize feed fouling potential for reverse osmosis operations

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**DEVELOPMENT OF TECHNIQUES
TO CHARACTERIZE FEED FOULING POTENTIAL
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2014

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2. **A. H. Taheri**, S.T.V. Sim, L.N. Sim, T.H. Chong, W.B. Krantz ,A.G. Fane, Development of a new technique to predict reverse osmosis fouling, Journal of Membrane Science, 448 (2013) 12-22.
3. F. Zamani, F. Wicaksana, **A.H. Taheri**, A.W.K. Law, A.G. Fane, W.B. Krantz, Generalized criterion for the onset of particle deposition in crossflow microfiltration via DOTM ó Modeling and experimental validation, Journal of Membrane Science, 457 (2014) 128-138
4. S.T.V. Sim, **A.H. Tehari**, T.H. Chong, W.B. Krantz, A.G. Fane, Colloidal fouling and its metastability ó Effect of crossflow velocity, flux, salinity and colloids concentration, Journal of Membrane Science, Submitted.

➤ Conferences:

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LIST OF SYMBOLS

<i>Symbol</i>	<i>Description (unit)</i>
A_m	membrane filtration area (m^2)
A_q	piezoelectrically active crystal area (m^2)
a	particle radius (m),
C_b	concentration of solute in bulk solution (kg/m^3)
C_w	concentration of solute at membrane surface (kg/m^3)
C_p	concentration of solute in permeate (kg/m^3)
C_{NaCl}	salt bulk concentration (kg/m^3)
CP	concentration polarization
CFS-MFI	Crossflow sampler - Modified Fouling Index (s/L^2)
CFS-MFI _{UF}	Crossflow sampler - Modified Fouling Index Ultrafiltration (s/L^2)
D	diffusion coefficient (m^2/s)
D_c	diffusion coefficient of the solute in the cake layer
d_p	diameter of particle (m)
d_h	hydraulic diameter (m)
f	frequency (Hz)
f_0	resonant frequency (Hz) of the sensor
FFM	feed fouling monitor
h	flow channel (m)
I	cake resistivity (m^{-2})
I_r	cake resistivity of RO (m^{-2})
J	water fluxFlux ($l/m^2.hr$)
J_r	RO permeate flux ($l/m^2.hr$)
J_{cr-RO}	RO critical flux ($l/m^2.hr$)
$J_{cr.FFM}$	FFM critical flux ($l/m^2.hr$)
k	Boltzmann's constant ($= 1.38 \times 10^{-23} J/mol.K$)
k_c	mass transfer in the fouled section
k_{eff}	overall mass transfer coefficient
k_{uf}	mass transfer in the un-fouled section
L	membrane length (m)
L_c	channel length (m)
MFI	Modified Fouling Index
MFI-UF _{const flux}	Modified Fouling Index ó Ultrafiltration constant flux (s/L^2)
MFI-UF _{const pressure}	Modified Fouling Index ó Ultrafiltration constant flux (s/L^2)
MWCO	Molecular weight cut-off (Da)
n	cake compressibility coefficient
R_c	cake resistance (m^{-1})
R_m	membrane resistance (m^{-1})
R_g	universal gas constant ($8.314 J/k.mol$)

Re	Reynolds number
SDI	silt density index
Sh	Sherwood number
Sc	Schmidt number
$t_i(SDI)$	initial time required to collect 500 mL of sample (s)
$t_f(SDI)$	time required to collect 500 mL of sample after elapsed time
$T(SDI)$	total elapsed flow time, min (usually 15 min)
T	absolute temperature (K)
TMP	transmembrane pressure (Pa)
TMP_s	trans-membrane pressure of the system during the salt pulsation
v	crossflow velocity (m/s)
V	permeate volume (m ³)

Greek Symbols

α	specific cake resistance (m/kg)
α_0	specific cake resistance at the reference salinity (m/kg)
α_r	specific cake resistance in RO
δ	CP layer thickness (m)
δ_c	cake layer thickness (m)
$\Delta\Pi_b$	Osmotic pressure difference between feed and permeate solution (Pa)
$\Delta\Pi_{bs}$	Osmotic pressure difference between feed and permeate solution (Pa) during salt pulsation
$\Delta P_{membrane}$	pressure drops contributed by the membrane (Pa)
ΔP_{cake}	pressure drops contributed by deposited cake (Pa)
ΔP_{CEOP}	pressure drops contributed by CEOP (Pa)
ΔTMP	total pressure drop across the cake (Pa)
Δm	change in mass adsorbed (kg) on the crystal sensor
ε	cake porosity
θ	deposition factor
β	cake ratio
μ	fluid viscosity (Pa.s)
ϕ	molar osmotic coefficient
ϕ_w	particle volume fraction at the membrane wall
ϕ_b	particle volume fraction in the bulk solution
γ	wall shear rate
ρ	density of solution (kg/m ³)
ρ_q	density of quartz (kg/m ³)
ν	kinematic viscosity (m ² /s)
η_q	shear modulus of the quartz (Pa)

ABSTRACT

Membrane filtration systems are successful methods to make high-quality water. An important issue and most challenging problem regarding these systems is fouling which arises from particle deposition in and on the membrane surface. Membrane fouling reduces performance of membranes and increases operational costs. Due to this problem, a reliable index to predict the fouling potential of feed water is important in preventing and characterizing membrane fouling and for monitoring the performance of pre-treatment during plant operation. The conventional fouling indices such, as SDI and MFI, are usually determined via off-line measurement techniques based on dead-end filtration, which does not consider the actual flow conditions.

To have a better understanding of the conventional fouling indices, the effect of several parameters on SDI, MFI, MFI-UF (constant pressure and constant flux) were investigated. In contrast with MFI, the SDI results confirmed the non-linear response to foulants concentration. The specific cake resistance for colloidal silica and humic acid was found to be maximum at low concentrations and gradually declined at higher concentrations. It was also highlighted that fouling by mixed foulants cannot be related simply to the individual MFIs. The effect of salt concentration on MFI-UF (constant pressure and constant flux) was also investigated over a broad range of NaCl (0 to 25,000 mg/L) for colloidal silica and humic acid. The results indicated that $\text{MFI-UF}_{\text{const.pressure}}$ of the colloidal silica passed through a maximum (under constant pressure filtration) while for humic acid $\text{MFI-UF}_{\text{const.pressure}}$ increased monotonically.

To overcome the limitations of these techniques, an on-line flow simulator, the feed fouling monitor (FFM), has been developed for characterization of the fouling propensity of feed water to RO. The FFM is based on the principle of particle deposition and cake layer formation on a small collection membrane in the device under cross flow conditions, which can be correlated to the particulate fouling (including colloidal particles and macromolecules) encountered in a RO operation. The information obtained from FFM was used to estimate cake resistance in RO in order to predict RO fouling profiles at the same hydrodynamic conditions. However, the predicted RO profiles were found to underestimate the actual RO performance due to ignoring the contribution of the cake-enhanced osmotic pressure (CEOP) effect.

The model was extended to include the contribution of CEOP and ultrasonic time domain reflectometry (UTDR) was used to monitor the rate of cake thickness increase in RO in order to estimate the cake-enhanced osmotic pressure (CEOP). The cake resistance (obtained from FFM) combined with CEOP could more accurately predict the RO fouling profiles using colloidal silica as a foulant model.

A salt tracer response technique (STRT) was also used to measure directly concentration polarization trends and estimate the contribution of CEOP under constant flux using both organic and inorganic foulant models. The predicted RO fouling profiles obtained from combination of FFM and STRT provided a good estimation of the transmembrane pressure (TMP) rise during RO fouling for both humic acid and colloidal silica. The contribution of CEOP to TMP rise was typically greater than the cake resistance.

CHAPTER 1

Introduction

1.1 Problem statement

One of the most important membrane processes is Reverse osmosis (RO) which is widely used to convert seawater and wastewater to clean water. A major challenge and concern associated with the use of RO technology is the fouling of the membrane. Membrane fouling causes a decline in permeability and changes the rejection of solutes over time and finally increases operational and energy costs of processing. One of the most important factors to determine membrane fouling is the property of the feed water [1, 2]. Hence, it is important to assess the quality of the feed water prior to operating a RO system. As a result, there is a need to develop reliable indices and methods to measure the particulate content and predict the fouling potential of RO feed water in order to prevent and characterize membrane fouling and for monitoring the performance of pre-treatment during plant operation.

There are several methods to determine the potential of feed water to foul the RO membrane. The most frequent and widely used method is the Silt Density Index (SDI) [3]. The SDI is an empirical method and does not provide a linear relationship with foulant concentration and cannot be used for quantitative modelling to predict RO fouling [4-7]. The basis of SDI was used to develop an improved method called the Modified Fouling Index (MFI) which has advantages over the SDI as it is more sensitive and is linear with the foulant load [8]. Due to the fact that $MFI_{0.45}$ is based on MF membrane and does not capture all potential foulants, the Modified Fouling Index ϕ Ultrafiltration (MFI-UF) was proposed

which uses ultrafiltration instead of microfiltration to trap more foulants [9]. However, these conventional fouling indices are usually off-line measurement techniques based on dead-end filtration, which does not consider the actual flow conditions.

To overcome this problem, the Crossflow Sampler ó Modified Fouling Index (CFS-MFI) was proposed using a cross-flow cell to simulate the hydrodynamic conditions in a RO process [10]. In this simulator a sampler membrane with large pores was located in the cross-flow cell operated at constant flux. The smaller particles pass through the sampler membrane and accumulate on a microfilter in a dead-end setup where the standard MFI is determined. Recently, Sim et al. (2010) [11] improved the CFS-MFI and incorporated UF instead of MF at constant flux. They found more accurate predicted fouling trends using CFS-MFI_{UF} compared to RO prediction using off-line MFI-UF under constant flux.

For salt-rejecting RO membranes such as RO, an important mechanism of fouling is cake-enhanced osmotic pressure (CEOP), in addition to cake filtration, which can increase the TMP and also create the favorable conditions to decrease salt rejection as filtration proceeds [12]. Hence, Sim et al. (2011) [13] attempted to include the effect of cake-enhanced osmotic pressure (CEOP) in their subsequent work to predict RO trends and this required measuring the rate of fouling deposition (by collection and weighing) and assuming a cake porosity.

1.2 Research objectives

Despite significant efforts to develop reliable fouling indices, there is still much to do to develop a comprehensive model that can relate a flow simulator to actual RO module performance. Hence, the objectives of this research are as follows:

- To develop a flow simulator as a feed fouling monitor (FFM) which can detect foulant load from a continuous sample passing over a small collection membrane. The developed FFM should be able to simulate the crossflow hydrodynamic conditions in a RO and operate under constant flux filtration. FFM development includes selection of a suitable membrane.
- To adapt a model based on cake filtration theory to allow analysis of the fouling propensity of the feed. This model would take data from the flow simulator and provide details of cake loading rate and specific cake resistance in order to project RO fouling performance in terms of the TMP rise.
- To modify the fouling prediction model in order to include the contribution of CEOP in RO fouling.
- To compare FFM projections with actual RO performance.

1.3 Thesis outline

The structure of this thesis is highlighted as follows:

Chapter 1: ***Introduction*** – Background information, problem statement as well as research objectives are provided.

- Chapter 2: ***Literature review:*** This chapter reviews the relevant literature on membrane, membrane fouling, specific cake resistance and cake enhanced osmotic pressure.
- Chapter 3: ***Review of membrane fouling indices:*** The available literature on existing membrane fouling indices is critically reviewed in this chapter.
- Chapter 4: ***Materials and methods:*** Detailed information about membranes, chemicals, experimental set up as well as analytical methods is provided.
- Chapter 5: ***Membrane fouling prediction indices – The effect of foulant type and operating mode:*** The influence of several factors on conventional fouling indices such as SDI, MFI, MFI-UF (under constant pressure and constant flux) were investigated. The fouling potential of colloidal (silica) and organic (humic) foulants, alone and in their mixture were studied. The specific cake resistance values obtained from constant pressure and constant flux filtration are compared in this chapter.
- Chapter 6: ***Principle of the feed fouling monitor and RO fouling prediction:*** The effects of several parameters such as foulants concentration, cross-flow velocity and applied flux on FFM were investigated. The RO fouling profiles were also predicted using the specific cake resistance values obtained from FFM at the same effective

hydrodynamic conditions. The predicted TMP profiles in this chapter were only based on hydraulic cake resistance while the effect of CEOP was not considered.

Chapter 7: ***Prediction of RO fouling by FFM – UTDR:*** The ability of the FFM combined with ultrasonic time domain reflectometry (UTDR) to predict RO colloidal fouling under constant flux filtration was investigated in this chapter. The UTDR was used to monitor the rate of cake thickness increase in order to estimate the CEOP. The developed model was extended to combine both the cake resistance (obtained from FFM) and the CEOP effect (estimated using data from FFM and UTDR) due to cake formation.

Chapter 8: ***Prediction of RO fouling by FFM and salt tracer response technique:*** the concentration polarization and CEOP contribution was estimated using the salt tracer response technique (STRT) under constant flux filtration using both organic and inorganic foulant models. The obtained information from STRT as well as FFM results was used to predict RO fouling behavior.

Chapter 9: ***Conclusions and Recommendations:*** The thesis conclusions and potential future research works are provided in this chapter.

Appendix: ***Preliminary observations of membrane regeneration by relaxation:*** These preliminary observations are included as an option for regeneration of the FFM.

CHAPTER 2

Literature Review

Membrane technologies have gained an important role in separation processes during past years. This chapter reviews the literature related to membrane and membrane processes and fouling. In chapter three the current techniques to predict and monitor the fouling are reviewed.

2.1 Definition of Membranes and Membrane Processes

A membrane can be defined as a thin and semi-permeable barrier between two phases which is selective towards some species over others. The concept of membranes has been studied since the middle of the eighteen century, however rapid growth of membrane processes has only occurred during the last four decades. A membrane can be classified in different ways, such as their material (polymeric, inorganic and liquid) or their structure (symmetric or asymmetric).

Despite many challenges, membrane technologies are nowadays successful methods in separation processes with a wide scope of applications. In many cases, membrane processes can compete with conventional separation processes regarding their advantages, which are highlighted as follows [14]:

- Membrane processes usually do not need phase change which reduces overall operational cost.
- These systems have less chemical usage compared to other conventional technologies and as a result are more green and environmental friendly.
- They are also easy to design and scale up with high efficiency.

- Since membrane systems are mostly assembled in module form, they require less space.
- Higher water recovery can be achieved by membrane processes than many other conventional treatment processes.

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are the four major membrane processes in water treatment which use pressure as driving force and are classified based on their pore size.

Microfiltration processes generally use porous membranes in a pore size range of 0.1 to about 10 μm to separate suspended particles as well as large microorganisms. Ultrafiltration refers to membranes with pore diameters from about 0.01 to 0.1 μm which can be applied to separate dissolved macromolecules by sieving mechanisms based on molecular size. NF and RO are considered as tight membranes which can reject divalent and monovalent ions respectively for softening and desalination purposes [15].

2.2 Membrane operational mode

2.2.1 Constant Flux and Constant Pressure Operation

In general, membrane systems can be operated under either constant pressure or constant flux. However in constant pressure systems, flux decline due to fouling can make it difficult to control system operation. For this reason in practice, industrial membrane processes typically operate at constant flux. In the constant flux mode, the trans membrane pressure (TMP) will rise over time due to membrane fouling in order to keep the flux constant by adjusting the pump delivery to supply higher feed

pressure. When the maximum capacity of the pump is reached, flux will decline in consequence of fouling. The differences between these operational modes are illustrated in Figure 2.1. For a fixed pressure mode, the deposit layer causes a drop in the flux with time and for constant flux it causes a rise in TMP with time. It should be noted that fixed pressure is “self-limiting” and constant flux is “self-accelerating”.

Figure 2.1: Schematic of TMP and flux profile, (a) constant pressure operation, and (b) constant flux operation

This means that during constant pressure mode, the flux keeps dropping as the cake layer forms and the rate of particle deposition changes due to variable driving force. In contrast, driving force and the rate of particle deposition during constant flux filtration are constant leading to a steady TMP rise over time. However in practice the rate of TMP rise is not always constant which can be due to cake compression or metastability of colloidal foulants [16-18].

2.2.2 Dead-end versus cross-flow filtration

Membrane processes can be operated under two main modes called dead-end and cross-flow filtration. Dead-end filtration is where there is no flow tangential to the

membrane surface and the concentrate stream and rejected material are retained. It is useful for dilute feeds. However, for concentrated feeds the membrane may foul quickly and flux can drop to unacceptable levels (Figure 2.2 A). In crossflow filtration the feed flows tangentially to the membrane surface (Figure 2.2, B), and this introduces surface shear that limit the accumulation of retained material. Tangential flow is usually provided by pumping but can be provided by bubbling, stirring etc.

Figure 2.2: Schematic of dead-end (A) and crossflow (B) filtration

2.2.3 Particle transport mechanism

In dead-end filtration, the flow direction is perpendicular to membrane surface. As a result, the particles continue to deposit and cake continuously develops until the end of filtration while the particles back transport can be considered negligible. In contrast with dead-end, particle transport in crossflow filtration includes both convection (permeate flux is perpendicular to membrane surface) and particle back transport due to tangential flow along the membrane [19-21].

In general, the back transport of particles during crossflow filtration could occur by several mechanisms such as Brownian diffusion [22], shear induced diffusion [23] and inertial lift [24].

2.2.3.1 Brownian diffusion

For crossflow filtration of very small (typically < 0.1 μm) or highly compressible particles, a thin layer of cake will develop on the membrane surface at the beginning of filtration which can cause a quick reduction of flux to a steady state value. At steady state conditions, the rate of particle movement toward the membrane due to the drag force of permeate flow is balanced by Brownian diffusion of particles away from the membrane surface to the bulk solution. The relationship for steady state flux for Brownian diffusion under laminar flow is given by Belfort et al. (1994) [19] as:

$$J = 0.114 \left(\frac{k^2 T^2}{\mu^2 a^2 L_c} \right)^{1/3} \ln \left(\frac{\phi_w}{\phi_b} \right) \gamma^{1/3} \quad (2.1)$$

Where k is Boltzmann's constant $1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}$, T is absolute temperature, μ is the fluid viscosity, a is the particle radius, L_c is the channel length, ϕ_w is the particle volume fraction at the membrane wall, ϕ_b is the particle volume fraction in the bulk solution and γ is the wall shear rate.

From Equation (2.1) it can be seen that the estimated flux based on the Brownian diffusion mechanism would be expected to increase with decrease in particle size $J \sim \frac{1}{a}$ and also increase with shear rate $J \sim \gamma^{1/3}$.

2.2.3.2 Shear-induced diffusion

The shear induced diffusion model was first introduced by Zydney and Colton (1986) [23] for crossflow microfiltration and assumes particles move toward the region of lower shear rate. In another words, Shear-induced hydrodynamic diffusion

of particles takes place due to the random displacement of individual particles, from streamlines in a shear flow as they interact with and tumble over other particles [19].

The length average flux for micron-sized particles (typically $> 0.2 \text{ }\mu\text{m}$) in laminar flow, based on shear-inducing diffusion model is represented by [23]:

$$J = 0.078 \left(\frac{a^4}{L_c} \right)^{1/3} \gamma \ln \left(\frac{\phi_w}{\phi_b} \right) \quad (2.2)$$

Based on equation (2.2), the averaged flux is predicted to increase with particle size $a \sim a^{4/3}$ and shear rate $\gamma \sim \gamma$

2.2.3.3 Inertial lift

For large and spherical particles, the lateral migration induced by inertial lift on the particles can be an important mechanism in particle transport during crossflow filtration where the Reynolds number based on the particle size is not negligible [24]. For fast laminar flow, the predicted steady state flux based on the inertial lift mechanism is as follows [24]:

$$J = \frac{0.036 \rho a^3 \gamma^2}{\mu} \quad (2.3)$$

where ρ is the density of solution.

Based on Equation (2.3), it is clear that flux is very sensitive to both particle size $a \sim a^3$ and shear rate $\gamma \sim \gamma^2$. Therefore, it is expected that the inertial lift model is a dominant mechanism for large particles.

2.2.4 Deposition factor

In contrast to dead-end filtration, only a fraction of the feed water passes through the membrane during crossflow filtration. In other words, not all the particles entering the module will be retained by membrane filtration under the crossflow process while during dead-end filtration, all the particles bigger than the membrane pore size would be trapped on the membrane surface. The deposition factor concept was first introduced by Schippers et al. (1981) [25] for reverse osmosis systems and was defined as the fraction of particles deposited or accumulated on the membrane relative to that present in that fraction of feed water. A positive value of deposition factor (less than one) refers to fractional accumulation of particles on membrane surface, while negative value indicates negligible particle deposition or that some particles are detached from the membrane. Boerlage et al. (2003) [26] reported negative deposition factors for both River Rhine and Ijssel Lake Plants. They suggested that tangential flow in crossflow filtration could possibly change the composition of the cake layer on the RO membranes over the time. Chong et al. (2008) [27] investigated the effect of cross flow velocity on deposition factor. A significant influence of cross flow velocity on particle deposition was observed in their study as only a fraction of the convected particles to membrane surface were successfully deposited. In another study, Sioutopoulos and co-workers (2010) [28] conducted a series of experiments to find the deposition factor by comparing the actual foulant amounts on the RO membrane surface and theoretical one. Deposition factors were estimated to be 1, 0.9 and 0.6 for ferric oxide, alginate and humic acid respectively.

The value of θ varied from about 1.0 (complete deposition) to 0.1 (partial

deposition). For values of $\theta < 1.0$ it is assumed that the upper regions of the polarized layer are mobile and moving tangentially due to surface shear. Evidence of such movement includes NMR micro-imaging of concentration polarization of colloidal silica suspensions in a tubular UF system [29]. The value of θ can be anticipated to vary with the nature of the foulant, imposed flux and hydrodynamics. For model foulants it may be possible to develop a priori prediction of θ , for example following the approach of Knutsen and Davis [30]. However in most applications this will be difficult. In this study we have treated θ as an empirical factor and deduced its value from best-fit of fouling trends.

2.2.5 Critical flux

It is important to find favorable fluxes in membrane systems to reduce operational costs, prolong membrane life and increase system performance. For this purpose, Field et al. (1995) [31] introduce the concept of critical flux for microfiltration which refers to a flux below which a decline of flux with time does not occur; above it fouling is observed. In general, the reason for the existence of critical flux is a balance between convective drag force of foulants toward the membrane by permeation flux and a back transport mechanism to the bulk [32, 33]. Several studies have reported that there is a negligible fouling at sub-critical flux during microfiltration of colloidal particles for example studies conducted by Howell et al. (1995) and Pollice et al. (2005) [34, 35].

The critical flux has usually been measured for MF and UF membranes by the pressure or flux stepping methods where flux is increased step by step and the change in TMP at the same time [33, 36-39]. The rate of TMP changes as a function

of time during filtration can increase remarkably above the critical flux. Direct observation through the membrane (DOTM) [40-42] and Particle mass balance measurement [37] are other methods to measure critical flux depending on feed type and filtration characteristics.

Numerous studies have investigated the effect of different factors (e.g. operational conditions, membrane characteristics, chemistry of feed solution) on critical flux [35, 37, 43-46]. Experimental values for Latex particles reported by Madaeni et al. (1997) highlighted the role of concentration, shear rate and particle size on critical flux measurement [43]. They found higher critical fluxes for larger particles, lower concentrations and higher crossflow velocities. However, Kwon et al. (1998) [44] observed different critical flux trends for different particle sizes. Regarding their experiments, critical flux decreased for small particles from 0.1 to 0.46 μm and then increased for larger particles from 0.46 to 11.9 μm . They explained this by concentration polarization model in cross flow microfiltration with different transport mechanisms depending on particle size. According to this model, Shear-induced diffusion mechanism (proportional to the square of particle size) is dominant for micron sized particles while Brownian diffusion (inversely proportional to the particle size) is important for sub-micron particles. Therefore, the decrease of critical flux in a range of 0.1 to 0.46 μm could be because of the Brownian effect for small particles. The more dominant shear-induced diffusion for larger particles (0.46 to 11.9 μm) resulted in higher critical flux for the larger particles [44].

2.3 Reverse osmosis (RO) processes

2.3.1 Fundamentals of Reverse Osmosis Membranes

Osmosis as a natural phenomenon that occurs when different concentrations of two solutions in the same solvent (usually water) are separated from each other by a thin and semi-permeable membrane. The water flow continues from the low concentration side into the more concentrated solution until the two solutions become equal in concentration or until the pressure of the more concentrated solution increases to a particular well-defined value (osmotic pressure). If a pressure at equilibrium condition is applied to the more concentrated side, then the water can pass into the dilute side. The name "reverse osmosis" is used to describe this process [47]. The concept of "osmosis" and "reverse osmosis" was discovered as early as 1748 by Abbe Nollet, nevertheless, application of reverse osmosis (RO) as a separation technology is relatively new. In the late 1950s, Professor Reid observed the capability of cellulose acetate RO membrane to separate salt from water and then in about 1960, Loeb and Sourirajan developed a hand-cast cellulose acetate (CA) membrane with relatively high water fluxes [48]. Since then, the development of different kinds of membranes such as asymmetric and composite membranes has resulted in many RO applications, in particular in water and wastewater treatment. The commercial RO membranes are mainly composite membranes which consist of an active layer and support layer and are prepared from different polymers such as polyamides and poly (ether/amide) [49]. These kinds of membranes are able to tolerate high operating pressure required for sea water desalination.

2.3.2 Membrane and Modules

There is a need for thousands of square meters of membrane for industrial membrane plants to produce an acceptable amount of clean water. As a result, economical methods to pack large areas of membranes are required. These packages are called membrane modules. There are some requirements of the membrane module for the feasibility of the process including: (1) acceptable mechanical support at different operating pressures specially in the case of RO processes, (2) that it offers minimal pressure drop across the module (3) that the module be moderately inexpensive and easy to change in the membrane systems [50].

A large number of module configurations are mentioned in the literature. However, the most commercial available membrane module systems can be classified into four main types [15]:

- Plate-and-frame
- Hollow-fiber
- Tubular
- Spiral-wound

The spiral wound module is the most commonly used configuration in the water desalination industry due to their high membrane area to volume ratio [51]. They are also well-suited to the TFC RO membranes that are produced in a flat-sheet format.

2.4 Concentration polarization (CP)

Concentration polarization (as illustrated in Figure 2.3) occurs when solutes and rejected particles accumulate at the membrane surface and the concentration near

the membrane surface increases gradually and will be greater than the concentration in the bulk. Figure 2.3 depicts the buildup of a laminar boundary layer.

Figure 2.3: Concentration Polarization (CP) within a Membrane Module

Increasing concentration polarization leads to higher osmotic pressure of the solution near to membrane surface which results in higher applied pressure being needed to achieve the same permeate flux or a decrease in flux at constant pressure operation. Also solute passage across the membrane may increase due to elevated solute concentration at the membrane wall.

The convective transport of solutes toward the membrane during membrane filtration will lead to concentration polarization at the surface of the membrane. A higher concentration in the boundary layer induces a back diffusion to the bulk concentration; the boundary conditions are illustrated in Figure 2.4.

Figure 2.4: Sketch of the concentration profile in the boundary layer toward the membrane

In the boundary film layer at the surface of membrane, with δ as a thickness, the solute concentration is increased from C_b (bulk concentration) to C_w (concentration at the membrane surface) due to the convective transport to the membrane. Steady state conditions will be obtained when diffusive transport of solutes ($D \frac{dc}{dx}$) into the bulk is balanced by the convective transport of solutes toward the membrane ($J.C_b$) and the transport of solutes that goes through the membrane as a permeate ($J.C_p$). dc/dx is the concentration gradient in the boundary layer and the diffusion coefficient is presented by D . Concentration polarization is described by the following first order differential equation [20]:

$$J \frac{dc}{dx} = D \frac{d^2c}{dx^2} + J C_b \quad \text{Boundary conditions: } \begin{cases} c = C_w & \text{at } x = 0 \\ \frac{dc}{dx} = 0 & \text{at } x = -\delta \end{cases} \quad (2.4)$$

Solving Equation (2.4) over the boundary conditions gives:

$$\frac{dc}{dx} = \frac{J C_b}{D} \left(\frac{e^{\frac{J}{D} x} - 1}{\frac{J}{D}} \right) = \frac{J C_b}{D} \left(\frac{e^{\frac{J}{D} x} - 1}{\frac{J}{D}} \right) \quad (2.5)$$

$$\frac{J \delta}{D} \ll 1:$$

$$\frac{dc}{dx} = \frac{J C_b}{D} \left(\frac{e^{\frac{J}{D} x} - 1}{\frac{J}{D}} \right) = \frac{J C_b}{D} \left(\frac{e^{\frac{J}{D} x} - 1}{\frac{J}{D}} \right) \quad (2.6)$$

This equation describes the relationship between the concentrations at the membrane surface, permeate, bulk and the flux. The term of $\left(\frac{C_m}{C_b}\right)$ is equal to $\frac{C_m}{C_b}$, where k is the mass transfer coefficient in the boundary layer. From Equation (2.6) it is obvious that there is an exponential relation between flux, diffusion coefficient and concentration polarization. It is seen that the value of concentration polarization increases with increasing flux, greater boundary layer thickness and lower diffusion coefficient. A large concentration polarization is usually not wanted due to the raised wall concentration C_m compared to the bulk concentration C_b and potentially a larger concentration in permeate. To mitigate this effect, it is often desirable to reduce the boundary layer thickness which leads to increase in the mass transfer coefficient k and as a consequence the back diffusion of solutes into the bulk solution. Based on Equation (2.6), an increased mass transfer coefficient will reduce membrane surface concentration C_m and thus decreases permeate concentration. It is possible to change the hydrodynamic conditions on the feed side to decrease the boundary layer thickness along the membrane surface to achieve better filtration performance.

The mass transfer coefficient for membrane filtration is usually obtained from a correlation of the form:

$$\text{Sherwood number} \quad Sh = \frac{k L}{D} = 2.0 \left(\frac{\mu}{\rho v L} \right)^{0.14} \left(\frac{\rho v L}{\mu} \right)^{0.75} \left(\frac{C_b}{C_m} \right)^{0.13} \quad (2.7)$$

$$\text{Reynolds number} \quad Re = \frac{\rho v L}{\mu} \quad (2.8)$$

$$\text{Schmidt number} \quad \text{Sc} = \frac{\nu}{D} \quad (2.9)$$

Where ν is kinematic viscosity and u_{cf} is cross flow velocity, d_h is hydraulic diameter and $\epsilon = 2H$ for a thin channel and L is the channel length. The constants n, a, b, c vary with the flow regime [22, 52].

2.5 Membrane fouling

The most challenging problem in membrane related technologies is fouling which decreases the performance and increases the operational costs. One general definition of fouling is as follows: "Undesirable accumulation or deposition of foulants on the membrane surface or in the pore structure which can reduce membrane permeability by closing pores and/or forming a layer on top of the membrane". Fouling is a complex phenomenon which is affected by several parameters, such as feed water quality, membrane properties, operational conditions etc. In constant pressure filtration, flux decreases due to fouling while during constant flux filtration, TMP increases to compensate for membrane fouling.

Membrane fouling can be classified into four main groups according to the fouling mechanism and foulant type as follows:

- Colloidal fouling
- Organic fouling
- Inorganic fouling or Scaling
- Biological fouling

2.5.1 Colloidal Fouling

In general, colloids are particles which have the particle size range from a lower

limit of about 1nm (0.001 μ m) to an upper limit of about 1000 nm (1 μ m) [53]. Various types of colloids exist in natural waters and some of them which are present in sea water are listed in Table 2.1[54].

Table 2.1: Colloidal matter in natural waters

Microorganisms
Biological debris (plant and animal)
Polysaccharides (gums, slime, plankton, fibrils)
Lipoproteins (secretions)
Clay (hydrous aluminum and iron silicates)
Silt
Oils
Kerogen (aged polysaccharides, marine snow)
Humic acids, lignins, tannins
Iron and manganese oxides
Calcium carbonate

During colloidal fouling, particles can accumulate on the surface of the membrane or within pores structure. As a result, it is important to discriminate dense and porous membranes. For porous membranes like MF and UF, colloidal particles can cause pore plugging followed by cake formation on the membrane surface [55-57]. In the case of RO and NF, colloidal fouling is mainly a surface phenomenon and caused by deposition and accumulation of foulants on the membrane surface which results in cake layer formation [58-60].

Numerous papers have been published over the years to describe the parameters affecting the fouling behavior of colloidal particles [59, 61, 62]. Gekas and Hallstorm (1990) [62] published a review of MF membranes, their types, potential applications, and fouling mechanisms.

Gourgues et al. (1992) [63] showed that higher permeate flux will enhance the particle deposition on the membrane surface. Mackley and Sherman (1993) [64]

reported that increasing cross-flow velocity leads to less particle deposition on the membrane surface and increase in permeate flux. The relative deposition of small size particles increases at lower cross-flow velocities because large particles have a higher back transport at lower cross-flow velocity than the small particles [65]. Thus it is found that the small particles have a greater tendency to deposit and cause membrane fouling [66].

2.5.2 Inorganic Fouling or Scaling

The expression *scaling* is applied to discriminate fouling caused by inorganic salt deposits from other types of fouling like organic fouling or biofouling. The presence of high concentrations of inorganic salts in RO feed water leads to undesirable deposition of salts on the membrane surface [67]. Particularly with salt rejecting membranes like NF and RO, the concentration of dissolved salts could be 2-10 times higher than feed concentration depending on the rejection and product recovery. The salt may precipitate on the membrane surface when the solubility of the salt is exceeded as a result of water recovery [68]. Ca^{2+} , Mg^{2+} , CO_3^{2-} , SO_4^{2-} , silica and iron are some of the most common inorganic salts that cause scaling on the membrane surface [69]. Other possible inorganic salts likely to cause inorganic fouling are Ba^{2+} , Sr^{2+} , Al^{3+} , Fe^{3+} and F^- [70].

2.5.3 Organic Fouling

One of the most significant groups of material that exist in RO feed waters is Natural Organic Matter (NOM). Humic substances, which are considered as a main component of dissolved NOM in surface waters, have a significant role in organic fouling of membranes. Organic fouling causes both reversible and irreversible flux

decline, thus removing NOM is an important step in many pre-treatment processes [71]. Investigations of the influence of NOM on membrane fouling were carried out by several researchers [72-75]. The study of Lahoussine-Turcaud et al. (1990) [76] on the ultrafiltration of natural water with different organic and inorganic macromolecules indicated that organic matter had a much greater effect on the flux decline than inorganic colloids which can be attributed to the different fouling mechanisms including adsorption, pore plugging or cake formation.

NOM is a complex heterogeneous mixture of compounds formed as a result of decomposition of animal and plant materials in the environment. The major fraction of NOM is composed of humic substances (HS). Although HS are often present in surface waters, it was shown that they constitute a significant fraction of residual organics in secondary effluents. Humic substance contains both aromatic as well as aliphatic components with primarily carboxylic and phenolic functional groups. As a result, humic substances are negatively charged in the pH range of natural waters [74].

2.5.4 Biofouling

The unwanted deposition and attachment of microorganisms, mainly bacteria, on the membrane surface followed by growth is generally called biofouling which usually contains a mixture of dead and live microorganisms and their associated extracellular polymeric substances [77].

Biofouling and its control remains a significant operating problem for many RO plants and may lead to severe loss of performance by increasing both salt passage and pressure drop across membrane elements and reduction of permeability as well

as costly cleaning operation [78]. Pretreatment of feed to reduce the concentration of microorganisms or reduce the concentration of nutrients is one of the most acceptable strategies to reduce biofouling in NF and RO operations. However, biofouling often occurs despite using pretreatment or other biofouling control strategies such as chlorination [78]. In general, a combination of pretreatment methods with physical and chemical cleaning can be more effective to prevent and control biofouling

2.6 Cake enhanced osmotic pressure (CEOP)

The term concentration polarization accounts for the accumulation of membrane rejected solute at the membrane surface and as a result a concentration gradient in the feed side and near membrane surface.

In the case of RO and NF processes, salt concentration polarization on the membrane surface creating an additional osmotic pressure drop across the membrane can be an important component of fouling in these types of membranes. In another words, fouling can also increase osmotic pressure and reduce driving force. This phenomenon is defined as cake-enhanced osmotic pressure (CEOP) and occurs when the back diffusion of the solutes is hindered by the foulant colloidal cake layer so the concentration of salt near the membrane surface increases and local osmotic pressure rises [12, 27].

The CEOP effect can cause decline of the flux or increase the TMP during colloidal and other foulant filtration and also increase the conditions for salt ions to transfer through the membrane, hence salt rejection decreases as filtration proceeds [12].

Regarding equation (2.6), the concentrations of salt ions near the membrane wall (C_m^*) increases due to hindered back diffusion of salt ions in the presence of the cake layer. The mass transfer coefficient for a clean membrane under laminar flow is defined by the Graetz-Leveque equation [79]:

$$K_m(0) = 1.62 \frac{D^{1/3} v^{2/3}}{L^{1/3} H^{2/3}} \quad (2.10)$$

Where D is the diffusion coefficient; v is the crossflow velocity; and L and H are the channel length and height, respectively.

The overall mass transfer coefficient (K_m) in a fouled channel is contributed by mass transfer in the un-fouled section (k_p) and mass transfer in the fouled section (k_c) which are described as:

$$\frac{1}{K_m} = \frac{1}{k_p} + \frac{1}{k_c} = \frac{1}{K_m(0)} + \frac{K_m(0)}{D} \frac{2\delta_c^2 \exp(-\frac{2\delta_c^2 K_m(0)}{D})}{\delta_c} \quad (2.11)$$

Where D is the Diffusion coefficient of solute in bulk solution, δ_c is cake layer thickness and ϵ_c represents cake porosity.

By combining equation (2.6) and equation (2.11) for constant flux filtration:

$$\frac{C_m(t)}{C_m(0)} = \exp \left[-\frac{2\delta_c^2 K_m(0)}{D} \frac{2\delta_c^2 \exp(-\frac{2\delta_c^2 K_m(0)}{D})}{\delta_c} \right] \quad (2.12)$$

Equation (2.12) shows the significant effect of flux, cake porosity and cake layer thickness on the concentration polarization as it is an exponential function of these parameters.

Hoek et al. (2003) [12] investigated the fouling caused by inorganic foulants on RO membranes and included the ionic strength based on film theory. They reported that a thin foulant cake layer may cause significant reduction in flux due to both cake resistance and increase in concentration polarization. Their results also noted the impact of membrane geometry and shear rate on the CEOP effect whereby applying higher shear rate caused a slight reduction of CEOP [79]. In addition, the effect of cake thickness and cake porosity on the diffusion coefficient of solutes in the cake and its impact on CEOP was also investigated [12]. The lower the porosity and the higher cake thickness attributed with the greater CEOP effect which was expected by equation (2.12). Chong et al. [27, 80] have recently applied experimental method called salt tracer response technique for cake resistance and CEOP studies using colloidal silica in RO system under constant flux filtration. They used sodium chloride as a salt tracer in their work to inject in RO and monitor change in TMP of the system. To determine the concentration polarization of salt under constant flux filtration, TMP can be measured and compared with the immediate response in TMP due to salt injection. Their experimental results highlighted the significant role and contribution of CEOP on RO fouling as well as hydraulic cake resistance. CEOP was also found to be sensitive to operational conditions such as cross flow velocity and flux with higher CEOP value obtained at higher flow and lower crossflow velocity.

2.7 Specific cake resistance

The structure of the cake layer on the membrane is affected by hydrodynamics, environmental conditions and foulant interactions; hence the specific cake resistance and cake porosity can be strongly affected by factors such as flux,

temperature, pressure, ionic environment and etc. Numerous papers, mainly in the filtration literature, have been published to investigate different parameters that influence cake resistance. It is convenient to express the cake resistance (R_c) as:

$$R_c = m \cdot \alpha \quad (2.13)$$

Where m is the cake load (kg/m^2) and α is the specific cake resistance (resistance per unit mass of cake).

The specific cake resistance can be expressed as a function of mean particle size, particle shape, and cake porosity and particle density. It usually increases with reduced porosity (ϵ) and reduced particles (d_p) size based on the Carman-Kozeny [81] equation:

$$\alpha = \frac{180(1-\epsilon)^2}{\epsilon^3 d_p^2} \quad (2.14)$$

Also, solution conditions like pH and salinity can affect foulant-foulant interactions and change inter-particle distance and as a result the variation of porosity and specific cake resistance [58, 82-84].

It has been shown that in membrane filtration, the specific cake resistance is affected by the applied pressure [85]. In practice, most cake layers are highly compressible [86]. Therefore, as the pressure drop increases the cake particles compress and porosity reduces. As a result, the specific cake resistance increases [17, 28, 87-90]. The specific resistance of the cake layer can be expressed as a function of pressure using the following power equation:

$$\alpha = \alpha_0 \cdot \Delta P^n \quad (2.15)$$

Where;

r = is specific cake resistance (m/kg)

α = is an empirical coefficient

n = cake compressibility coefficient

For an incompressible cake layer, $n=0$. The n value is larger for a more compressible cake layer and when compression is complete n is equal to 1. The range of n has been reported between 0.4 to 1 for MF and UF membranes by Hamachi et al. (1999) [91]. For ultrafiltration of colloidal silica, Singh and Song (2006) [92] reported an n value of ~ 0.82 , and by increasing ionic strength as a background (0.1 M), this value was reduced to 0.36. A silica gel layer was found to be compressible ($n \sim 0.5-0.6$) by Vladisavljevic et al. (1992) [87]. Iritani et al. (2002) [93] observed compressible cake layers ($n \sim 0.7$) for bovine serum albumin (BSA) foulant layers at pH 7 and an almost incompressible foulant layer at its isoelectric point (pH=4.7).

Mousa (2007) [94] reported that the specific cake resistance depends on the membrane type and is inversely proportional to membrane pore diameter or the MWCO. The explanation for this is transmission of small particles through large pore size membranes, and the formation of a cake by large particles. As a result the average particle size and porosity of the cake is larger and specific cake resistance is smaller.

Inter-particle voids between particles maybe filled by small colloids, which can significantly reduce porosity and increase cake resistance [95, 96]. In addition, cake

structure with larger and looser particles generally leads to lower specific cake resistance [95-98].

Vladisavljevic et al. (1992) [87] investigated the effect of temperature on the specific resistance of a silica gel layer. They observed that the rise of temperature causes the formation of a denser gel layer corresponding to a higher specific cake resistance. They reported that this may be due to swelling of the gel material.

For filtration of a settled mixed liquor, Parameshwaran et al. (2001) [88] reported stable specific cake resistance for a maximum TMP of 20 kPa. However for a TMP of 50 kPa the specific cake resistance was higher and tended to increase with increased in imposed flux due to compressible cake formation.

Specific cake resistance can also vary with solids content. For example, specific cake resistance was found to increase with increasing bulk concentration of silica when it changed from 3.5-28 kg/m³ (3,500-28,000 mg/l) as a result of increase of silica gel mass [89]. This relationship was in good agreement with the results reported by Vladisavljevic et al. (1992) [87]. Based on their experiments for silica suspension, specific cake resistance increased when concentration increased from 10-107 kg/m³ (10,000-107,000 mg/l). However, Parameshwaran et al. (2001) [88] observed the specific cake resistance to decrease with increasing feed solid content from 40 to 160 mg/l due to change in particle size distribution and the presence of larger particles at higher feed concentrations.

The situation in cross flow filtration due to the presence or absence of shear is more complex. In fact, specific resistance is not easy to measure in crossflow filtration.

Shear can change or even control the size of aggregates and affect deposition and detachment behavior on the growing cake surface. Sioutopoulos et al. (2010) [28] suggested stirring of the feed may cause partial re-suspension of the deposited particles leading to a thinner cake layer which is composed of smaller particles and higher overall resistance. Thus, specific cake resistance in crossflow systems with a distribution of particle sizes may be greater than dead-end specific resistance of the same feed solution [99].

CHAPTER 3

Review of Membrane Fouling Indices

3.1 Introduction

For the past few decades reverse osmosis (RO) technology has played a significant role in water and waste water treatment and desalination. However, this technology has a major drawback, namely membrane fouling. Membrane fouling not only increases operational costs, energy demand and cleaning frequency, but also affects the water quality produced. Therefore it is important to find solutions to prevent or minimize fouling and warrant the sustainability of RO technology.

One way to reduce fouling problems is via monitoring the fouling propensity of RO feed waters. The information gathered can potentially be extended to predict the performance of the RO process. No doubt, the foulants present on the membrane originated from the feed water. Typically feed waters to RO processes contain high amounts of total dissolved solids (TDS) with various cations, anions, natural organic matters, particulate matter and living organisms. For seawater, TDS is in the range of 30,000 to 50,000 mg/L while TDS for brackish water is up to about 10,000 mg/L. The RO membrane serves as the selective/separation layer that allows only water to pass through while retaining the dissolved solids, and achieves a final rejection of > 99 %. Some of the rejected solutes tend to accumulate on the membrane surface and are potential fouling agents. The deposits commonly found on RO membrane surfaces are particulate, crystalline, organic and biological materials. Apart from predicting the long term performance of the RO process,

effective monitors could assist in selection of an appropriate pre-treatment method in order to meet the criteria set by the RO manufacturers as well as serve as a tool to assess the efficiency of the pre-treatment process.

3.2 Features of fouling

As mentioned, fouling is defined as the accumulation or deposition of unwanted materials on the surface membrane (section 2.5). Fouling causes a decline in flux at constant pressure operation or causes transmembrane pressure to rise at constant flux operation. In practical situations, RO plants tend to be operated at fixed production rate that requires constant flux operation. Thus in the event of fouling, higher feed pressure is supplied by adjusting the pump until the maximum capacity of the pump is reached, only then the permeate flux starts to decline, which is equivalent to operation at fixed pressure mode. The fouling rates for fixed pressure and constant flux cases are different since the fouling process slows down in the former, fouling becomes “self-limiting” whereas fouling is “self accelerating” as foulants steadily accumulate and concentration polarization accelerates in the latter [100]. Despite the differences in the fouling patterns, the majority of lab based studies involving RO fouling have been performed under fixed pressure conditions. It is necessary to compare the fouling process occurring under fixed pressure and constant flux operation as they may give different fouling dynamics and mechanisms.

The effect of fouling can be reflected in the basic relationship to describe flux and driving force [101]:

$$J = \frac{\text{TMP} - CP\Delta\Pi_b}{\mu(R_m + R_c)} \quad (3.1)$$

where J is the permeate flux; TMP refers to transmembrane pressure; $\Delta\Pi_b$ is the difference in the osmotic pressure across the membrane between the feed in the bulk and permeate solution; μ is the viscosity of the permeate; R_m is the clean membrane resistance; R_c is the resistance of the fouling layer; and CP is the concentration polarization due to retention of solute by the RO membrane (section 2.4).

3.3 Membrane Fouling Indices

An important factor for membrane fouling is the property of the feedwater [1, 2]. It is important to assess and measure the quality of feedwater in order to predict the fouling potential of the feed water to membrane filtration systems by routine analysis. In addition, this analysis method can be used to evaluate the pre-treatment efficiency or to monitor the (fouling) state of the membrane process. The application of fouling indices is complicated by the complexity of fouling with different types of foulant. Several fouling indices have been developed in the past to provide appropriate signals for membrane fouling potential prediction. Various fouling indices are reviewed as follows relating to different fouling types.

3.3.1 Assessment of Colloidal Fouling Propensity

3.3.1.1 Silt Density Index (SDI)

The silt density index (SDI) is the most common and widely accepted tool for characterization of the fouling potential of water. This method conforms to the ASTM D-4189 standard [3]. Before the publication of öASTMö in 1995 [102], the

SDI test was called different names: Plugging Index (PI) by Channabasappa [103], Fouling Index (FI) [69].

SDI is an indication of the quantity of particulates in water, based on filtration of feed water through a microfilter membrane. It is typically applied on low fouling potential water such as pre-treated water feeding reverse osmosis or nanofiltration. Determination of SDI is based on measuring the required time to filter 500 mL of feed solution through a standard 0.45 μ m pore size microfiltration membrane under a constant given pressure of 30 psi (2.1 bar). The SDI calculates from the rate of plugging the filter using the following equation:

$$SDI = \frac{1 - \frac{t_i}{t_f}}{T} \times 100 \quad (3.2)$$

Where t_i = initial time required to collect 500 mL of sample

t_f = time required to collect 500 mL of sample after elapsed time

T = total elapsed flow time, min (usually 15 min)

Either time (T) or permeate volume (V) can be varied where $T = 5, 10$ or 15 min and $V = 500, 250$ or 100 mL. T is usually taken as 15 min but if the expression (

$1 - \frac{t_i}{t_f}$) exceeded 75%, T is reduced to 10 or 5 min [8].

Even though SDI has been the standard test to predict membrane fouling for many years, it does not have a good theoretical basis, and therefore is of limited use. SDI was found unreliable in numerous studies [4, 8, 104-107]. The main reason is that SDI was not derived from the filtration mechanism and therefore has no relationship

with the colloid content [8]. There is always a maximum value for SDI regardless of the foulant concentration. When $t_f \gg t_i$, the SDI is equal to $100/T$, so SDI_5 and SDI_{10} have the maximum value of 20 and 10 respectively, while SDI_{15} value approaches an asymptotic maximum of 6.67 at high concentration [8]. Thus, according to the ASTM D4189-95, SDI test is only applicable to relatively low turbidity waters with values less than 1.0 NTU. Turbidity and SDI are both used as process evaluation parameters but there is no direct correlation between them [108]. However, when the turbidity is higher than a certain value, the SDI is not measurable [109, 110]. Durham (1999) observed that SDI was not measurable when the solid content of the water sample had a turbidity value of 50 NTU [110]. Therefore, without knowing the concentration of colloidal particles in the feed, RO fouling prediction based on the SDI value is not possible [7].

Lipp et al. (1990) [105] have conducted a series of experiments which measure the SDI for different concentrations of potential organic (a flocculating agent with high molecular polyacrylic amide and cationic character, called Praestol 664BC) and inorganic ($BaSO_4$, $CaSO_4$ and $Fe(OH)_3$) foulants present in the feed in practical RO systems and compared the results with their crossflow RO experiment. Besides claiming that SDI has no relationship with the solute concentration, they also reported that SDI failed to represent the fouling in RO their RO experiments. For instance, their results revealed that a feed which had SDI_{15} values approaching 6.67 showed no flux decline after 25 hours of RO filtration. In contrast, a low SDI_{15} feed with values of about 3.5 feed waters caused almost 50 % decline of the RO flux.

A major problem with the SDI test is that it uses microfiltration membranes with pore sizes of 0.45 μm , thus the test does not effectively account for the presence of foulants that are smaller than this size. In contrast, RO feed has often been treated with MF or UF filtration, thus the feed mostly contains colloids and organics which are normally smaller than 0.45 μm . These foulants which are not retained by the test membranes can be responsible for the observed RO fouling and might be overlooked during the test [25].

The other problem is that when filtering these smaller colloids and organic foulants through the SDI membrane, not only cake formation but other fouling mechanisms such as pore blockage and pore adsorption can occur and be responsible for controlling the fouling rate [111]. These mechanisms do not occur with non-porous RO membranes.

Another major limitation of the SDI measurement protocol is that the difference between the crossflow fluid dynamics and the constant flux filtration in an operating RO and the dead-end constant pressure filtration on the SDI membrane has not been accounted for. Due to these limitations, SDI is not sometimes conservative enough to be used to predict fouling in RO.

However, there are some contradictory studies [2, 112]. White claimed that SDI is not an entirely empirical method as it has a sound theoretical basis and its validity can be verified using the classical filtration laws modified for water which has low solids content [112]. Kremen and Tranner (1998) [2] used a simplified mathematical hypothesis to show there can be a relationship between the measured SDI value and the corresponding amount of foulant deposited on the test filter. They

obtained positive results in which the increase in measured SDI values corresponded to a geometric increase in the amount of foulant deposited [2].

It should be noted that measurement of SDI depends on many parameters, such as the membrane used in the test [5, 113]. Mosset et al. (2008) reported differences between SDI values for two batches of membrane with the same material and the same manufacturer [4]. They suggested performing the SDI test with new and the same batch of membrane. The effect of membrane materials on the SDI was also studied by Hong et al. (2009) [111]. They reported that fouling propensity of PVDF membranes was clearly higher than cellulose ester membranes. Recently, Alhadidi et al. (2011) [114] investigated the influence of membrane properties on the SDI. They observed significant difference between SDI obtained from membranes with difference properties. Their research concluded that for a reliable SDI measurement, it is very important to have uniform and constant membrane properties. Another study conducted by Alhadidi et al. (2011) [115], highlighted the effect of feed temperature on the SDI. They observed higher SDI values with the increase of feed water temperature. This could be due to the lower viscosity leading to higher fluxes and more permeate proceed in the deposit time T.

3.3.1.2 Modified Fouling Index (MFI)

The non-linear relationship of the SDI with particle concentration is a significant disadvantage of the SDI method. To solve this problem, the MFI is a fouling index introduced by Schippers (1980) [8] which is based on the fouling mechanism. They proposed that dead-end filtration at constant pressure takes place in three steps in sequence:

- Pore blocking;
- Cake filtration without compression;
- Formation of a compressible cake.

This is depicted in Figure 3.1, which describes the ratio of t/V as a function of V , where V is filtration volume collected in time t .

Figure 3.1: Ratio of t/V as a function of V under the three filtration mechanisms: Blocking filtration, cake filtration and cake filtration with compression

According to the membrane blocking laws, there is a linear relationship between t/V and V during the cake filtration period [116]. The Modified Fouling Index can be described by following equation, considering resistances in series:

$$J = \frac{1}{A} \frac{dV}{dt} = \frac{P}{(R_m + R_c)\mu} \quad (3.3)$$

Where:

J = permeate flux across the membrane [$\text{m}^3/\text{m}^2\text{s}$]

A = membrane area [m^2]

V = filtration volume [m^3]

t = time [s]

$\hat{P}$ = applied transmembrane pressure [N/m^2]

R_m = clean membrane resistance [$1/\text{m}$]

R_c = cake/fouling resistance [$1/\text{m}$]

μ = fluid viscosity [Ns/m^2]

An assumption usually made is that during constant pressure filtration the resistance of the cake formed is proportional to the amount of the solid mass deposited on the surface of the membrane, so that:

$$R_c = \frac{V}{A} \times \alpha C_b \quad (3.4)$$

where α is the specific cake resistance [m/kg] and C_b [kg/m^3] is the feed concentration of particles per unit volume of filtrate.

Equation (3.4) can be re-written in the following form:

$$R_c = \frac{V}{A} \times I \quad (3.5)$$

where I is the fouling index, which is a measure of the fouling potential of the feedwater for the membrane.

$$I(t) = \alpha(t) C_b \cdot R_{ej} \quad (3.6)$$

Eq. (3.6) is also considered the incomplete species rejection by the UF membrane. The obtained specific cake resistance under constant pressure is constant for incompressible cakes and can be estimated using the Carman-Kozeny relationship (Equation 2.14 ó see chapter 2) [81].

By substituting Equation (3.5) in Equation(3-6) and integrating at constant $\hat{e}P$:

$$t = \frac{\mu VR_m}{\Delta PA} + \frac{\mu V^2 I}{2\Delta PA^2} \quad (3.7)$$

To analyse experimental data, (3-7) is re-written in the following form:

$$\frac{t}{V} = \frac{\mu R_m}{\Delta PA} + \frac{\mu I}{2\Delta PA^2} \times V \quad (3.8)$$

In a $\frac{t}{V}$ vs. V , the slope of the linear region is recognized as the MFI.

$$MFI = \frac{\mu I}{2\Delta PA^2} \quad (3.9)$$

Combining the Carman-Kozeny equations (2.14) and (3.7) substituting for fouling index in equation (3.9), gives:

$$MFI = \frac{\mu 90(1-\varepsilon)C_b}{d_p^2 \Delta PA^2} \quad (3.10)$$

Therefore, it is evident that MFI is related to the nature and dimension of the particles (ε and d_p) and directly connected to the concentration of particles (C_b) in the feed water.

The cake thickness $\delta_c(t)$ based on porosity of the cake and cake mass can be measured from the following equation [79]:

$$\delta_c(t) = \frac{m_c(t)}{\rho_c(1-\varepsilon(t)) \times A_m} \quad (3.11)$$

where ρ_c represents the density of the cake (kg/m^3) and A_f is the filtration area (m^2).

The number of cake layers can be determined from the cake thickness:

$$\text{Number of cake layers} = \frac{\delta_c(t)}{d_p} \quad (3.12)$$

It should be emphasized that MFI is also applicable for compressible cakes, when the pressure drop over the cake (ΔP_c) is dominant. The fouling index I related to the cake compression is defined as follows:

$$I = \frac{1}{\alpha} \left(\frac{\Delta P_c}{P_c} \right)^w C_b \quad (3.13)$$

where α is the compressibility coefficient and $\frac{1}{\alpha}$ is a constant. In the case of incompressible cakes, $w = 0$ and the higher the compressibility coefficient means the more compressible the cake [26].

The $\text{MFI}_{0.45}$ is calculated using the same procedure, equipment and membrane used for the SDI, except that the volume is measured every 30 seconds over a 15-minute filtration period.

Recently, a mathematical relation between SDI and MFI has been developed by Alhadidi et al. [115, 117]. This relation is based on the assumption that cake filtration occurs as the only fouling mechanism during the test which is only strictly valid for large particles. The SDI was found to be depended on the pressure, temperature as well as membrane resistance. The developed SDI/MFI relation was proven to be valid for both γ -Alumina suspension as model water and seawater.

MFI still has some limitations for prediction of RO fouling. Some of these limitations are listed below:

- $MFI_{0.45}$ is based on the dead-end filtration mode, while RO is in cross flow filtration mode which affects the nature of fouling and concentration polarization.
- Permeate flux in MF is much higher than RO, which affects the rate of particle deposition and foulant layer structure.
- As the MFI measurement is carried out using 0.45 μm membrane and cannot capture all particles, the fouling ability of smaller particles and macromolecules tends to be ignored.
- The cakes formed on RO and MF probably has different structures due to various operational conditions and different applied pressures.

Due to some of these drawbacks, a new fouling index based on ultrafiltration was developed.

3.3.1.3 Modified Fouling Index - Ultrafiltration

Schippers et al. (1981) [25] demonstrated the effect of membrane pore size on the MFI value using the same type of feed. MFI value was found to increase dramatically with decreasing membrane pore size indicating that $MFI_{0.45}$ is not capable of accounting for the presence of small colloidal particles. This was confirmed by Braun et al. (2002) who stated that it would be more appropriate and practical to have the fouling test based on pore size relevant to the real situation [118].

It has been shown that colloidal particles smaller than 0.45 μm can be responsible for colloidal fouling of the RO membrane surface. Hence, Boerlage et al. (2001, 2002) developed a new fouling index called the Modified Fouling Index-Ultrafiltration (MFI-UF) which is based on ultrafiltration membranes [119, 120]. The MFI-UF is performed with the same procedure and equipment as the $\text{MFI}_{0.45}$ and SDI and under constant pressure and temperature. The only difference between the indexes is the use of an UF membrane instead of a MF membrane.

Boerlage et al. (1998) [121] reported stable MFI-UF values in long-term experiments. Lower fluxes for UF compared to MF leads to the stability of MFI-UF in long term tests. The MFI-UF value is much higher than MFI due to capturing of smaller particles by UF membranes [122].

Most RO membrane processes are conducted under a constant flux with increasing pressure due to fouling phenomena. As both pressure and flux may cause cake compression, measurement of the MFI-UF in constant flux mode is expected to more closely predict particulate fouling in RO. The application of MFI-UF for constant flux has been developed by Boerlage et al. (2004) [9]. Substituting ΔP for constant flux and R_c from Equation (3.5) into Equation (3.3) gives:

$$J = \frac{\Delta P}{\mu(R_m + \frac{V}{A} \times I)} \quad (3.14)$$

By re-writing $\frac{V}{A}$ as $J \cdot t$ and rearranging gives the following equation:

$$\Delta P = J R_m + J^2 I t \quad (3.15)$$

Equation (3.15) indicates the pressure increase required to keep a constant flux as a result of particles deposition and cake formation on a membrane surface.

The fouling index I_F can be determined at time (t) from the slope of the linear region in a plot of ΔP as a function of time according to the following equation:

$$I_F = \frac{\Delta P - J\mu R_m}{J^2 \mu t} \quad (3.16)$$

MFI-UF values can then be determined as follow:

$$MFI-UF_{const.flux} = \frac{\mu I_F}{2\Delta P_0 A^2} \quad (3.17)$$

For comparison purposes, ΔP_0 is taken at the standard pressure of 2×10^5 Pa (2bar). Boerlage et al. (2004) [9] showed that MFI-UF under constant flux filtration can be obtained within a shorter time compare to MFI-UF under constant pressure operation. Sim et al. (2011) [123] performed two experiments with similar initial pressure and initial flux to compare MFI-UF under both constant flux and constant pressure. They reported higher resistivity and lower MFI-UF for constant flux versus constant pressure which indicates the cake formed under these two conditions varied significantly. However they noted that it is not possible to directly compare the $MFI-UF_{const.flux}$ and $MFI-UF_{const.pressure}$ as this may cause misleading information on the fouling propensity of the given feed.

3.3.1.4 Crossflow Sampler Modified Fouling Index (CFS-MFI)

Recently, the Crossflow Sampler Modified Fouling Index (CFS-MFI) was developed to simulate the crossflow hydrodynamic conditions in a RO processes during fouling index measurement [10, 124]. In this method, a cross-flow

membrane sampler with large pores was located upstream; the smaller particles pass through the membrane into the permeate and deposited on a microfilter in a dead-end setup in the permeate line where the standard MFI was determined. Javeed et al. (2009) used a 0.45 μm microfiltration membrane for both CFS-MFI and MFI under constant pressure mode [124]. They reported that the SDI and MFI values measured from CFS-MFI are not proportional to the standard MFI values. However the use of constant pressure, rather than constant flux, negates the aim of simulating the RO hydrodynamics in the crossflow sampler. Recently, Sim et al. (2010) [11] improved the CFS-MFI and used UF instead of MF and conducted the test under constant flux. This index is known as Crossflow Sampler Modified Fouling Index UF (CFS-MFI_{UF}); it was found that the CFS-MFI tend to be a lower value than the standard MFI. To investigate the accuracy and sensitivity of the CFS-MFI_{UF}, RO experiments performed and the results indicated a good agreement for the CFS-MFI_{UF} trend with the actual RO fouling behaviour.

However when tested with a solution of high salt concentration (6 g/L), the CFS-MFI_{UF} predicted trend was found to significantly underestimate the actual RO fouling behaviour. The discrepancy is probably due to the potential contribution of cake-enhanced osmotic pressure (CEOP) in RO fouling (see chapter 2- section 2.6), which has been neglected in the CFS-MFI_{UF} measurement. It should be noted that conventional SDI and MFI do not take into account the effect of CEOP. Sim et al. (2010) [13] further extended the concept of CFS-MFI_{UF} to incorporate the CEOP effect in the fouling prediction model. This required ex-situ of foulant cake load and estimation of cake porosity. Their preliminary results indicated that the model combining CFS-MFI_{UF} and CEOP effects provides a good estimation on the RO

fouling profile. Hence, CFS-MFI_{UF} combined with CEOP appears to be a more realistic approach to determine the fouling propensity of feed water prior to the RO units.

3.3.1.5 Other Fouling Indices

There have been several other fouling indices for colloids proposed over the years in addition to those mentioned above to predict the fouling potential of feed water.

The mini-plugging factor index (MPFI) is determined by plotting the change in flowrate (l/s) as a function of time (s). The MPFI test uses the same equipment as SDI and MFI test. Like MFI, MPFI is defined as the slope of the linear part of the curve which is attributed to the cake filtration mechanism. However, MFI is a more sensitive test to characterize the fouling as compared to MPFI because it is based on throughput volume [125].

Khirani et al. (2005) [126] developed the concept of MFI-NF to improve the MFI test by using a nanofiltration membrane in order to capture smaller particles and macromolecules. However, the measured MFI-NF (0.5 kDa) values for seawater were nearly similar to the MFI-UF (30kDa), indicating that full retention of dissolved organics cannot be achieved. The MFI-NF is also reportedly a longer duration test. Thus, this index may not be the most appropriate for determining the fouling potential of sea water.

The concept of the unified membrane fouling index (UMFI) was developed by Huang et al. (2008) [127] based on Hermia's filtration model [116] for the assessment of fouling in low pressure membranes. The UMFI is based on cake

filtration theory and is introduced as the slope of the curve of the reciprocal of normalized membrane specific flux as a function of unit permeate throughput (i.e., accumulated permeate volume per unit membrane area, v). The greater the UMFI value, the higher the membrane fouling potential.

UMFI is defined as a slope term in the linear equation:

$$\frac{1}{J'_s} = 1 + (\text{UMFI}) \cdot V_s \quad (3.18)$$

Where normalized specific flux (J'_s) is defined as:

$$J'_s = \frac{J_s}{J_{s0}} \quad (3.19)$$

J_s equals the flux divided by pressure ($J_s = J/P$) where J [m/s] is the permeate flux and J_{s0} is J_s at time zero. The UMFI has units of m^{-1} , or m^2/L if V_s has units of L/m^2 . The UMFI is compatible with various modes of low pressure membranes and can be applied to both constant-flux and constant-pressure filtration [127, 128]. However, this test is operated using a hollow fiber module, hence selective deposition of particles and the flow dynamics of crossflow filtration are not considered.

A new fouling index (CFI: combined fouling index) was introduced by Choi et al. (2009) [129] who used a set of different membrane filters for better prediction of the fouling potential of mixed foulants in RO/NF. In this method, three MF/UF membranes were applied for MFI tests in order to increase the sensitivity of the index and CFI was evaluated by assuming a linear combination of each fouling index. According to this method, it is possible to consider the contribution of particles, colloids and organic matters to RO/NF fouling at the same time. To verify

the ability of CFI to predict fouling potential of feed water, the flux decline rate (FDR) was defined. If the relationship between FDR and CFI is linear, the fouling index can be used as a promising technique for measuring the potential of RO/NF fouling in their study. Choi et al. (2009) reported linear correlation between FDR and CFI which indicated that the CFI can successfully predict the NF flux decline by considering the impact of different foulants. However it is surprising that fouling by mixed foulants can be related simply to the individual MFIs, and this concept will be tested in this study.

Recently, Yu et al. (2010) [130] extended the work of Choi et al. (2009) [129] and developed a new approach for assessment of fouling potential for various feed waters; called the multiple membrane array system (MMAS). Based on this method, a multiple membrane system including microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) membranes were configured in series in one system. Particulate, colloids, and organic matters were continuously separated by MF, UF, and NF membranes, and the modified fouling index (MFI) was measured during each separation instead of measuring MFI values at each step separately and independently. During the test, the feed water passed to the MF membrane to evaluate fouling potential of particulates. Permeate from the first MF membrane was then introduced to the second UF membrane to determine the fouling potential of nano-colloids. Finally the UF permeate which is mainly contaminated by organic foulants is fed to the NF membrane and, consequently, the organic fouling potential was measured with minimum interference by of other foulants. The resulting three MFI values were plotted schematically in a triangle manner. To confirm the applicability of the MMAS the fouling potential of the raw and pre-treated

seawaters were measured for each step (Particle-MFI, Colloid-MFI, and Organic-MFI) as well the conventional SDI value. The results were compared with the actual flux decline rate (FDR) data given from the lab-scale RO setup. The results showed that the prediction of actual flux decline by MMAS was most accurate, but the SDI failed to predict the actual flux-decline behavior. Yu et al. (2010) [130] suggested, MMAS could provide a better technique to predict fouling potential and select proper pre-treatment processes. However, it should be noted that MMAS measures fouling resistance and does not give information to estimate the CEOP effect.

Indices based on filtration with porous membranes cannot measure scaling potential. For assessment of inorganic fouling (scaling), the commonly used indices are the Langelier Saturation Index (LSI) [131] and its modifications, i.e. the Ryznar Saturation Index (RSI) [132] and the Stiff and Davis Saturation Index (SDSI) [133]. All of these indices offer rough estimates for the tendency of water for CaCO_3 precipitation. To determine these indices, the calcium hardness, alkalinity, the temperature and total dissolved solids must be measured. A positive LSI implies CaCO_3 saturation, and scale is expected to form. In a same way, scaling propensity is expected for $\text{SDSI} > 0$ and $\text{RSI} < 6$. These indices provide qualitative indication of potential fouling, and cannot be used for predictive preposes.

Binovi (1983) [134], proposed the permanganate demand (PD) as an index to characterize the concentration of humics to predict organic fouling in RO processes. However, this index was only developed on the basis of humic acid and other organic matter and particles were not studied. Another disadvantage of this index is duration of the test which takes several hours. Due to these limitations, there has

been no published data of this index available since it was first developed.

3.4 Concluding remarks

This chapter provides a comprehensive review of various fouling indices to characterize the RO feed water fouling potential. Several fouling indices have been developed to provide appropriate information for the measurement of membrane fouling potential.

Even though the simplicity of the SDI may be attractive, it is an empirical technique which has no fundamental relationship with the concentration of foulants. MFI on the other hand indicates a linear relation with concentration and is based on cake filtration mechanism. However, both SDI and MFI techniques operate using a microfiltration membrane (0.45 μm) under constant pressure filtration.

As RO fouling is mainly contributed by smaller particles ($<0.45 \mu\text{m}$), the MFI-UF was introduced which uses UF rather than MF to simulate better the fouling of a RO membrane under both constant pressure and constant flux filtration.

The aforementioned fouling indices are off-line techniques conducted under dead-end filtration. To overcome this, the Crossflow SampleróModified Fouling Index (CFS-MFI) was proposed utilising a cross-flow cell to simulate the hydrodynamic conditions in an RO process.

In summary, several fouling indices have been developed to provide information on membrane fouling potential for RO and UF. The key limitations of these indices are:

- The lack of allowance for cake enhanced osmotic pressure (except for the recent work of Sim et al. (2010) [11].
- The lack of on-line capability in index measurement.

This study will address these limitations.

CHAPTER 4

Materials and Methods

In this section the materials and methodology of experiments are explained. Information about membranes, chemicals, model foulants as well as experimental apparatus and analytical methods is also presented. However in order to prevent unnecessary repetition, the specific details regarding different topics are described in related chapters followed by the associated results and discussion.

4.1 Membranes

Flat sheet ultrafiltration membranes (regenerated cellulose-RC) from Millipore (PLTK15005) with MWCO of 30 kDa as well as mixed cellulose esters (Millipore) with pore size of 0.45 μm were used in the studies. RO membranes (DOW FilmTec, BW30) with a membrane resistance of about $1.12 \times 10^{14} \text{ m}^{-1}$ were also used. The pure water (Milli-Q) flux was first measured in the filtration experiments to stabilize the membranes and to obtain the intrinsic membrane resistance (R_m). A new membrane was used for each filtration test.

4.2 Model foulants

Bentonite (Sigma-Aldrich 18609), colloidal silica (Sigma Aldrich, Ludox TMA) and humic acid (Sigma-Aldrich) were used as model fouling agents in the experiments. The humic acid concentration was determined by a TOC analyzer (Shimadzu TOC-V CSH) to determine the rejection of the organic foulant by the UF membrane.

The colloidal silica was supplied in the form of 34 wt% suspension in deionised water at pH 7.0. The particle size of the colloidal silica was 20 nm as reported by the manufacturer. Sodium chloride (Sigma Aldrich) was used in some experiments as background ionic solution. Sodium chloride solutions were filtered with a 0.45 μ m filter (Millipore, Model HAWP04700) before use to remove possible contaminants. Ultra pure water (Milli-Q) was used to prepare the concentrated bentonite, silica, humic acid and sodium chloride solutions.

4.3 Reproducibility of results

A set of three experiments was performed for SDI and MFI tests using MF membranes to account for experimental error. Relative errors were within 10% for SDI and MFI measurements

To ensure proper experimental reproducibility for MFI-UF and FFM experiments, several membranes such as PVDF, PES and RC were tested. Among these membranes, RC provided the most stable flux and membrane resistance. Hence RC membrane was selected as a UF for all experiments. The results showed an error of about 5% to 8% for MFI-UF and FFM experiments.

4.4 Experimental apparatus

4.4.1 Dead-end filtration set-up

The dead end filtration was used to measure fouling indices and the specific cake resistance and the set up is depicted in Figure 4.1. A stainless steel feed reservoir (2 Liter capacity) was connected to a dead-end filtration cell (maximum capacity of 120 ml, Custom made) with an active membrane area of 0.0012 m². The required

trans-membrane pressure (TMP) in constant pressure filtration was supplied via a nitrogen gas cylinder. The permeate volume and TMP were measured with an electronic weighing balance (Mettler Toledo, Model PB3002-L) and pressure transducer, respectively. Data from the weighing balance and pressure transducers were recorded using a data acquisition system (National Instrument, Model PCI 6014 and LabView 7). To conduct experiments under constant flux mode, a peristaltic pump (Masterflex L/S pump) was installed in the permeate line of the dead-end cell to maintain constant flow of permeate.

Figure 4.1: Schematic diagram of dead-end constant pressure filtration device

4.4.2 Low pressure cross-flow filtration set-up

A cross-flow filtration set-up which was used in this study to conduct critical flux measurements for UF membranes and Feed Fouling Monitor (FFM) experiments (refer to chapter 6) is depicted in Figure 4.2.

Figure 4.2: Schematic of low pressure cross-flow filtration setup

The crossflow membrane cell was made from acrylic with an effective membrane area of 0.0012 m^2 . The channel of the cell is 60mm long, 20 mm in width and 7 mm in height. The feed solution was introduced from a 10 L feed tank using a gear pump (Cole Palmer Model 75211-15) to the system. The temperature of the feed solution was maintained constant at a certain temperature (25°C) with cooling water from a chiller (Polyscience, Model 9106AA2P). The feed tank was equipped with a stirrer (Panasonics Model M81X25GD4W2) to ensure the solution was well mixed. The feed pressure and flow rate were monitored with a pressure gauge (Ashcroft) and two flow meters (Gilmont Instrument) respectively. A high precision pressure transducer (Cole Palmer Model 206) was used to measure the supplied pressure on the retentate (P1) and permeate side (P2) of the membrane. A mass-flow controller (Brooks instrument, Model 5882/D1A1C3800) was used in the experiments to control the flux. For all experiments NI PCI-6221, M Series data acquisition system (DAS) and Labview 8 were used for data collection.

4.4.3 Cross-flow RO filtration set-up

The flow sheet of the experimental setup for crossflow reverse osmosis system is shown in Figure 4.3.

Figure 4.3: Schematic diagram of reverse osmosis set-up for colloidal fouling studies

The custom made stainless steel RO cell which was used for this study had a flow channel of $320\text{mm} \times 60\text{mm} \times 0.8\text{mm}$ with an effective membrane area of 0.0186m^2 . The feed solution was pumped from a 20L feed tank using a high-pressure pump (Hydra-Cell Pump) to the RO unit and a mass flow controller (Brooks Instrument, Model 5882) were used to adjust and control permeate flow. The feed water temperature was kept constant at $25 \pm 1^\circ\text{C}$ using a chiller (Polyscience, Model 9112) while permeate and concentrate flow were recycled back to the feed tank during filtration. An overhead stirrer (Panasonics, Model MX8G5B) was used to mix the feed solution in the feed tank during filtration and a back pressure regulator (Swagelok, Model KBP) was applied to control the system pressure and flow during

filtration. Feed and permeate pressure were monitored using high accuracy pressure transducers (Ashcroft digital industrial gauge- 30 2174 SD 02L) while two flow-meters (Cole Palmer-PMR1-010640 and PMR1-010810) were used to monitor feed flow rate. The conductivity and temperature of feed and permeate were monitored by conductivity meters (Eutech Alpha Cond500). A data acquisition system (DAQ system) National Instrument, Model PCI 6014 was used to record parameters such as temperature, flux and conductivity.

Other instruments were also connected to the RO setup to conduct further experiments like ultrasonic time domain Reflectometry (UTDR) measurements and sodium chloride tracer response experiments. More details of these techniques are described in chapters 7 and 8 respectively.

4.5 Analytical methods

4.5.1 Zeta potential measurement

The Zeta potential of model foulants was measured using the Laser Doppler Velocimetry (LDV) method (Malvern ZetaSizer Nano ZS) [135]. Sample solutions were freshly prepared using Mili-Q water. Prepared samples were slowly injected into a zeta potential cell to avoid any interference by bubbles during measurement. Each test was repeated at least three times to ensure consistency of the results.

4.5.2 Membrane surface charge measurement

A SurPASS electrokinetic analyzer [136] was used to characterize the original membrane surface charge (zeta potential) based on streaming potential measurement. The zeta potential was measured at pH of 5-6 using an electrolyte

solution of 10 mM potassium chloride (KCl, Merck, Singapore). An electrolyte solution was circulated in a setup containing the flat sheet membrane sample. The Ag/AgCl electrodes located on both sides of the membrane were used to detect the streaming potential of the sample. The Fairbrother-Mastin method was applied to calculate the zeta potential of the membrane [136].

4.5.3 Quartz crystal microbalance with dissipation (QCM-D)

Quartz crystal microbalance with dissipation (QCM-D) measurement was conducted to study and quantify any interaction between humic acid and colloidal silica. QCM-D can provide a real time measurement of organic adsorption on inorganic surfaces [137, 138]. Silica-coated quartz crystal sensors with 14 mm diameter (Q-Sense, QSX 301, Sweden) and fundamental resonant frequency of 4.95 MHZ, were used to simulate the surface of the colloidal silica foulant.

To verify the fundamental frequency of each crystal, experiments were first conducted under dry air conditions followed by Milli-Q water for 10 mins to stabilize the sensor. Then humic acid solution (15 mg/L) was fed into the flow chamber at a flow rate of 10 $\mu\text{L}/\text{min}$ for 60 minutes and any changes of resonance frequency and energy dissipation measured. According to the Sauerbrey Equation (4.1) [139] the change in frequency is related to the adsorbed amount of humic acid on the sensor per unit surface.

$$\Delta F = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (4.1)$$

where Δm is change in mass adsorbed (kg) on the crystal sensor, f is the frequency (Hz), f_0 is the resonant frequency (Hz) of the sensor, A_q is the piezoelectrically active crystal area (m^2), ρ_q is the density of quartz (kg/m^3), and μ_q is the shear modulus of the quartz (Pa). Figure 4.4 represents QCM-D experimental setup.

Figure 4.4: QCM-D experimental set-up

Before each experiment, the sensor was pre-cleaned using 2% sodium dodecyl sulfate (SDS) solution and then rinsed by Milli-Q water followed by drying with ultrapure N_2 gas. This method is explained in more detail in chapter 5.

CHAPTER 5

Membrane Fouling Prediction Indices – The Effect of Foulant Type and Operating Mode

5.1 Abstract

Several factors affecting conventional fouling indices including SDI, MFI, MFI-UF (under constant pressure and constant flux) were investigated in this chapter. The very non-linear response of SDI to concentration was confirmed whereas the MFI results showed more linear behaviour. Analysis of the MFI-UF for colloidal silica and humic acid showed that the specific cake resistance was highest at low concentration and gradually declined at higher concentrations. For the mixed foulants the presence of modest amounts of humic acid (≤ 15 mg/L) tended to reduce both MFI-UF and specific resistance below that of the colloidal silica alone (50-150 mg/L). At high concentrations of humic the MFI-UF of the combined foulants exceeded that of silica alone. Over a broad range of NaCl the MFI-UF (constant pressure and constant flux) of the silica was observed to pass through a maximum, and this was explained by changes to particle-particle interactions as salt concentration increased. In contrast with colloidal silica, a maximum of MFI-UF was not observed in the range of NaCl concentration in this study.

5.2 Introduction

Reverse osmosis (RO) is widely used for water reclamation and desalination. The

This chapter is based on: "The fouling potential of colloidal silica and humic acid and their mixtures" by A.H. Taheri, L.N. Sim, C.T. Haur, E. Akhondi, and A.G. Fane. Published in Journal of Membrane Science, 433 (2013) 112-120.

SDI is an empirical method and frequently provides misleading information on the quality of feed water for RO membranes [7, 140]. However due to its simplicity, this fouling index is popular for characterizing the fouling potential of feed water for RO membranes. Another common method is the MFI (the modified fouling index) which has advantages over the SDI as it is more sensitive, reliable and linear with the foulant load [8, 25]. Both SDI and MFI are based on filtration of the feed by 0.45 μm membranes [8, 25, 141]. However the MF based $\text{MFI}_{0.45}$ may not capture all potential foulants, and the Modified Fouling Index δ Ultrafiltration (MFI-UF) has been proposed as an alternative to capture smaller colloidal particles than that by the $\text{MFI}_{0.45}$ [9, 119, 120].

This chapter provides a fundamental understanding on the influence of solution chemistry and operating conditions towards the indices. Parameters such as foulant concentration and salinity on the fouling indices such as SDI, $\text{MFI}_{0.45}$, MFI-UF constant pressure and MFI-UF constant flux are investigated.

5.3 Determination of SDI and $\text{MFI}_{0.45}$

The standard measurement of SDI and MFI was described in detail in Sections 3.3.1.1 and 3.3.1.2, respectively.

5.3.1 Experimental procedure

All membranes were compressed under constant pressure of 250 kPa with ultra pure water (Milli-Q) for 15 minutes before the main filtration test to have stable water flux as well as measurement of the intrinsic membrane resistance (R_m).

As described in Section 3.3.1.1, to determine SDI, the test solution was filtered

through a 0.45 μm membrane at constant applied pressure of 207 kPa (30 psig), and the rate of plugging of membrane was measured. The SDI test was performed with the dead end filtration setup (Figure 4.1).

The experimental procedure was as follows:

1. Assemble the set up as shown in (Figure 4.1).
2. Flush the feed tank to remove any possible contaminants and then fill it with test solution.
3. Adjust the pressure regulator to 207 kPa (30 psig). Put 0.45 μm membrane filter (47 mm diameter) in the membrane holder.
4. Completely open the flow control valve and simultaneously control the pressure.
5. Measure the time required to collect volume of 500 ml and record it as (t_i).
6. Maintain the filtration for a total time of 5, 10 or 15 minutes (T) (depends on type of SDI which is going to measure).
7. Measure the times required to collect a second 500 ml (t_f).
8. After completion of the test, calculate SDI by Equation (3.2).
9. Empty and clean the system and feed tank with MQ Water

The modified fouling index (MFI) tests used the same equipment and procedure as the SDI test, except that the permeate volume was measured and recorded continuously every 30 seconds over a 15 minutes filtration period. As mentioned in section (3.3.1.2), the MFI is defined by equation (3.7). The value of MFI can be determined graphically by plotting ($\frac{t}{V}$) as function of permeate volume (V).

5.3.2 Silt Density Index (SDI)

Table 5.1 and Figure 5.1 summarize the SDI measurements (SDI_{15} , SDI_{10} and SDI_5) with different concentrations of bentonite as a model foulant. Several experiments were repeated up to 3 times to ensure the reproducibility. Relative errors were within $\pm 10\%$ for SDI and MFI measurements.

Test No.	Membrane	Concentration of bentonite (mg/l)	SDI 15	SDI 10	SDI 5	$R_m(m^{-1})$
1	mixed cellulose esters 0.45 μm	1	0.63	0.46	0.35	1.43E+08
2	mixed cellulose esters 0.45 μm	2	0.5	0.37	0.004	1.40E+08
3	mixed cellulose esters 0.45 μm	3	0.8	0.53	0.45	1.40E+08
4	mixed cellulose esters 0.45 μm	6	4.16	5.24	5.94	1.38E+08
5	mixed cellulose esters 0.45 μm	10	4.92	6.84	11	1.42E+08

Figure 5.1: Effect of concentration of bentonite on SDI

The results show that the SDI values increased non-linearly with the concentrations of bentonite, e.g. the SDI_{15} values varied from 0.63 to 4.92 when the bentonite concentrations were in the range of 1-10 mg/L. It shall be noted there were no significant difference between SDI values at very low concentrations of bentonite

(<3 mg/L) which suggested this method was insensitive to determine the fouling potential of solutions with low concentrations of bentonite.

The results are in good agreement with previous studies. Park et al. (2006) [142] studied the effect of different foulants at various concentrations on SDI. They reported SDI values increased slowly with increasing NOM (natural organic matter) concentrations up to a certain level and then increased severely and finally became flat at higher concentration region (approaching the asymptote). Other research on the effect of concentrations of humic acid on SDI also confirmed a similar pattern [74].

It is anticipated that SDI values would approach a limiting asymptotic values (see section 3.3.1.1). The limit values are 6.67, 10 and 20 for SDI_{15} , SDI_{10} and SDI_5 respectively. For the concentration test the Maximum SDI values were 74%, 68% and 55% of the limit. This suggests the SDI_5 may be more sensitive at higher concentration.

5.3.3 Modified Fouling Index (MFI)

The results from the MFI tests are presented in Table 5.2 for different concentrations of bentonite using microfiltration (0.45 μ m).

Table 5.2: Modified Fouling Index (MFI) measurements for bentonite					
Test	Membrane	Feed	Concentration (mg/l)	MFI (s/L ²)	Rm
1	mixed cellulose esters 0.45 μ m	Bentonite	1	2.45	1.43E+08
2	mixed cellulose esters 0.45 μ m	Bentonite	2	3.57	1.40E+08
3	mixed cellulose esters 0.45 μ m	Bentonite	3	4.86	1.40E+08
4	mixed cellulose esters 0.45 μ m	Bentonite	6	9.34	1.38E+08
5	mixed cellulose esters 0.45 μ m	Bentonite	10	22	1.42E+08

As mentioned earlier, the value of MFI can be measured graphically by plotting $\frac{t}{V}$ as a function of permeate volume (V). The linear part of the curve shows the cake filtration which is representing MFI. To find the MFI value, the slope of each curve is plotted as a function of permeate volume and the minimum or the stable value of the slope is taken to represent the MFI (Figure 5.2).

Figure 5.2: Slope of filtration curve as a function of permeate volume (L)

Figure 5.3 presents variations of modified fouling index (MFI) for different concentrations of bentonite.

Figure 5.3: MFI measurements under various feed (bentonite) concentration

The MFI experiments results show a positive (quasi) linear relationship between the MFI values and the concentration of bentonite. Many researchers have observed linear relationships between MFI and concentration using different types of feed and under constant pressure [8, 74, 143]. The definition of fouling index ($I = C_b \alpha$) suggests that I (and MFI) should increase with C_b . The slight curvature in Figure 5.3 must be due to small changes to α caused by cake formation with different concentration feeds. With other types of feed (see below) a departure from linearity was also observed.

5.4 Determination of MFI- $UF_{\text{const.pressure}}$

Due to the instability of bentonite suspension and due to their particle sizes, bentonite is not appropriate in representing particulate contaminant in RO feed water. As such, colloidal silica and humic acid were selected as the model foulant for subsequent experiments. The resistances of all membranes were first determined by measuring the Mili-Q water flux at a constant pressure.

The typical results from plotting t/V as a function of V for 100 mg/L silica and 15 mg/L humic acid are plotted in Figure 5.4.

Figure 5.4: Filtration curve ($\frac{t}{V}$) vs. (V) for 15 mg/L HA and 100 mg/L SiO₂, constant pressure of 210 kPa

According to Equation (3.8), MFI-UF pressure refers to the slope of ($\frac{t}{V}$) vs. (V).

In this case, silica and humic acid have MFI-UF values of 186058 s/L² and 16713 s/L², respectively. These values of MFI are much larger than for bentonite particulate foulant.

5.4.1 Inorganic fouling experiments with silica

Filtration experiments were conducted with UF membranes (RC 30 kDa) to study inorganic colloidal fouling on MFI-UF. The silica concentration was in the range of 15-800 mg/L, and a constant pressure of 210 kPa was applied.

The effect of silica concentration on the MFI-UF is presented in Figure 5.5.

Figure 5.5: MFI-UF as a function of silica concentration in the feed water, constant pressure of 210 kPa

According to Figure 5.5, the results confirmed the direct relation of the modified fouling index (MFI-UF) value to the concentration of particles over most of the concentration range as anticipated by Equation (3.6). Similar trends for colloidal silica particles, humic acid and formazine under constant pressure filtration have been observed by others [8, 11, 74, 94, 142]. However the trend in the lower concentration ranges (below 100 mg/L) was non-linear, and this is more evident in the specific resistances. Using the MFI-UF values, it is possible to obtain specific cake resistance () based on Equation (3.6). Figure 5.6 shows specific cake resistance as a function of silica concentration.

Figure 5.6: Specific cake resistance of silica deposit as a function of silica concentrations, constant pressure of 210 kPa

The specific cake resistance shows a rapid increase and then steadily decreases to a plateau value when particle concentration increases. The initial value for specific cake resistance is anomalously low, probably due to the poorly dispersed cake formation at very low particle concentration where the cake layer is not mature due to insufficiency of the convected solids in the bulk. The subsequent trend from low to raised to a lower constant value can be explained by changes in effective cake structure for different solids concentrations. At low solid concentrations, the deposition process can be orderly producing layers with few defects. This low porosity structure would have raised α . As the concentration increases, the cake layering becomes more disordered with more random voids, causing higher porosity and lower specific cake resistance [88]. The cake layering process is influenced by net solids convection as determined by flux and concentration leading to the observed plateau in α .

5.4.2 Organic fouling experiments with humic acid

Humic substances, which are considered as a main component of dissolved natural organic matter (NOM) in surface waters, have a significant role in organic fouling of membranes. Organic fouling causes both reversible and irreversible flux decline, thus removing NOM is an important step in many pre-treatment processes [71]. Investigations of the influence of NOM on membrane fouling have been carried out by several researchers [72, 74, 75, 144]. For example, the ultrafiltration of natural water with various organic macromolecules and inorganic colloids indicated that organic matter had a much greater effect on the flux decline than inorganic colloids which can be attributed to the different fouling mechanisms, including pore plugging or cake formation [76].

Ultrafiltration experiments were performed with humic acid solutions in the range of 1-50 mg/L. The effect of humic acid on the MFI-UF values and specific cake resistance are presented in Figure 5.7 and Figure 5.8, respectively. Note that the total permeate volume was used to measure the rejection of humic acid by the UF membrane (Rejection = $55 \pm 10\%$).

Figure 5.7: MFI-UF as a function of humic acid concentration, constant pressure of 210 kPa

Figure 5.8: Specific cake resistance as a function of humic acid concentration, constant pressure of 210 kPa

In common with the colloidal data the MFI-UF values for humic acid showed a generally linear relationship with the concentration of humic acid shown in Figure 5.7. However in the low concentration range (<10 mg/L) the values were above trend, as observed with the silica. This is reflected in the calculated specific resistance shown in Figure 5.8. In agreement with colloidal fouling experiments,

there is a significant decline in specific resistance as concentration increases from 1-10 mg/L and then negligible increase in from 10-50 mg/L humic acid.

5.4.3 Combined fouling experiments

Most fouling index studies have concentrated on individual organic or inorganic foulants and the effect of combined foulants on membrane filtration remain relatively poorly understood. Therefore the objective of this section is to study the influence of concentration for both colloidal (silica) and organic (humic) foulants, alone and in mixtures, on membrane fouling potential under constant pressure filtration. The trends in MFI-UF and specific cake resistances are also compared.

5.4.3.1 Characterization of model foulants and membrane surface

5.4.3.1.1 Zeta potential of foulants

Surface charge of foulants was measured by the Laser Doppler Velocimetry (LDV) method (Malvern ZetaSizer Nano ZS). Surface zeta potentials of humic acid, colloidal silica and their mixture were measured under the same solution conditions used in the experiments (pH~7) and are summarized in Table 5.3.

Table 5.3: Surface zeta potential of model foulants *

Model foulants	Zeta potential (mV)
Colloidal silica (100 mg/L)	-39.6±2.3
Humic acid (15 mg/L)	-59.9±2.2
Colloidal silica (100 mg/L) + humic acid (15 mg/L)	-52.4±1.4

* Reported values are the average of three measurements with standard deviation.

Silica (100 mg/L) had a negative surface zeta potential of -39.6±2.3 mV whereas

humic acid (15 mg/L) had a significantly higher negative surface zeta potential - 59.9 ± 2.2 mV. Surface zeta potential for the mixture of humic acid (15 mg/L) and colloidal silica (100 mg/L) was measured as -52.4 ± 1.4 which is more negatively charged than colloidal silica, but less negatively charged than humic acid alone. This is assumed to be due to the interaction of humic acid and silica that resulted in changes to the surface properties of the colloidal silica (see 5.4.3.1.3).

5.4.3.1.2 Membrane surface charge measurement

The surface charge (zeta potential) of the UF membrane (RC 30 kDa) at a pH of ~ 7 was also measured based on the streaming potential measurement by using a SurPASS electrokinetic analyzer [136]. The membrane was negatively charged with a zeta potential of approximately -21 mV (in 10 mM KCl).

5.4.3.1.3 Adsorption by QCMD

Figure 5.9 shows the amounts of humic acid adsorbed onto the silica-coated quartz crystal sensor (experimental details in 4.4.3).

Figure 5.9: Amounts of humic acid adsorbed on silica-coated quartz crystals sensor as a function of time

According to the surface zeta potential measurements, both the silica and the humic acid had significant negative charge, so electrostatic repulsion between these model foulants should limit adsorption of HA on silica. This finding is in good agreement with Contreras et al. (2009) [145] who observed very low adsorption of humic acid on the surface of colloidal silica. To put the amount adsorbed into perspective a monolayer of humic acid on the silica particles could be equivalent to 1-10 mg/m², which is order of magnitude higher than the measured value (~10 ng/m²). However the data in Table 5.3 implies some surface interaction.

5.4.3.2 Effect of humic acid in the presence of colloidal silica

In these experiments the humic acid concentration was increased from 2.5 mg/L to 50 mg/L while the silica concentration was kept constant at 100 mg/L. Figure 5.10 compares the MFI-UF for organic, colloid and combined fouling experiments as well as the sum of individual organic and colloidal foulants. The calculated MFI-UF refers to sum of individual MFI-UF for HA and SiO₂ ($MFI_{\text{calculated}} = MFI_{\text{SiO}_2} + MFI_{\text{HA}}$). However, the measured MFI-UF refers to the MFI-UF value obtained from filtration using mixed foulants.

Figure 5.10: MFI-UF for different feed: humic acid (various concentrations), colloidal silica (100 mg/L), combined foulants (various concentrations of HA and 100 mg/L silica), constant pressure of 210 kPa

The measured MFI-UF increased as the concentration of humic acid increased, and the MFI-UF for the mixture was higher than the fouling index of individual humic acid at all concentrations. However, at low concentration of humic acid (< 15 mg/L), the measured MFI-UF of the combined fouling was lower than the silica alone or the summation of the fouling indices for silica and humic acid. At higher concentrations (> 20 mg/L) the measured MFI-UF was greater than the MFI-UF of the silica alone. To explain this behavior there is a need to consider the likely effects of foulant interactions during filtration of complex solutions containing both organic and colloidal particles. According to surface zeta potential values (Table 5.3), adsorption of HA on the membrane surface would increase the electrostatic repulsion between the membrane and colloidal silica. This would hinder deposition of colloidal silica on the membrane and as a result create a more porous initial cake layer. However, $\frac{t}{V}$ versus V plot used to provide MFI-UF uses the slope

generated by multiple layers of foulant and therefore characterizes foulant-foulant deposition. Although QCM-D experiments revealed low adsorption of HA on colloidal silica, it could still increase the net repulsion either by increasing the surface charge or by penetrating between silica particles. Humic acid has higher negative charge compared to silica and could increase the net repulsive forces within the deposit leading to higher cake porosity with lower fouling potential. However, the data in Figure 5.10 suggests that beyond a certain load of humic acid the interparticle voids start to become blocked and the cake becomes less porous, giving a higher MFI-UF. Figure 5.11 illustrates these ideas for the mixed foulant cake. The organic-filled void model is analogous to a bacterial cake, where the presence or absence of extra-cellular organic substances has been shown to make a significant difference in cake resistance [146].

Figure 5.11: Schematic of cake layer on the membrane surface, (a): silica, (b): silica in the presence of low concentration of humic acid (c): silica in the presence of high concentration of humic acid

Li and Elimelech (2006) [147] also studied fouling mechanism of colloids and natural organic matter and suggested that there is a synergistic effect due to hindered back diffusion. They claimed that the back diffusion of one model foulant can be hindered by the presence of other types of foulants and thereby increase the cake resistance. Thus, possible explanations for the trends at higher humic acid content might be either due to hindered back diffusion or filling the voids between colloidal particles and infiltration of humic acid in the silica cake layer. It is also possible that both mechanisms apply. The combined effect would be a cake with a low porosity, a greater resistance and therefore a higher MFI-UF. Not surprisingly the sum of the individual MFI-UFs does not match the mixture MFI-UF very well. This highlights the fact that knowledge of the fouling propensity of the individual foulants does not lead to the fouling propensity of the mixture. This interpretation contrasts with that of Choi et al. (2009) who reported that fouling by mixed foulants can be related simply to the individual MFIs [148]. Figure 5.12 shows the specific cake resistance results obtained from experiments for the mixture of silica at different humic acid concentrations.

Figure 5.12: Specific cake resistance for different feed: humic acid (various concentrations), colloidal silica (100 mg/L), combined foulants (various concentrations of HA and 100 mg/L silica), constant pressure of 210 kPa

The trends mirror those for MFI-UF, and emphasize the significant effect a small amount of humic acid can have on the specific resistance of the silica cake (a 32% drop at 2 mg/L humic).

5.4.3.3 Effect of colloidal silica in the presence of humic acid

In these experiments the humic acid concentration was fixed at 15 mg/L and the silica concentration increased from 15 to 150 mg/L. Figure 5.13 presents the MFI-UF data and Figure 5.14 the specific resistances from dead-end filtration under constant pressure for humic acid, silica and their mixture.

Figure 5.13: MFI-UF results: Humic acid (15 mg/L), colloidal silica (various concentrations), combined foulants (various concentrations of Silica and 15 mg/L HA), constant pressure of 210 kPa

Figure 5.14: Specific cake resistance results: Humic acid (15 mg/L), colloidal silica (various concentrations), combined foulants (various concentrations of Silica and 15 mg/L HA), constant pressure of 210 kPa

The measured MFI-UF increased by increasing the silica concentration in the presence of humic acid. At low concentrations of silica (≤ 25 mg/L) the MFI-UF for the mixture was greater than that for silica alone. At higher values of silica, the mixture MFI-UF was less than for silica alone. Whether the MFI-UF is enhanced or

diminished appears to depend on the relative amounts of humic and colloid. When the proportion of humic is low the MFI-UF is diminished; this is also evident in Figure 5.10. Under these conditions humic acid may promote interparticle repulsion and increasing porosity. With more humic acid present the results imply a loss of cake porosity, presumably due to interstitial loading by humic acid. The data also confirm that knowledge of the individual MFI-UFs cannot be used reliably to predict the fouling potential of the mixture. The trends in specific cake resistance are similar. Over most of the silica concentration range the specific cake resistance of the mixture of foulants is significantly smaller than that of the silica alone. However, this trend is dependent on the selected humic concentration (here 15 mg/L) as evident from Figure 5.12.

5.4.4 Effect of salinity on fouling (MFI-UF_{const. Pressure})

5.4.4.1 Colloidal silica

The influence of salinity (ionic strength) on NF and RO membrane fouling has been investigated by many researchers. Hong and Elimelech (1997)[149] observed reduction in NF permeability with an increase in ionic strength. In general, increasing salinity of a feedwater has been reported to aggravate fouling in many studies [58, 59, 150-152]. Typically, stable colloidal particles in surface water have negative charge due to their high zeta potential. Also, the membrane surface typically has a negative charge and develops a double layer in water. High ionic strength decreases electrostatic charge repulsion and compresses the double layer at the membrane surface which leads to reduction of pure water permeability. Furthermore, higher salinity compresses double layers around particles, allowing

them to accumulate more densely on the membrane surface which increases the specific cake resistance. Cho et al. (2000) [153] reported higher rejection of polyethylene glycols PEGs and decrease in pores size of a UF membrane at higher ionic strength. Chong et al. (2008) [27] observed the porosity of the cake layer using colloidal silica decreased with increasing ionic strength, ranging from 0.6 to 0.4 when NaCl concentration increased from zero to 10000 mg/L NaCl. As noted above, this observation can be due to the suppression of the electrostatic double layer repulsion under high ionic strength causing the formation of a more compact cake layer.

The influence of salinity on MFI-UF under constant pressure filtration was investigated in this section. Some of the data have been used in Chapter 7 and Chapter 8 as input to a predictive fouling model. A 30 kDa RC membranes were used for all experiments at constant pressure (2.1 bar). Various NaCl concentrations were prepared as the ionic background and 200 mg/l SiO₂ was used as the model foulant.

The value of MFI-UF under constant applied pressure can be determined from the slope of the linear part of the graphs by plotting ($\frac{t}{V}$) as function of permeate volume (V) as detailed in section 5.3.3. The obtained MFI-UF values to assess the effect of salinity are presented in Figure 5.15.

Figure 5.15: The MFI-UF of feedwater for 200 mg/L SiO₂ as a function of NaCl

The MFI-UF initially increased with increasing salinity reaching a maximum at about 10000 mg/l NaCl followed by a decrease in MFI-UF values as the salinity increase. The observed trend is similar to that reported by Sim et al. (2010) [11] who studied on the impact of salt concentration on the fouling indices using silica mixture (20nm to 100nm). They also observed the maximum of fouling indices occurred between 0.15M (8700mg/L) and 0.2M (11600mg/L) of NaCl. The initial increase is possible due to reduction in cake porosity (increasing specific cake resistance) as the inter-particle distance between particles in the cake layer decreased. On the other hand, subsequent decrease in MFI-UF is probably due to the increase in salinity above the critical concentration of coagulation (CCC) where the particles becomes less negatively charged and the zeta potential value approach zero at high concentration of NaCl. This indicated that the electrostatic repulsion between particles are significantly reduced and hence easily aggregated.

Figure 5.16 shows the zeta potential of silica suspension as a function of NaCl

concentration. Sim et al. (2010) [11] also observed a significant shift from small particle size to large particle size when the salinity increasing. The larger particles formed would lead to a more permeable cake via the CarmanóKozeny Equation (2.14).

Figure 5.16: Zeta potential of colloidal silica (200 mg/L) as a function of NaCl Concentration

Similar behavior was also observed by several researchers. Boerlage et al. (2003) [26] studied on the effect of ionic strength on the MFI-UF using tap water. The maximum MFI-UF with tap water was observed at 0.1 M as an ionic strength in their experiments. Bacchin et al. (1996) [154] reported a change for the specific cake resistance of bentonite in cross-flow ultrafiltration using KCl in the range of 10^{-5} to 0.1 M. The bentonite specific cake resistance was independent of ionic strength up to 0.001 M, and then it increased to a maximum at 0.003M and then decreased to below that measured at 10^{-5} M of salt concentration.

Figure 5.17: Specific cake resistance and porosity of cake layer as a function of NaCl concentration. Feed: 200 mg/L SiO₂

As seen from Figure 5.17, specific cake resistance mirrors the MFI trend and increases as the ionic strength was increases at zero to 10,000 mg/L NaCl then decrease from 10,000 mg/L NaCl to 25,000 mg/L NaCl.

5.4.4.2 Humic Acid

Investigations of the influence of the salt concentration on MFI-UF and specific cake resistance of humic acid (15 mg/L) were carried out using different NaCl concentrations. The effect of salt concentration on the MFI-UF values is presented in Figure 5.18.

Figure 5.18 The MFI-UF of feedwater for 15 mg/L HA as a function of NaCl

In contrast with colloidal silica, the MFI-UF for humic acid increased with NaCl concentration over the range 0-25000 mg/L of NaCl. There was no evidence of a decline at higher NaCl concentrations. Similar to silica, humic acid experienced a reduction of electrostatic double layer and become less negatively charged when NaCl was added to the solution. This allows the molecules to deposit and accumulate more densely at the membrane surface and form thick deposit layer [149]. However, the concentration of NaCl has not yet reach to its CCC, which is why coagulation of humic acid to a bigger particle is not expected in this range of NaCl concentration. Several researchers also observed that at high ionic strength, humic macromolecules become coiled and shift to smaller apparent conformation with a more spherical shape and as a result can form a more compact fouling layer [72, 75]. This explanation is supported by the zeta potential vs. NaCl concentration plot, Figure 5.19 at which the zeta potential is about -25mV at salt concentration of 25000mg/L.

Figure 5.19: Zeta potential of HA (15 mg/L) as a function of NaCl Concentration

Figure 5.20 shows the specific cake resistance as a function of salt concentration.

Figure 5.20: Specific cake resistance of cake layer as a function of NaCl concentration

5.5 Determination of $\text{MFI-UF}_{\text{const. flux}}$

As described in section 3.3.1.3, it may be more appropriate to determine MFI-UF in constant flux mode as most of the RO plants operate at constant flux. $\text{MFI-UF}_{\text{constant}}$

J_{flux} can be determined from the fouling index (I) versus time plot as a minimum or stable fouling index [9] or based on the linearity of the pressure versus time plot.

Figure 5.21 demonstrates typical data for the TMP vs. time during a MFI-UF test, using a 30 kDa RC membrane at a constant flux of $166 \text{ l/m}^2 \cdot \text{hr}$.

Figure 5.21: TMP as a function of time. Conditions: 100 mg/L SiO_2 , 0 mg/L NaCl, UF membrane (RC, 30 kDa), Constant Flux ($166 \text{ l/m}^2 \cdot \text{hr}$)

Due to the nature of the feed or operational conditions, the TMP relation as a function of time may not be linear in all cases. According to the TMP profile in Figure 5.21, it is clear that there are two different slopes which represent different types of fouling mechanisms. It is assumed that the initial slope of the curve is caused by cake filtration whereas the second slope is due to cake filtration with compression. In this study, $\text{MFI-UF}_{\text{consant.flux}}$ values are determined using the initial slope of the TMP vs. time curves which is assumed to be related to cake filtration phenomena.

A layer by layer deposition of particle on the membrane surface creates additional hydraulic resistance known as cake resistance. To obtain representative MFI values, it is necessary to have multiple layers of foulant. The cake mass and number of cake layers on the membrane surface can be determined using equations (3.11) and (3.12), respectively. For the example of Figure 5.21, the formation of five layers of colloidal silica on the membrane surface would have taken only 7 seconds.

5.5.1 Effect of Particle Concentration on $\text{MFI-UF}_{\text{const.flux}}$

The relationship of MFI-UF under constant flux with foulant load has been investigated for different concentrations. The same filtration mechanisms in constant pressure were anticipated as in constant flux mode. Thus, the initial slope in the curve (pressure vs. time) was due to cake filtration followed by cake compression which is more evident at higher particle concentrations.

5.5.1.1 Inorganic fouling experiments using silica

The development of the pressure increase over time for various particle concentrations of silica is plotted in Figure 5.22.

Figure 5.22: TMP vs. Time. Conditions: 0 mg/L NaCl, constant flux: (75 l/m².hr), UF membrane (RC, 30 kDa)

The modified fouling index determined for various concentrations of silica is plotted in Figure 5.23, where the initial slope of the curve (TMP vs. Time) was used to calculate the fouling index.

Figure 5.23: MFI-UF constant flux: (75 l/m².hr), 0 mg/L NaCl, UF membrane (RC, 30 kDa)

Figure 5.23 shows that the MFI-UF increased linearly with increasing concentration of particles. Linearity of MFI-UF with particle concentration is anticipated as a result of the cake filtration based on equation (3.6) and (3.17). These results show that fouling index is proportional with particle concentration and confirm the assurance of cake filtration in the MFI-UF test under constant flux filtration. Boerlage (2004) [9] reported a linear dependence of MFI-UF under constant flux with the particulate concentration for canal water and tap dilution. It should be noted that the values of $\text{MFI-UF}_{\text{const.flux}}$ were considerably smaller than $\text{MFI-UF}_{\text{const.pressure}}$. This difference is described in section 5.6.

Figure 5.24 presents the specific cake resistance results obtained from experiments for the constant flux filtration of silica at different concentrations.

Figure 5.24: Specific cake resistance of silica deposit as a function of Silica concentrations; Flux: (75 l/m².hr), 30kDa RC, 0 mg/L NaCl

According to Figure 5.24, a plateau value of specific cake resistance was obtained after rapid increase and subsequent decrease of specific cake resistance. The low

value of specific cake resistance is probably because of a poorly dispersed cake layer at very low silica concentration. At modest concentration of silica (50 mg/L), the particles can deposit homogenously which makes a cake layer with few defects and high specific cake resistance. The more disordered cake layer created as the particle concentration increases leads to higher cake porosity and lower specific cake resistance [88]. The same trend for specific cake resistance as a function of particle concentration was observed during constant pressure filtration of colloidal silica Figure 5.6. However the magnitudes differ and this is discussed in section 5.6.

5.5.1.2 Organic fouling experiments using humic acid

Ultrafiltration experiments were performed with humic acid solutions in the range 1-30 mg/L. The effect of humic acid on the MFI-UF values and specific cake resistance are presented in Figure 5.25 and Figure 5.26, respectively.

Figure 5.25: MFI-UF a function of HA concentrations; constant flux: (75 l/m².hr), UF membrane (RC, 30 kDa), 0 mg/L NaCl

Figure 5.26: Specific cake resistance of silica deposit as a function of HA concentrations;
Flux: (75 l/m².hr), 30kDa RC, 0 mg/L NaCl

According to equation (3.6), linear relationship of fouling index and concentration is anticipated. Figure 5.25 shows the linear increase of MFI-UF as a function of humic acid concentration for constant flux filtration. Similar observation was also obtained by Sim et al. (2010) [11] who investigated the linearity of MFI-UF under constant flux for various concentrations of humic acid.

Figure 5.26 shows specific cake resistance reaches to plateau value at higher concentration of humic acid. At low concentration of HA (1-5 mg/L), the foulants can deposit homogenously which would make for a higher specific cake resistance. The more random particle deposition at higher concentration creates a cake with higher cake porosity and lower specific cake resistance [88]. It can be seen that both MFI and specific cake resistance for humic acid at constant flux and constant pressure are not too dissimilar. Section 5.6 discussed the difference and similarities between constant flux and constant pressure operation.

5.5.2 Effect of Applied Flux on $\text{MFI-UF}_{\text{const.flux}}$

The effect of applied flux in the range of 30-170 $\text{l/m}^2\cdot\text{hr}$ on the $\text{MFI-UF}_{\text{constant.flux}}$ was investigated using colloidal silica as a foulant model. The results for TMP versus time are depicted in Figure 5.27 for different applied fluxes.

Figure 5.27: TMP vs. Time. Conditions: 100 mg/L SiO_2 , 0 mg/L NaCl, UF membrane (RC, 30 kDa) different applied flux

The obtained MFI-UF values to assess the effect of applied flux are presented in Figure 5.28. $\text{MFI-UF}_{\text{consant.flux}}$ values are determined using initial slope of the TMP vs. time curves.

Figure 5.28: Effect of applied flux on MFI-UF, Conditions: 100 mg/L SiO₂, 0 mg/L NaCl, UF membrane (RC, 30 kDa)

The MFI-UF at constant flux was found to increase when applied flux increased. This is presumably due to greater permeate drag force that bring the colloidal particles closer and reduce the cake porosity. A similar trend was reported by Boerlage (2004) [9] when investigating the effect of applied flux (70 to 110 L/m².hr) on MFI-UF_{constant.flux} using tap and canal water. They reported that at higher flux the particles impinge on the membrane surface at higher velocity and the cake may then assume a higher specific cake resistance than at a lower applied flux. Sim et al. (2010) [11], also reported that MFI-UF increased as applied flux increased for the filtration of 50 mg/L silica colloidal in buffer under constant flux operation.

5.5.3 Effect of salinity on fouling (MFI-UF_{const.flux})

The effect of salinity on MFI-UF under constant flux filtration was investigated in this section using colloidal silica and humic acid as model foulants. A 30 kDa RC membrane was used for all experiments. The initial slope of TMP as a function of time was used to measure MFI-UF values.

5.5.3.1 Colloidal silica

The effect of salinity on the rate of colloidal fouling and cake properties was studied using a 200 mg/L colloidal silica solution over a broad range of NaCl concentrations (2000 to 16000 mg/L). Figure 5.29 shows the TMP as a function of NaCl concentration for dead-end filtration under a constant flux (95 l/m².hr).

Figure 5.29: Effect of NaCl concentration on MFI-UF, Conditions: 200 mg/L SiO₂, UF membrane, constant flux: 95 l/m².hr, (RC, 30 kDa)

The results are consistent with high ionic strength that compresses the double layer around the particles and allows them to pack more densely in the deposited cake.

Figure 5.30 shows the experimentally determined specific cake resistance as a function of the NaCl concentration.

Figure 5.30: Specific cake resistance for colloidal silica fouling as a function of NaCl concentration, Flux: (95 l/m².hr), 200 mg/L SiO₂, 30 kDa RC

This figure mirrors the MFI-UF and indicates that the specific cake resistance increased as the ionic strength increased owing to a concentration increase from 2000 to 16000 mg/L NaCl. A similar trend in the specific cake resistance was observed by Chong et al. (2008) [27] for colloidal silica fouling at different NaCl concentrations under constant pressure filtration. They reported that the specific cake resistance increased with increasing ionic strength, from zero to 10,000 mg/L NaCl due to the suppression of the electrostatic double layer repulsion under high ionic strength. The correlation obtained from calculated α value as a function of NaCl concentrations for constant flux filtration between 0 to 16,000 mg/L of NaCl is:

$$\alpha = (-3 \times 10^{-8} C_{NaCl}^2 + 0.001 C_{NaCl} + 4.1333) \times 10^{14} \quad (5.1)$$

Equation (5.1) was used to estimate the specific cake resistance of foulant layer based on salt concentration of a solution in the fouling prediction model (Chapter 7 and Chapter 8).

5.5.3.2 Humic acid

To investigate the influence of the salt concentration on MFI-UF and specific cake resistance of humic acid (20 mg/L) under constant flux filtration several experiments were carried out using different NaCl concentrations. The effect of salt concentration on the MFI-UF values is presented in Figure 5.31.

Figure 5.31: Effect of NaCl concentration on MFI-UF, Conditions: 20 mg/L HA, UF membrane (RC, 30 kDa), constant flux: 95 l/m².hr

It is generally observed that fouling of humic substance in a higher ionic strength environment is more severe [155]. Figure 5.31 indicates that a higher NaCl concentration increases the MFI-UF under constant flux which is in good agreement with experiments under constant pressure filtration (Figure 5.18). At higher salt concentration, humic acid molecules change configuration and would creates a

more dense cake layer. As a result, specific cake resistance with increased in the salt concentration would increase as observed in Figure 5.32.

Figure 5.32: Effect of NaCl concentration on specific cake resistance, Conditions: 20 mg/L HA, UF membrane (RC, 30 kDa), constant flux: 95 l/m².hr,

The correlation calculated from measured specific cake resistance as a function of salt concentrations for constant flux filtration between 0 to 15,000 mg/L of NaCl is:

$$\alpha = (2 \times 10^{-8} C_{NaCl}^2 + 0.0001 C_{NaCl} + 2.3972) \times 10^{14} \quad (5.2)$$

This Equation (5.2) was used to estimate the change of specific cake resistance with salt concentration in a solution for RO fouling prediction purposes (Chapter 8).

5.6 Comparison between constant pressure and constant flux

It can be seen from Figure 5.5 and Figure 5.23 that for colloidal silica the MFI-UF_{const.pressure} values were considerably greater than MFI-UF_{const.flux}. The MFI-UF_{const.pressure} was in the range of 74,000 s/L² to 295,000 s/L², while under constant flux (75 l/m².hr) the values ranged from 2,700 s/L² to 42,000 s/L² as the colloidal

silica concentration varied from 25 to 200 mg/L. Sim. et al. (2011) [123] claimed that a direct comparison between $\text{MFI-UF}_{\text{const.pressure}}$ and $\text{MFI-UF}_{\text{const.flux}}$ may give misleading information on the fouling propensity of the feed due to scaling the $\text{MFI-UF}_{\text{const.flux}}$ to the standard pressure of 2 bar based on Equation (3.17). However, from Figure 5.6 and Figure 5.24 it was found that specific cake resistance values of experiments under constant pressure was significantly higher than those under constant flux.

The specific cake resistance values obtained from two experiments under constant pressure and constant flux for colloidal silica are compared in Figure 5. 33.

Figure 5. 33: Specific cake resistance: Constant flux vs. Constant pressure.
100 mg/L SiO_2 , 0 mg/L NaCl, Constant pressure: 210 kPa, Constant flux: 75 $\text{l/m}^2\cdot\text{hr}$

As shown in Figure 5. 33 the specific cake resistance for colloidal silica obtained from the experiment at constant pressure is about one order of magnitude greater than the specific cake resistance determined from constant flux filtration. According to the Carman-Kozeny relationship (Equation 2.15), the differences between the

specific cake resistance values indicates that the cake formed under constant pressure has a lower porosity compared to the cake formed under constant flux. This observation can presumably be due to greater initial flux and drag force on constant pressure filtration flux which can compress the cake and decrease the overall cake porosity. Figure 5.34 compares the flux versus permeate volume to illustrate the large differences in foulants convective transport for constant pressure and constant flux filtration.

Figure 5.34: Flux vs. permeate volume for constant flux and Constant pressure filtration. 100 mg/L SiO₂, 0 mg/L NaCl, Constant pressure: 210 kPa, Constant flux: 75 l/m².hr

The figure above indicates that the initial flux for constant pressure ($\sim 730 \text{ l/m}^2\text{.hr}$) is around 10 times higher than the constant flux filtration ($75 \text{ l/m}^2\text{.hr}$). At higher initial flux, the colloidal silica experiences greater hydrodynamic drag force towards the membrane, resulting in lower cake porosity and greater specific cake resistance. To confirm this, the compressibility factor of colloidal silica was investigated using Equation (2.15) [156]. The compressibility factor of colloidal silica was estimated by plotting $\log \epsilon$ versus $\log \hat{p}$ where compressibility factor is

the slope of the line. For compressible cakes, the slope is 1 and the lesser the compressibility, the lesser the slope (See Chapter 2, section 2.7). 100 mg/L colloidal silica was used to investigate the dependency of specific cake resistance on applied pressure (Figure 5.35).

Figure 5.35: Compressibility check for 100 mg/L SiO_2 , 0 mg/L NaCl

The compressibility factor of colloidal silica was found to be around 0.9 as shown in Figure 5.35. This indicates that the specific cake resistance of colloidal silica is very dependent on the applied pressure/flux and supports the explanation for the differences between in constant pressure and constant flux. The porosity difference between constant pressure and constant flux can also be estimated from the measured specific cake resistance values and the Carman-Kozeny Equation (2.14). This shows values of porosity of about 0.43 and 0.68 for constant pressure and constant flux of dead-end filtration of 100 mg/L SiO_2 , respectively.

However the trends for humic acid are different. From

Figure 5.8 and Figure 5.26, it is seen that the specific cake resistance for humic acid under constant flux is slightly higher than the specific cake resistance at constant pressure. The specific cake resistance and the flux versus permeate volume from two experiments under constant pressure and constant flux for 20 mg/L HA are depicted in

Figure 5.36 and Figure 5.37.

Figure 5.36: Specific cake resistance: Constant flux vs. Constant pressure.
20 mg/L HA, 0 mg/L NaCl, Constant pressure: 210 kPa, Constant flux: 75 l/m².hr

Figure 5.37: Flux vs. permeate volume for constant flux and Constant pressure filtration.
 20 mg/L HA, 0 mg/L NaCl, Constant pressure: 210 kPa, Constant flux: 75 l/m².hr

As shown in Figure 5.36, the specific cake resistance obtained from constant flux (11.53×10^{14} m/kg) is higher than the in constant pressure (7.87×10^{14} m/kg), even though the initial flux in constant pressure filtration (~ 756 l/m².hr) is around 10 times higher than constant flux filtration (75 l/m².hr). These results suggest that the specific cake resistance of humic acid is independent of applied flux which is in contrast with colloidal silica. To investigate the dependency of humic acid resistance on the applied pressure, the compressibility factor of 20 mg/L humic acid was measured using Equation (2.15).

Figure 5.38: Compressibility check for 20 mg/L HA, 0 mg/L NaCl

According to Figure 5.38, the compressibility of humic acid was around 0.45 which is significantly lower than colloidal silica. This shows that humic acid is less compressible than colloidal silica and that higher initial fluxes would have less effect on the cake porosity and specific cake resistance. Another factor that may contribute to the trends is that the high initial flux in constant pressure filtration could generate aggregation of macromolecules such as humic acid and thereby reduce their specific cake resistance [157, 158].

5.7 Conclusions

The effects of different factors on membrane fouling indices with colloidal silica and humic acid under both constant pressure and constant flux were investigated. Based on the experimental results, the following conclusions can be made:

- The very non-linear response of SDI to concentration was confirmed whereas the MFI results showed a more linear behaviour (in line with the literature).

- A linear response of $\text{MFI-UF}_{\text{const.pressure}}$ was observed for both humic acid and colloidal silica, except at the lowest concentrations. A rapid increase was observed for the specific cake resistance of colloidal silica followed by a steady decrease when particle concentration increased. The initial low value of the specific cake resistance is assumed to be due to dispersed cake formation at low particle concentration and subsequent decline was due to inhomogeneous deposition of particles on the membrane at higher concentration.

- In a mixture of silica and humic acid the increasing humic acid at a constant concentration of colloidal silica could result in an increase in the $\text{MFI-UF}_{\text{const.pressure}}$ value. At low concentrations of humic acid the $\text{MFI-UF}_{\text{const.pressure}}$ of the combined foulants was less than that of silica alone. This may be due to repulsion of humic acid and silica and creation of a more porous cake layer. At higher concentrations of humic the $\text{MFI-UF}_{\text{const.pressure}}$ of the combined foulants exceeded that of silica alone. This may be due to infiltration of humic acid into the silica cake layer, or hindered back diffusion effects, creating a lower porosity cake.

- Similar behavior was observed when the concentration of colloidal silica increased and the HA was kept constant. Over most of the silica concentration range the $\text{MFI-UF}_{\text{const.pressure}}$ value was lower than that of the silica alone.

- Over a broad range of NaCl (0 to 25,000 mg/L) the $\text{MFI-UF}_{\text{const.pressure}}$ of the colloidal silica was observed to pass through a maximum, and this was explained by changes to particle-particle interactions as salt concentration increased.

- In contrast with colloidal silica the $\text{MFI-UF}_{\text{const.pressure}}$ for humic acid increased monotonically over the range of 0-25000 mg/L NaCl due to changes in humic substances size to smaller apparent conformation and formation of a more compact cake layer.
- A linear relationship of $\text{MFI-UF}_{\text{const.flux}}$ concentration was obtained for both humic and colloidal silica. The results also highlighted that $\text{MFI-UF}_{\text{const.flux}}$ increased as the applied flux increased. Over a broad range of NaCl Concentration (0-16000 mg/L) $\text{MFI-UF}_{\text{const.flux}}$ increased for both humic acid and colloidal silica concentration.
- The specific cake resistance of colloidal silica was found to be sensitive to the initial flux and the applied pressure. The results indicated greater values for constant pressure filtration of colloidal silica than constant flux. The greater drag force in constant pressure operation could change the structure of the cake and decrease the porosity. However, for humic acid the specific cake resistance of humic acid in constant pressure filtration was less than for constant flux and may be due to the lower compressibility value and aggregation of foulants at higher flux.

CHAPTER 6

Principle of the Feed Fouling Monitor and RO

Fouling Prediction

6.1 Introduction

The conventional fouling indices are usually determined by off-line measurement techniques based on dead-end filtration, which does not consider the effect of the actual flow conditions. To overcome this problem, the Crossflow Sampler Modified Fouling Index (CFS-MFI) was proposed using a cross-flow cell to simulate the hydrodynamic conditions in a RO process [10, 124]. In this simulator a sampler membrane, with supra-micron pores, is located in the crossflow cell operated at constant flux. The smaller (foulant) particles pass through the sampler membrane with the permeate and deposit on a microfilter in a dead-end setup where the standard MFI is determined. Recently, Sim et al. (2010) [11] studied the Crossflow Sampler Modified Fouling Index UF (CFS-MFI_{UF}) and found that the CFS-MFI had a lower value than the standard MFI on the same feed. To investigate the accuracy and sensitivity of the CFS-MFI_{UF}, RO experiments were performed for which the results indicated good agreement between the CFS-MFI_{UF} trend and the actual RO fouling behaviour. The fouling trend predicted by the CFS-MFI_{UF} deviated by only 11% from the actual RO transmembrane pressure (TMP) profile in the absence of concentration polarization of salt. However, in the presence of 6 g/L NaCl, the predicted RO profile was significantly smaller than the actual RO fouling profile, which suggested that the potential effect of cake-enhanced osmotic pressure (CEOP) cannot be neglected. In a subsequent paper Sim et al. (2011) included the

effect of CEOP. However this required measuring the rate of fouling deposition (by collection and weighing) and assuming a cake porosity [13].

The aforementioned fouling indices have been proven to not be reliable for predicting RO performance due to lack of a comprehensive model that can relate the simulator to actual RO module performance or the proper physics to go from the simulator to the actual RO module. Another major challenge is selection of a suitable membrane for the simulator since it is important to quickly assess the fouling potential of the feed.

Therefore, the focus of this work is 1) To develop a flow simulator as a feed fouling monitor (FFM) including selection of a suitable membrane, 2) To adapt models for the TMP that will permit taking data from the simulator in order to project RO fouling performance in terms of the TMP rise, 3) To compare FFM projections with actual RO performance.

6.2 Feed Fouling Monitor

To overcome the limitations of aforementioned fouling prediction techniques, an on-line flow simulator has been developed for characterization of the fouling propensity of feed water to RO which is called the feed fouling monitor or FFM. The feed fouling monitor (FFM) is an adaptation of the integrity sensor (IS) developed by the Singapore Membrane Technology Center [159, 160]. The FFM is based on the TMP rise due to particle deposition, and is designed for cross-flow. Its performance needs to be correlated to the particulate fouling (colloidal particles and/or macromolecules) encountered in RO. The FFM was used to incorporate the effect of cross-flow hydrodynamics and also detect foulant loads from a sample

stream continuously passing over a small collection UF membrane. A UF rather than a RO membrane was used because it is more sensitive to deposition and can provide reasonably rapid assessment of the fouling potential using the FFM (See 7.4.1 for further discussions). Since the deposits captured by the FFM are potential RO foulants, the specific cake resistance and cake porosity obtained from this simulator can be used to predict the TMP rise for a RO membrane. A schematic of the FFM experimental setup is shown in Figure 4.2. The concept is that the developed FFM can be connected upstream of the RO system to provide on-line monitoring of the feed quality and assist in predicting RO performance.

It should be noted that in this chapter the effect of CEOP is not considered. The predictions are based on fouling resistance development and compared with RO fouling. The CEOP contribution is considered in Chapter 7 and Chapter 8.

6.3 Theory

Most RO membrane processes are operated under constant flux with increasing TMP due to fouling. Since both pressure and flux may cause cake compression, conducting FFM experiments under the constant flux mode and with cross-flow should better simulate RO fouling behaviour. Hence, the FFM experiments were run with the same feed solutions as the RO experiments to measure the TMP as a function of time.

A RO fouling prediction model has been previously developed for both constant pressure and constant flux operation [161]. The model is briefly described as follows. The TMP of a RO system as a function of filtration time is given by:

$$\text{TMP}_r = \Delta P_{\text{membrane}} + \Delta P_{\text{cake}} \quad (6.1)$$

Where $\Delta P_{\text{membrane}}$ and ΔP_{cake} are the pressure drops contributed by the membrane and deposited cake, respectively. As noted above the effect of CEOP is neglected, but will be considered in the analysis in Chapter 7 and Chapter 8. So from Equation (6.1):

$$\text{TMP}_r = J_r \mu_r R_{mr} + J_r (J_r - J_{crit}) \mu_r I_r t_r \quad (6.2)$$

Where the subscript r refers to a RO membrane. J_r is the permeate flux, μ_r is the fluid viscosity.

The resistivity is defined as [9, 26, 120]:

$$I(t) = \alpha_c(t) \cdot C_b \cdot \text{Rej} \quad (6.3)$$

Where, α_c is the specific cake resistance and C_b is the foulant concentration in the bulk.

In this study the resistivity of RO (I_r) is related to the resistivity obtained from the FFM (I) using the corrections for the particle deposition (θ) factor and cake ratio (β):

$$I_r = \beta I \quad (6.4)$$

The cake ratio (β) accounts for the possible differences between the cake formed on the FFM and that deposited during RO which is assumed in this study to be equal to 1. The second term in equation (6.2) assumes that all the foulant convected towards

the membrane remains in the cake. However Chong et al. (2008) [27] observed that this is not necessarily the case and this is depicted in Figure 6.1.

Figure 6.1: Cake accumulation, illustrating fractional deposition factor (θ)

Equation (6.2) can be corrected for this by introducing the fractional deposition factor (θ), so,

$$TMP_r = J_r \mu_r R_{mr} + J_r (J_r - J_{crit}) \mu_r I_r \theta t_r \quad (6.5)$$

Chong et al. (2008) [27] investigated the effect of cross-flow velocity on the observed deposition factor for colloidal silica. They observed a significant influence of the cross-flow velocity on the fraction of convected particles that were deposited on the membrane surface. In current study we have treated θ as an empirical factor and deduced its value from best-fit of fouling trends.

Hence, for the FFM, equation (6.5) can be re-written as follows:

$$TMP = J \mu R_{mr} + J(J - J_{crit}) \mu I t \quad (6.6)$$

Equations (6.6) and (6.3) imply that the specific cake resistance can be determined from the slope of the TMP versus time plot for constant flux filtration using the

FFM. It should be noted that use of this plot requires independent measurement of critical flux, J_{crit} .

6.4 Critical flux measurement

For the FFM to simulate RO fouling it is necessary to operate at net fluxes similar to the RO. The net flux is the difference between the imposed flux, J , and the critical flux, J_{crit} ; that is J_{Net} it is equal to $J - J_{crit}$ [162]. The critical flux refers to that flux below which negligible fouling occurs and above which a membrane is fouled [31]. It cannot be assumed that the critical fluxes in UF and RO are the same due to the differences in membrane properties and ionic environment. Hence, in this study the critical fluxes for both the RO and UF membrane (i.e., as used in the FFM) were measured for the same feed and crossflow conditions. The critical flux was measured using the step-by-step method [31].

6.5 Materials and methods

6.5.1 Membranes and Materials

UF regenerated cellulose (RC) membranes with a molecular weight cut-off (MWCO) of 30 kDa (Millipore - PLTK15005) were used for the FFM experiments to capture model foulants. The filtration tests were initiated with pure water (Milli-Q) to stabilize the membrane and to measure its intrinsic resistance (R_m). RO membranes (DOW FilmTecBW30) with a membrane resistance of $1.12 \times 10^{14} \text{ m}^{-1}$ (equivalent to water permeability of about $2.5 \text{ l/m}^2\cdot\text{hr}$ per bar) were also used in this study.

A 34 wt% suspension of colloidal silica (Sigma Aldrich, Ludox TMA) in deionised water at pH 7.0 diluted to 200 mg/L was used as a model inorganic foulant. A particle size of 20 nm for the colloidal silica was reported by the manufacturer. Humic acid (Sigma-Aldrich) were also selected as a model organic foulant. The desired concentration of Sodium chloride (Sigma Aldrich) was used in experiments as background ionic solution. All feed solutions were prepared using Milli-Q water.

6.5.2 Experimental apparatus

The description of the FFM and crossflow RO setup was presented in Chapter 4, section 4.3.2 and section 4.3.3, respectively.

6.6 Results and discussion

6.6.1 FFM experiments

Since most RO processes are operated under constant flux, FFM experiments were conducted under the constant flux mode and cross-flow for prediction purposes.

6.6.1.1 Critical flux in FFM

The critical flux for the FFM measured by the flux stepping method was $J_{cr.FFM.SiO_2} = 83 \pm 5 \text{ l/m}^2 \cdot \text{hr}$ and $J_{cr.FFM.HA} = 80 \pm 5 \text{ l/m}^2 \cdot \text{hr}$ for colloidal silica and humic acid, respectively. This critical flux was significantly higher than the critical flux measured for the same feed with the RO membrane under similar hydrodynamic conditions. The critical flux of colloidal silica (200 mg/L) for the RO experiments (section 6.6.2) was measured using the step-by-step method and was found to be $J_{cr-RO} = 20 \pm 2 \text{ l/m}^2 \cdot \text{hr}$. The differences in membrane properties and ionic

environment could explain the differences in J_{critUF} and $J_{crit RO}$. The lower critical flux for RO could be due to both a lower barrier to deposition [113, 163] and an additional transport mechanism [164, 165]. Table 6.1 shows that the RO membrane has a lower zeta potential than the UF membrane and this would provide a lower particle-membrane repulsion.

Table 6.1: Surface zeta potential of membranes and model foulants*.

Sample	Zeta potential (mV)
RO membrane	-8±1.2
UF membrane	-21±1.9
Humic Acid	-59.9±2.2
Colloidal silica	-39.6±2.3

* Reported values are the average of three measurements with standard deviation

In addition to this the RO membrane has a salt concentration gradient in the boundary layer, whereas the UF membrane does not. The ϕ diffusiophoresis ϕ phenomenon, which transports colloids up a salt gradient [164, 165], could have a role in RO but not in UF. Both electrokinetic and diffusiophoretic effects would tend to give a lower critical flux for RO conditions. These observations warrant further study.

6.6.1.2 The influence of concentration

The influence of humic acid concentration (10-40 mg/L) on the fouling rate under cross-flow and constant flux is reported in this section. The obtained results are presented as TMP versus time in Figure 6.2.

Figure 6.2: Effect of humic acid concentration on TMP, cross-flow velocity: 0.1 m/s, 2000 mg/L NaCl, Flux: 125 l/m².hr, membrane: 30 kDa RC

The results in Figure 6.2 indicate higher fouling rate ($dTMP/dt$) at higher concentrations of humic acid. This is presumably due to the greater rate of convective foulant transport towards the membrane surface at higher concentrations. Hence, the overall rate of humic acid deposition on the membrane surface and hydraulic cake resistance increased as concentration increased.

6.6.1.3 The effect of cross-flow velocity

Hydrodynamic conditions such as cross-flow velocity have a significant influence on membrane fouling [166]. The effect of cross-flow velocity of constant flux filtration for colloidal silica is depicted in Figure 6.3.

Figure 6.3: Effect of cross-flow velocity on TMP, 200 mg/L SiO₂, 2000 mg/L NaCl, Flux: 125 l/m².hr, membrane: 30 kDa RC

It can be seen from Figure 6.3 that reduction of cross-flow velocity increased fouling rate ($dTMP/dt$). This is in good agreement with the literature that suggests increasing the cross-flow velocity will increase surface shear and can reduce the concentration polarization on the membrane surface by improving mass transfer and particle back transport mechanisms [167, 168]. Similar data are reported by Chong et al. (2008) [27] who reported that RO fouling behavior increased as the cross-flow decreased for filtration of colloidal silica. They also found greater amounts of particle deposition at lower cross-flow velocity. However, there are some conflicting reports regarding the interpretation of the effect of cross-flow velocity on membrane fouling. Sim et al. (2011) [123] observed two different fouling trends for the CFS-MFI running over a wide range of cross-flow velocities for both raw seawater and a mixture of colloidal silica. For low cross-flow velocity, they reported that CFS-MFI decreases as cross-flow increases while subsequent increase

in cross-flow after a certain value (~ 0.37 m/s) leads to higher CFS-MFI due to reduction of particles size in deposit cake layer.

6.6.1.4 The effect of applied flux

6.6.1.4.1 Inorganic fouling experiment with Silica

Silica is one of the most common inorganic foulants in feed waters in membrane processes. The effect of flux in the range of 95-155 $\text{l/m}^2\cdot\text{hr}$ on the fouling was investigated using 200 mg/L SiO_2 as the model foulant and 2000 mg/L NaCl as the ionic buffer. The cross-flow velocity was kept constant at 0.1 m/s for all experiments. It should be noted that the net fluxes (see 6.4) were in the range 12 to 72 $\text{l/m}^2\cdot\text{hr}$.

Figure 6.4: TMP as a function of time for different fluxes under a cross-velocity of 0.1 m/s for a feed containing 200 mg/L SiO_2 and 2000 mg/L NaCl

Figure 6.4 shows the TMP as a function of time for fouling in cross-flow at different fluxes. The higher fluxes associated with a more rapid fouling rate can be explained by an increase in permeate drag force on the foulant layer and an increase

in the particle deposition rate [169]. Zue et al. (1997) [58] observed the important role of permeate drag force caused by the flux on colloidal deposition and membrane fouling. Their results indicated that the fouling rate is controlled by the permeate drag in a high ionic strength environment due to reduction of the double layer repulsion force. They suggested that if the permeate drag can overcome the double layer repulsive forces; the particles can migrate and deposit on the membrane surface. In general increasing colloidal fouling potential at higher flux can be related to: 1) higher concentration polarization and deposition rate of foulants 2) greater permeate drag force towards the membrane surface. Higher operational flux would also result in greater permeate volume and more deposited particles. Figure 6.5 presents the TMP as a function of permeate volume at different fluxes for cross-flow filtration of colloidal silica.

Figure 6.5: TMP as a function of permeate volume for different fluxes under a cross-velocity of 0.1 m/s for a feed containing 200 mg/L SiO₂ and 2000 mg/L NaCl

The results of fouling experiments at different fluxes (Figure 6.5), demonstrate that the rate of the TMP rise significantly increased as applied flux increased.

To investigate the effect of applied flux on the cake properties equations (6.3) and (6.6) were used to obtain the specific cake resistance α calculated from the slope of the TMP as a function of time. Since silica particle size is known, the cake porosity can be determined from the specific cake resistance using the Carman-Kozeny equation (2.14). The resulting specific cake resistances and cake porosities are plotted in Figure 6.6. The critical flux (J_{UF}) measured in the FFM was 85 ± 5 l/m²hr, and the imposed fluxes were in the range 95 to 155 l/m²hr, so that the net fluxes in the FFM were in the range 12 to 72 l/m²hr. These net fluxes covered and extended those for the RO experiments (J_{Net} = 10 to 28 l/m²hr).

Figure 6.6: Experimentally determined specific cake resistance and porosity for a colloidal silica cake layer as a function of flux for a cross- flow velocity of 0.1 m/s, 200 mg/L SiO₂ and 2000 mg/L NaCl

This figure indicates that the specific cake resistance increases monotonically and the cake porosity decreases monotonically with increasing flux. However, for compressible foulants, the cake layer can be compacted at high fluxes. At higher fluxes the specific cake resistance is larger, thereby implying reduced cake porosity

[9, 123]. Consequently, the TMP rise in Figure 6.3 is probably due to both accelerated cake layer growth and a denser cake layer at higher fluxes. These results will be used to predict RO fouling potential performance.

6.6.1.4.2 Organic fouling experiments using humic acid

The effect of applied flux in the range of 110-155 l/m².hr on the fouling was investigated in this section using 20 mg/L Humic acid and 2000 mg/L NaCl as the as background ionic solution. The cross-flow velocity was kept constant at 0.1 m/s for all experiments. The TMP as a function of time and permeate volume for humic acid are depicted in Figure 6.7 and Figure 6.8, respectively.

Figure 6.7: TMP as a function of time for different fluxes under a cross-velocity of 0.1 m/s for a feed containing 20 mg/L HA and 2000 mg/L NaCl

Figure 6.8: TMP as a function of permeate volume for different fluxes under a cross-velocity of 0.1 m/s for a feed containing 20 mg/L HA and 2000 mg/L NaCl

In good agreement with the colloidal silica experiments, the results of fouling experiments for humic acid also demonstrated that the rate of the TMP increased as flux increased. Equation (6.6) was used to calculate specific cake resistance of humic acid from the slope of the TMP as a function of time.

Figure 6.9 : Experimentally determined specific cake resistance for humic acid cake layer as a function of flux. Cross-flow velocity: 0.1 m/s, 20 mg/L HA, 2000 mg/L NaCl

Figure 6.9 presents the obtained specific cake resistance for humic acid under various fluxes. To calculate specific cake resistance, the critical flux for cross-flow filtration of 20 mg/L of humic acid was measured using the step-by-step method ($J_{cr.FFM} = 80 \pm 5 \text{ l/m}^2 \cdot \text{hr}$). Equation (6.6) was used to calculate specific cake resistance of humic acid from the slope of the TMP as a function of flux. The obtained results show a direct relation between specific cake resistance of humic acid and filtration flux. According to Boerlage (2004) [9], the specific cake resistance increase with increasing flux probably related to reduction of porosity by increasing flux.

6.6.2 RO experiments

Several RO fouling experiments under different applied fluxes were carried out using humic acid (20 mg/L) and colloidal silica (200 mg/L) with 2000 mg/L NaCl as ionic background. The RO TMP profiles as a function of time for range of fluxes using colloidal silica are plotted in Figure 6.10.

Figure 6.10: TMP as a function of time for different fluxes under a cross-flow velocity of 0.1 m/s for a feed solution containing 200 mg/L SiO_2 and 2000 mg/L NaCl

Figure 6.10 indicates that the TMP and fouling rate ($d\text{TMP}/dt$) increased with

increasing flux for colloidal silica fouling experiments. In the case of RO processes, salt concentration polarization can also be increased due to the fouling. This phenomenon is defined as cake-enhanced osmotic pressure (CEOP) which occurs by hindered back diffusion of the solutes by the foulant colloidal cake layer (see Chapter 2, section 2.6). The concentration of salt near the membrane surface increases and local osmotic pressure rises [12, 27]. Several studies indicate that for RO systems, CEOP contributes more to the fouling than changes in the cake resistance [12, 27, 163, 170]. Hoek and Elimelech [12] reported a strong effect of flux on CEOP. Their results suggested insignificant CEOP at low fluxes due to negligible cake deposition, while at moderate to high fluxes, the contribution of CEOP steadily increased. Chong et al. [27, 80] also observed a severe CEOP effect at higher fluxes due to a thicker cake layer.

For RO performance prediction it is also important to calculate the effective net flux which is the actual flux minus the critical flux. With an RO critical flux of 20 l/m².hr (see 6.6.1.1) the net fluxes were in the range 10 to 22.1 l/m².hr.

6.6.3 RO fouling prediction

In this section we assess whether the RO fouling trend running at different fluxes for colloidal silica can be predicted using the resistivity (I) or specific cake resistance obtained from FFM at the same hydrodynamic conditions. Equation 6.4 shows that the resistivity of RO (I_r) can be related to the resistivity obtained from the FFM. Hence, the TMP profile of RO can be predicted from equation 6.2 and the predicted trends are also compared against actual RO performance.

Figure 6.11 shows a comparison for a range of RO fluxes between the experimentally determined TMP profiles and those predicted by the model using the FFM data. Note that for prediction purposes, FFM experiments were conducted at same net flux as RO experiments.

Figure 6.11: TMP versus time for a range of RO fluxes showing the measured (solid lines) and predicted values (dashed lines) based on FFM running a same net flux with RO, cross-flow velocity of 0.1m/s and feed containing 200mg/L of colloidal silica and 2000 mg/L NaCl

The results indicate that the model using the FFM measurements provides a good estimate of the TMP profile for RO fouling only for RO operating at 30 l/m².hr (effective flux=10 l/m².hr). At higher fluxes, the predicted RO profile was found to underestimate the TMP rise and to deviate from the actual RO fouling trend as flux increases.

Many studies have demonstrated that the deposited foulant layer can also cause the cake-enhanced osmotic pressure (CEOP) as well as hydraulic resistance in RO systems [27, 79, 80, 170]. In fact, the CEOP effect could be the dominant

mechanism in RO systems. According to equation (2.13), concentration polarization is expected to increase exponentially with flux and therefore, the CEOP contribution on TMP rise is assumed to be greater at higher flux.

However, predicted TMP profiles in this section were only linked to hydraulic cake resistance; the effect of CEOP has not been considered for RO fouling prediction. Hence, it is clear from Figure 6.11 that the prediction by FFM underestimated the RO fouling at higher applied fluxes due to ignoring the CEOP contribution.

The potential contribution of CEOP on RO fouling will be incorporated into the developed model in the following chapters.

6.7 Conclusion

A novel fouling simulator, the feed fouling monitor (FFM), that employs a UF membrane was developed to predict RO fouling under the same flow conditions. Fouling was studied using colloidal silica and humic acid as the model foulants and sodium chloride as an ionic buffer for both the FFM and RO experiments.

A higher fouling rate ($dTMP/dt$) was observed at higher concentrations of humic acid due to greater rate of convective foulants transport toward the membrane surface at higher concentration. The rate of fouling ($dTMP/dt$) for filtration of colloidal silica was also increased as cross-flow velocity decreased.

The effect of flux on the fouling rate and cake properties was investigated for both RO and the FFM. The results showed that higher fluxes caused an increased fouling rate for both RO and the FFM. In the FFM studies the TMP increased more rapidly at higher fluxes presumably owing to a higher particle deposition rate and a

decrease in the cake porosity. The predicted fouling trends for RO based on the information obtained from FFM were found potentially to be smaller than the actual RO fouling profiles which highlight the significant effect of cake enhanced osmotic pressure. This is addressed in Chapter 7 and 8.

CHAPTER 7

Prediction of RO Fouling by FFM – UTDR

7.1 Abstract

In this chapter RO colloidal fouling was predicted using the on-line feed fouling monitor (FFM) (described in chapter 6) combined with a monitor based on ultrasonic time domain reflectometry (UTDR) under constant flux filtration. The fouling simulator (FFM) incorporated the relevant cross-flow conditions and detected the development of foulant load and resistance from a continuous sample passing over a small UF membrane. The UTDR was coupled to a RO membrane cell to monitor the rate of cake thickness increase, which is required information for the estimation of cake-enhanced osmotic pressure (CEOP). A model was developed to predict fouling in RO using data from the two monitors and combined both the cake resistance and the CEOP effect due to cake formation.

RO and FFM fouling experiments were performed at different constant fluxes using the same feed solutions (200 mg/L SiO₂, 2000 mg/L NaCl) and the same cross-flow velocity (0.1 m/s). The results showed that higher fluxes caused an increased fouling rate for both RO and the FFM. The foulant layer thickness measured by UTDR in the RO experiments increased faster at higher applied fluxes and the estimated CEOP effect was also strongly influenced by the flux.

The results show that the new model, combined with the FFM and UTDR

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measurements, can provide a good estimation of the RO fouling profile over a range of applied fluxes. This study also underscores the importance of CEOP in contributing to the increase in transmembrane pressure due to colloidal fouling in RO of saline feeds.

7.2 Introduction

For salt-rejecting NF and RO membranes fouling is often related to salt concentration polarization on the membrane surface, thereby creating an additional osmotic pressure barrier across the membrane. During filtration, the back diffusion of NaCl is hindered by the fouling layer and the concentration of NaCl is elevated near the membrane surface. As a result the osmotic pressure increases, which is defined as the cake-enhanced osmotic pressure (CEOP) [12, 27] (See Chapter 2, section 2.6).

The contribution of CEOP in RO fouling has been the subject of several recent studies [12, 27, 79, 80, 170]. The CEOP concept was introduced by Hoek et al. [12, 171] who developed a mathematic model for the CEOP mechanism due to the hindered back diffusion of salt. It is important to note that CEOP increases as cake height increases and for higher fluxes.

Hoek et al. (2003) [12] found that a thin foulant cake layer may cause significant reduction in flux due to both cake resistance and increase in concentration polarization. They reported that the contribution of CEOP to the RO performance loss can be higher than the hydraulic cake resistance. They also investigated the effect of cake porosity and cake thickness on the diffusion coefficient of solutes in the cake and its impact on CEOP. The greater the cake thickness and lower the

porosity contributed to a greater CEOP effect which is expected from Equation (2.13). Existing fouling indices which were described in chapter 3 are based only on the cake resistance; the effect of CEOP has not been considered for RO fouling prediction. Chong et al. [27, 80] confirmed the importance of cake height and flux experimentally using a sodium chloride tracer response technique to measure the CEOP effect during RO fouling.

In Chapter 6, an online fouling simulator, known as the Feed Fouling Monitor (FFM) has been proposed that allows estimation of the hydraulic cake resistance on the RO membrane surface. To include the contribution of CEOP in RO fouling the FFM is coupled with ultrasonic time domain reflectometry (UTDR) in this chapter.

In the present Chapter the UTDR was used to measure the height of the developing cake layer in the RO system which permitted estimation of the evolution of CEOP during filtration. UTDR has been successfully used to monitor membrane processes and was first applied to membranes by Greenberg and Krantz. It has been used to measure membrane fouling and cleaning and membrane compaction in RO systems [172-178]

UTDR is based on reflection of acoustic signals from membrane and fouling layers. In the present chapter UTDR was used to measure the height of the developing cake layer in the RO system which permitted estimation of the evolution of CEOP during filtration. To predict fouling in RO, a mathematical model developed in chapter 6 is extended to include both cake resistance and the CEOP effect due to cake formation.

Thus this chapter makes use of two monitors to provide the data required to predict transmembrane pressure (TMP) rise in RO due to colloidal fouling. The online Feed Fouling Monitor (FFM) is an adaptation of an integrity sensor that responds to changes in water quality [160, 179]. The FFM measures fouling resistance and specific cake resistance and this coupled with measured critical fluxes, allows prediction of the evolution of fouling resistance. The FFM data also provide estimates of fouling cake porosity. The UTDR measures the growth of fouling layer height and this, with knowledge of cake porosity, allows prediction of CEOP development. The predicted TMP profile combines the effects of resistance and CEOP.

Specific issues addressed in the chapter are: 1) development of a model to estimate TMP rise from trends in fouling resistance and cake height; 2) development of the FFM to provide online data on fouling characteristics, including selection of the most suitable FFM membrane; 3) using UTDR to measure fouling height trends; 4) comparison of experimental TMP rise in RO for a range of imposed fluxes with the predicted TMP profiles using monitor input.

7.3 Fundamentals of UTDR

The ultrasonic measurement technique, which is also known as the ultrasonic time domain reflectometry (UTDR), was first applied as a noninvasive, real-time technique to monitor membrane processes by Greenberg and Krantz [172-175]. This technique was used to characterize membrane compaction and investigate membrane fouling and cleaning in a flat sheet RO module [180]. The method was later applied to the more industrially important spiral-wound modules [181, 182].

Since then, many studies have employed the ultrasonic technique to monitor the fouling progress caused by various types of foulants [183-186]. Recently, the UTDR has been successfully used to detect biofouling on polymeric membrane surfaces [187].

When an ultrasonic wave encounters an interface, reflection, transmission, and mode conversion can occur while changes in the transit time, attenuation, scattering or frequency content of a waveform provide information on the media properties. The magnitude of the transmitted and reflected waves depends on the difference between the acoustic impedance of the media it is travelling through $(Z_2 - Z_1)$, where the acoustic impedance is a function of the sound velocity and density of the medium $(Z_i = \rho_i c_i)$. Subscripts 1 and 2 refer to the medium from which and into which, respectively, the wave is propagating.

For an incident wave perpendicular to an interface, the amplitude (A) of the reflected wave relative to the incident wave is given by:

$$A = \frac{Z_2 - Z_1}{Z_2 + Z_1} \quad (7.1)$$

A storage oscilloscope or electronic digitizer during UTDR measurements determines the time between wave transmission and its reflection. The arrival time (t) for a wave reflection is related to the distance between the reflecting interface and the transducer (Δd) and the wave velocity:

$$t = \frac{2\Delta d}{c} \quad (7.2)$$

Figure 7.1 presents typical UTDR data for instantaneous voltage of the reflected wave versus time which gives the amplitude, arrival time and phase modulation of the reflected waves.

Figure 7.1: (1) Schematic flat-sheet membrane module represents a UTDR transducer and reflected wave (A), membrane surface (B) and top of fouling layer (C), (2) Reflected wave amplitude versus time for typical UTDR measurements
As can be seen from

Figure 7.1, reflection from the interface between the feed solution and the top plate of the membrane module (2-A) can be observed in a shorter time than the reflection from the interface between the membrane surface and the feed solution (2-B). Note that deposition of foulants on the membrane surface will reduce the arrival time (2-C). The arrival times attributed to reflections B and C can be used to calculate the amount of membrane compaction or thickness of cake layer while reflection A provides a stationary reference point.

The UTDR has been largely applied to study fouling in flat sheet membranes, and have proven to be able to detect the initiation and growth of the fouling layer on flat sheet RO membrane. While most of the work that has been done in lab-scale

systems, Chai et al. (2007) applied UTDR to the more industrially important spiral-wound modules [188]. Applying UTDR to a spiral-wound module is complicated by multiple reflections that occur from each of the interfaces associated with the wrapping material and concentric membrane, membrane support, and channel-spacer. However, UTDR can be easily fitted to a canaryø side-stream cell. The advantage of using the side stream monitor (or canaryø) is that it has its own controlled crossflow and flux, which make it possible to allow exploration of how plant changes could influence fouling. This will provide a feedback for proper process control and recommend an operating boundary for the safeguard of the plant.

7.4 Materials and Methods

7.4.1 Membranes and materials

The RO experiments (fouling runs and UTDR measurements) used the Dow Filmtec BW30 TFC membrane in flat sheet form. This membrane has a typical water permeability of $2.5 \text{ l/m}^2\text{hr}$ per bar. For the FFM a UF membrane was used. This was the regenerated cellulose Millipore PLTK 15005, with a molecular weight cut-off (MWCO) of 30 kDa, selected for its consistent properties. The UF membrane has a typical water permeability of about $300 \text{ l/m}^2\text{hr}$ per bar, i.e. about two orders of magnitude more permeable than the RO membranes. The advantages of using UF in the FFM are that it provides a sensitive and rapid response to fouling resistance development. The challenge in using UF in the FFM is to operate at a net fouling rate similar to the RO system. For this it is necessary to determine the critical fluxes of both UF and RO for the same feed and hydrodynamics.

The filtration tests were initiated with pure water (Milli-Q) to stabilize the membrane and to measure its intrinsic resistance (R_m). A 34 wt% suspension of colloidal silica (Sigma Aldrich, Ludox TMA) in deionised water at pH 7.0 was diluted to 200 mg/l and used as the model foulant. A particle size of 20 nm for the colloidal silica was reported by the manufacturer. All feed solutions were prepared using Milli-Q water.

7.4.2 Analytical methods

The Laser Doppler Velocimetry (LDV) method (Malvern ZetaSizer Nano ZS) was used to measure the zeta potential of other foulants (section 4.4.1) while the original surface zeta potential of membranes were measured using surPASS electrokinetic analyzer (section 4.4.2).

7.4.3 Experimental apparatus

7.4.3.1 RO setup and UTDR facilities

The cross-flow RO setup is shown in Figure 7.2.

Figure 7.2: Schematic of RO system with UTDR measurement facility

The stainless steel RO cell had a flow channel of $320 \times 60 \times 0.8$ mm with an effective membrane area of 0.0186 m^2 . A detail description of the crossflow RO setup was presented in Chapter 4, section 4.3.3.

The UTDR measurement system involved three components, the signal pulser and receiver, the ultrasonic transducers and electronic digitizer. The UTDR system used a 5 MHz ultrasonic transducer (Olympus Model VentriScan) and a 300 MHz digitizer (National Instruments, Model PCI-5152) with a sensitivity of 0.5 ns/div (39 mV/div) coupled to the top and centre of the RO cell using silicone oil (Olympus, Model C2) as a couplant as shown in Figure 7.2.

7.4.3.2 Feed Fouling Monitor (FFM)

An on-line flow simulator, the feed fouling monitor (FFM), based on the principle of particle deposition was designed for cross-flow. Description of the developed FFM setup was presented in detail in chapter 4, section 4.3.2.

7.4.3.3 Dead-end setup

In contrast to RO, UF does not reject salt; hence, the differences between the specific cake resistance due to salinity in UF and RO filtration systems was investigated using a dead-end setup to isolate the effect of the ion environment on the double layer. Description of the developed dead-end setup was presented in detail in chapter 4, section 4.3.1.

7.4.4 Experiment Design Considerations

7.4.4.1 Fouling prediction model

A RO fouling model, (described in Chapter 6) has been extended to incorporate the cake-enhanced osmotic pressure, and is described in section 7.5. The required inputs to the model determined the design and operation of the FFM and UTDR experiments.

7.4.4.2 RO-UTDR experiments

In order to assess whether the data from the monitors can predict RO performance, the actual RO fouling performance must be measured. Hence, cross-flow RO experiments were conducted over a range of constant fluxes for which the TMP was monitored as a function of time. The RO fouling layer thickness was also measured as a function of time by UTDR to incorporate the effect of cake height on CEOP in the model. Prior work has already verified the accuracy of UTDR measurements on both the thicknesses of biofilms [61] and inorganic silica foulant layer [48]. The time, t , required for a wave to travel from a reflecting interface is a function of the

distance between the reflecting interface and the transducer, Δd , and the wave velocity and is given by:

$$t = \frac{2\Delta d}{c} \quad (7.3)$$

7.4.4.2.1 Analysis of Acoustic Signature

Figure 7.3 shows plots of the amplitude of the acoustic wave response in volts for peaks A and B of interest as a function of the arrival time in microseconds: (i) full reflected signals of the cell and (ii) enlarged region for peaks A and B.

Figure 7.3: Peak Amplitude versus arrival time for a crossflow velocity of 0.10 m/s, an aqueous sodium chloride solution of 2 g/L and a constant flux of 48.1 LMH: (i) full reflected signals of the cell and (ii) peaks A and B of interest. Peak (A) is the reflection from the fixed top plate/feed solution interface, Peak (B) is the reflection from the permeate support/fixed bottom plate interface.

The peaks of interest are peaks A and B corresponding to the reflected acoustic wave generated from the following interfaces; feed solution/membrane, and permeate support/fixed bottom plate, respectively. To calculate the theoretical arrival time of the peaks of interest using equation (7.3), the following sound velocities are assumed for the materials; 2800 m/s for Perspex, 2000 m/s for the polymeric membrane material [63] and 1500 m/s for water. The thickness of the top Perspex plate is 26 mm and the thickness of the membrane after compaction is assumed to be 120 μ m [64]. The permeate support is a commercial product spacer of thickness of about 0.2 mm used in a spiral wound reverse osmosis module. Therefore, the theoretical arrival time of peaks A and B are calculated to be 19.63 μ s and 20.02 μ s, respectively, which are in close agreement with the actual arrival times of peaks A and B in Figure 7.3 (ii). Since the incident sound wave must pass through the relatively thick feed solution twice, whereas the foulant layer is relatively thin, the transit time for the sound wave reflected from the foulant layer interface will be determined primarily by the speed of sound in water. In summary, the foulant layer thickness is calculated using equation (7.3) for which the sound velocity is assumed to be 1500m/s, the same as that of water.

7.4.4.3 Design of the Feed Fouling Monitor

An on-line flow simulator, the feed fouling monitor (FFM), based on the principle of particle deposition at controlled flux was designed for cross-flow operation. An aim is to correlate its performance to the fouling (colloidal particles and/or macromolecules) encountered in RO. As explained above a UF, rather than a RO, membrane was used to provide rapid assessment of the fouling potential using the FFM. It is assumed that since the deposits captured by the FFM are potential RO

foulants, the specific cake resistance and cake porosity obtained can be used to predict the resistance component of TMP rise for a RO membrane. The CEOP contribution was ignored in the model for the FFM data analysis since the UF membrane passes salt. However, the CEOP contribution was retained in the model for predicting RO performance.

7.4.4.4 FFM experiments

Since most RO membrane processes are operated under constant flux with increasing TMP due to fouling, conducting FFM experiments under the constant flux mode and with cross-flow should simulate RO fouling behaviour. Hence, the FFM experiments were run with the same feed solutions as the RO experiments to measure the TMP as a function of time at the same net fluxes as the RO (see Chapter 6, section 6.4). In order to calculate the specific cake resistance and cake porosity, the model adapted for RO was used. The CEOP contribution was ignored in the model for the FFM data analysis since the UF membrane passes salt. However, the CEOP contribution was retained in the model for predicting RO performance.

7.4.4.5 Effect of salt concentration on the cake porosity

In contrast to RO, UF does not reject salt and salt concentration polarization does not occur. However, models are available to account for salt concentration polarization in RO systems. Hence, the difference between the salinity in the UF and RO filtration systems must be considered for prediction purposes. In addition to concentration polarization, the salt concentration can also influence the double layer around the foulant particles and change the foulant layer properties, such as

porosity. To allow for this the effect of salt concentration on the specific cake resistance and cake porosity has been investigated. In order to isolate the effect of the ion environment on the double layer, these measurements were conducted using a dead-end apparatus that eliminates the complications introduced by cross-flow (see 7.4.2.3). The TMP was monitored as a function of time for constant flux filtration using the dead-end filtration set up.

7.4.4.6 RO fouling prediction

Data collected from the FFM, RO-UTDR and the dead-end experiments were used to predict RO performance by the model adapted for RO. Actual RO performance was compared with the predicted TMP profiles.

7.5 Theory

7.5.1 Model development

7.5.1.1 Cross-flow RO filtration

A RO fouling prediction model has been previously developed in chapter 6 for constant flux operation and based on earlier works [161]. The model has been modified here to include the effect of CEOP. The TMP of a RO system as a function of filtration time is given by:

$$\text{TMP}_r = \Delta P_{\text{membrane}} + \Delta P_{\text{cake}} + \Delta P_{\text{CEOP}} \quad (7.4)$$

Where $\Delta P_{\text{membrane}}$ and ΔP_{cake} and ΔP_{CEOP} are the pressure drops contributed by the membrane, deposited cake and CEOP, respectively.

$$\text{TMP}_r = J_r \mu_r R_{mr} + J_r (J_r - J_{crit}) \mu_r I_r t_r + \text{CP} \cdot \Delta \Pi_m \quad (7.5)$$

where the subscript r refers to a RO membrane. J_r is the permeate flux, μ_r is the fluid viscosity, CP is concentration polarization modulus and $\Delta\Pi_m$ is the osmotic pressure difference. Equation (7.5) accounts for the fact that the fouling layer deposited on a salt-rejecting RO membrane hinders the diffusion of salt ions from the membrane surface back to the bulk solution. Thus the first two terms in equation (7.5) apply to UF, and the third term is added for RO.

According to Equation (6.4), the resistivity of RO (I_r) is related to the resistivity obtained from the FFM (I) using corrections for the particle deposition (θ) factor and cake ratio (β). The cake ratio (β) accounts for the difference between the cake formed on the FFM and that deposited during RO. In this study (β) has been assumed to be equal to 1. In this study the deposition factor was considered as an empirical factor and deduced its value from best-fit of fouling trends.

The concentration polarization, CP, is related to the flux and mass transfer of the membrane system via the boundary layer film model [12, 27, 80]. When no fouling is present:

$$CP = \frac{C_w - C_p}{C_b - C_p} = \exp\left(\frac{J}{D/\delta}\right) = \exp\left(\frac{J}{k_m}\right) \quad (7.6)$$

Where C_w , C_b , and C_p are the membrane surface, bulk and local salt concentrations, respectively; D is the solute diffusivity, δ is the CP layer thickness and k_m is the mass-transfer coefficient. However, in the presence of a cake layer, the salt concentration near the membrane wall C_w is increased due to the hindered back diffusion:

$$CP = \frac{C_w - C_p}{C_b - C_p} = \exp\left(\frac{J}{k_{eff}}\right) \quad (7.7)$$

The overall mass transfer coefficient (k_{eff}) in a fouled channel, consists of contributions from the unfouled section (k_{uf}) and the cake (k_c), and is described by [189]:

$$\frac{1}{k_{eff}} = \frac{1}{k_c} + \frac{1}{k_{uf}} \quad (7.8)$$

The mass transfer in the cake layer (k_c) can be determined as follows:

$$k_c = \frac{D_c}{\delta_c} \quad (7.9)$$

Where D_c is the diffusion coefficient of the solute in the cake layer and can be estimated by [190]:

$$D_c(t) = D \left(\frac{\varepsilon(t)}{1 - \ln \varepsilon(t)^2} \right) \quad (7.10)$$

Where ε is the porosity of the cake layer. Hence, k_c as a function of time is given by:

$$k_c(t) = \frac{D}{\delta_c(t)} \left(\frac{\varepsilon(t)}{1 - \ln \varepsilon(t)^2} \right) \quad (7.11)$$

The mass transfer coefficient in the unfouled section of channel (k_{uf}) can be determined from the GraetzóLeveque equation for laminar flow in an empty channel over an impermeable unfouled surface by [79]:

$$k_{uf} = 1.62 \left[\frac{vD^2}{2hL} \right]^{1/3} \quad (7.12)$$

Where D is the diffusion coefficient, v is the cross-flow velocity, and h and L are the channel length and height, respectively. Substituting equation (7.11) into equation (7.8) gives:

$$\frac{1}{k_{eff}} = \frac{1}{k_{uf}} + \frac{\delta_c(t)}{D} \left(\frac{1 - \ln \varepsilon(t)^2}{\varepsilon(t)} \right) \quad (7.13)$$

Concentration polarization as a function of time $CP(t)$ during constant flux filtration can be calculated by combining equations (7.7) and (7.13) and rearranging:

$$\frac{CP(t)}{CP(0)} = \exp \left\{ \frac{J\delta_c(t)}{D} \left(\frac{1 - \ln \varepsilon(t)^2}{\varepsilon(t)} \right) \right\} \quad (7.14)$$

$CP(0)$ is the concentration polarization at the beginning of filtration and before foulant deposition. Since the flux, thickness, and porosity of the cake layer appear in the argument of the exponential in equation (7.14), they have a significant effect on the concentration polarization.

7.5.1.2 FFM experiments

Since UF membranes do not reject salt, salt concentration polarization and CEOP do not occur in the FFM experiments. Hence, fouling index and specific cake resistance for the FFM experiments can be obtained from Equation (6.6).

In this study, since particle density ρ_p and d_p are known, the measured specific

cake resistance can be used to estimate the average cake porosity by the Carman-Kozeny equation [81]:

$$\alpha = \frac{180(1-\varepsilon)}{\rho_p d_p^2 \varepsilon^3} \quad (7.15)$$

For other feeds it would be necessary to identify an effective particle size if equation (7.15) is to be used for porosity estimation.

7.5.1.3 Dead-end filtration

The specific cake resistance and cake porosity for dead-end experiments under constant flux filtration can also be obtained using the appropriately simplified form of Equation (6.6):

$$\text{TMP} = J^2 \mu l t + J \mu R_{mr} \quad (7.16)$$

The specific cake resistance can be determined by combining equations (7.16) and (6.3) from a plot of the TMP as a function of time for dead-end experiments under constant flux filtration.

7.5.2 Ultrasonic time-domain reflectometry

The UTDR technique uses the amplitude and arrival time of an acoustic waveform to give information of the characteristics of the medium and the locations of moving or stationary interfaces. A high frequency transducer that is rigidly attached to the top plate of the membrane cell transmits and receives the acoustic waveform. The incident waveform reflects from the interfaces at the top plate, membrane surface, support plate and bottom plate, respectively. Fouling causes a change in amplitude and arrival time for the wave form reflected from the membrane surface, thereby

permitting real-time measurement of the cake layer thickness [173, 174]. The cake height data obtained by UTDR can be used in combination with equation (7.14) to determine the contribution of CEOP to the RO fouling prediction.

7.6 Experimental procedure

The RO experiments combined with UTDR were conducted for a range of constant fluxes. For these RO experiments TMP profiles and the cake layer thicknesses were measured.

The FFM tests were then carried out at a series of net fluxes to obtain estimates of specific cake resistances and cake porosities for RO at the same hydrodynamic conditions. The TMP profiles for these experiments were measured and the specific cake resistance values as well as the cake porosity were determined using the model adapted for UF.

The effects of salt concentration on the specific cake resistance and cake porosity were also investigated. Dead-end tests were done under constant flux and various salt concentrations (2 to 16 g/L NaCl). The changes in the specific cake resistance and cake porosity due to the salt concentration were determined by monitoring the TMP as a function of time and using the model. The results from the dead-end filtration experiments were used to infer how the salt would affect the cake porosity in the FFM and RO.

By combining the aforementioned results, the TMP for the RO tests was predicted and compared with that for the actual RO module. Figure 7.4 is a flow diagram to show how the specific cake resistance and cake porosity from FFM are combined

with the cake height from UTDR to estimate CEOP and cake resistance in order to predict the RO TMP profile. In this study the initial trends (5 to 10 hrs) in cake height and specific cake resistance were used to predict RO fouling at 45 hours. For long term operation the procedure could provide regular updates of predicted TMP based on new data from the FFM and UTDR.

Figure 7.4: Experimental procedure to predict TMP profile of RO

7.7 Results and Discussion

7.7.1 RO experiments

A series of RO experiments were conducted using the same feed solution, cross-flow velocity, and a range of fluxes. The height of the cake formed during the RO experiments was measured using UTDR from which the CEOP was estimated.

The TMP profiles as a function of time for a range of fluxes are shown in Figure 7.5.

Figure 7.5: TMP as a function of time for different fluxes under a cross-flow velocity of 0.1 m/s for a feed solution containing 200 mg/L SiO₂ and 2000 mg/L NaCl

Figure 7.5 indicates that the TMP and fouling rate ($dTMP/dt$) increased with increasing flux. Several studies indicate that for RO systems, CEOP contributes more to the fouling than changes in the cake resistance [12, 27, 163, 170]. Equation (7.14) shows that concentration polarization is strongly dependent on the flux, cake layer porosity, and cake thickness. Hoek and Elimelech [12] reported a strong effect of flux on CEOP. Their results suggested insignificant CEOP at low fluxes due to negligible cake deposition, while at moderate to high fluxes, the contribution of CEOP steadily increased. Chong et al. [27, 80] also observed a severe CEOP effect at higher fluxes due to a thicker cake layer.

According to equation (7.5), for RO performance prediction it is important to know the net flux, which is the imposed flux minus the critical flux. The critical flux of the colloidal silica for the RO membrane was measured using the flux stepping method and found to be $J_{cr-RO} = 20 \pm 2 \text{ l/m}^2 \cdot \text{hr}$.

7.7.2 RO-UTDR measurements

Since CEOP can contribute significantly to fouling in RO and is coupled to concentration polarization, the latter must be measured as a function of the flux, cake thickness, and porosity in order to be able to predict fouling from the FFM measurements. Figure 7.6 is a plot of the cake layer thickness measured by UTDR as a function of time during RO for different fluxes.

Figure 7.6: UTDR measured foulant thickness as a function of time at different RO fluxes.
Conditions: Feed: 200 mg/L silica and 2000 mg/L NaCl; Cross-flow velocity = 0.1m/s

Figure 7.6 indicates that the rate of cake layer growth increased from 0.375 to 0.513 $\mu\text{m/hr}$ owing to the more rapid deposition of particles as the imposed flux increased from 30 to 48.1 $\text{l/m}^2\cdot\text{hr}$. With a $J_{crit,RO}$ of 20 $\text{l/m}^2\cdot\text{hr}$ the net fluxes ($J - J_{crit,RO}$) were in the range 10 to 28 $\text{l/m}^2\cdot\text{hr}$. The rate of cake layer growth, which is assumed to be constant, is used in conjunction with the results from the FFM (section 7.7.3) to predict the potential RO fouling performance (section 7.7.5).

7.7.3 FFM experiments

Most RO membrane processes are operated under constant flux with an increasing TMP due to fouling. To simulate RO fouling behaviour the FFM was operated at various constant fluxes, at a crossflow velocity of 0.1 m/s and with RO feed using 200 mg/L SiO₂ as the model foulant and 2000 mg/L NaCl as the ionic buffer.

Note that the critical flux for FFM experiments was measured using the step-by-step method and found to be higher than the critical flux measured for RO membrane under the same conditions ($J_{cr.FFM} = 83 \pm 5 \text{ l/m}^2 \cdot \text{hr}$). The possible for these differences are discussed in section 6.6.1.1. The effect of applied flux on FFM fouling behaviour using colloidal silica was investigated and discussed in detail in 6.6.1.4.1.

7.7.4 Dead-end filtration

7.7.4.1 Effect of salt concentration

The effect of salinity on the rate of colloidal fouling and cake properties was studied using a 200 mg/L colloidal silica solution over a broad range of NaCl concentrations (2000 to 16000 mg/L).

Figure 7.7 presents the TMP as a function of time for dead-end filtration under a constant flux ($95 \text{ l/m}^2 \cdot \text{hr}$).

Figure 7.7: TMP as a function of time for constant flux ($95 \text{ l/m}^2\cdot\text{hr}$) dead-end filtration using a 200 mg/L SiO_2 solution for a range of NaCl concentrations

These results show that the fouling rate ($d\text{TMP}/dt$) increases with the salt concentration. Increasing the salinity of a feed-water has been reported to accelerate fouling [58, 150, 169]. Stable colloidal particles have a negative charge in water with a high zeta potential. A raised ionic strength compresses the double layer and decreases the electrostatic charge repulsion resulting in a lower porosity and more densely packed deposit on the membrane surface.

Figure 7.8 shows the experimentally determined specific cake resistance and cake porosity as a function of the NaCl concentration. This figure indicates that the specific cake resistance increased whereas the cake porosity estimated from the Carman-Kozeny (equation 7.14) decreased from 0.52 to 0.43 as the ionic strength increased from 2000 to 16000 mg/L NaCl .

Figure 7.8: Specific cake resistance and cake porosity for colloidal silica fouling as a function of NaCl concentration for a flux of 95 l/m².hr and a feed solution containing 200 mg/L SiO₂

A similar trend in the specific cake resistance was observed by Chong et al. (2008) [27] for colloidal silica fouling at different NaCl concentrations. They reported that the specific cake resistance increased with increasing ionic strength, from zero to 10,000 mg/L NaCl, due to suppression of the electrostatic double layer repulsion at high ionic strength.

7.7.4.2 Correction for specific cake resistance

Diffusion of salt back to the bulk solution can be hindered by the formation of a cake layer on the membrane surface during RO causing the osmotic pressure to be dramatically increased, this is the CEOP effect. In contrast to RO, UF does not reject salt and the difference between the salinity in UF and RO filtration systems should be considered in any attempt to predict fouling. Hence, the specific cake resistance at different salt concentrations (c) was compared with the specific cake

resistance at the reference salinity (α_0 at 2000 mg/L NaCl). For retentive membranes, equation (7.6) can be simplified as follows:

$$CP = \frac{C_w}{C_b} \quad \text{if} \quad C_p \ll C_w \quad (7.17)$$

Figure 7.9: Correction factor for specific cake resistance as a function of concentration polarization, Constant flux: 95 l/m².hr, 200 mg/L SiO₂

This ratio of the specific cake resistance normalized with respect to the reference value (α/α_0) is plotted as a function of the CP in Figure 7.9. These data are fitted by equation (7.18) that can be used to estimate the specific cake resistance in RO (α_r) at any concentration polarization based on the specific cake resistance determined from FFM measurements:

$$\alpha_r = \alpha_0 \times (-0.0243CP^2 + 0.3486CP + 0.7336) \quad (7.18)$$

Since $CP > 1$, equation (7.18) indicates that the specific cake resistance increases as CP increases. The cake porosity for RO can then be estimated from equation (7.18)

and the Carman-Kozeny (equation 7.14). These results are used in section 7.7.5 to convert the FFM results to predict the RO fouling potential

7.7.5 RO fouling prediction

The major aim of this chapter is to predict RO fouling using the online FFM combined with the UTDR monitor. Equation (7.4) indicates that in the presence of salt, both the cake resistance and CEOP contribute to fouling during RO. The cake resistance contribution was determined based on the specific cake resistance at an equivalent net flux for the same hydrodynamic conditions using the FFM (section 7.6.3). The cake porosities determined for different fluxes were modified for the effect of the salt concentration (section 7.6.4.2). The CEOP contribution was determined using the UTDR to measure the rate of change of cake thickness and the FFM to estimate the cake porosity (section 7.7.2 and section 7.7.3).

Figure 7.10 compares the predicted and measured TMP profiles for a range of RO fluxes. This figure indicates that the predicted TMP obtained from the FFM at a flux of $111 \text{ l/m}^2\cdot\text{hr}$ (effective flux = $28 \text{ l/m}^2\cdot\text{hr}$) agrees well with the measured RO TMP at a flux of $48.1 \text{ l/m}^2\cdot\text{hr}$ (effective flux = $28.1 \text{ l/m}^2\cdot\text{hr}$). However, the predicted RO profile begins to deviate from the actual RO fouling trend as the FFM flux increases from $95 \text{ l/m}^2\cdot\text{hr}$ to $150 \text{ l/m}^2\cdot\text{hr}$ (effective flux from 12 to $72 \text{ l/m}^2\cdot\text{hr}$).

Figure 7.10: TMP versus time showing the predictions for a range of fluxes and the measured results at an RO flux of $48.17 \text{ L/m}^2\cdot\text{h}$ for a cross-flow of 0.1 m/s and a feed containing 200 mg/L of colloidal silica and 2000 mg/L NaCl

The differences in predicted TMP profiles underscore the importance of obtaining cake properties such as the specific cake resistance and cake porosity, from the FFM at the correct conditions to predict the actual RO TMP profile. Figure 7.10 indicates that operating the FFM at the same effective net flux as the RO is an appropriate approach for RO fouling prediction purposes. As mentioned earlier, the TMP profile for RO can be determined from the resistance estimated via the FFM and the RO cake layer thickness determined using UTDR.

Figure 7.11 presents a comparison for a range of RO fluxes between the experimentally determined TMP profiles and those predicted by the model using the FFM and UTDR measurements.

Figure 7.11: TMP versus time for a range of RO fluxes showing the measured (solid lines) and predicted values (dashed lines) based on FFM running a same net flux with RO, cross-flow velocity of 0.1m/s and feed containing 200mg/L of colloidal silica and 2000 mg/L NaCl

The results confirm that the model in combination with the FFM and UTDR measurements provides a good estimate of the TMP profile for RO colloidal fouling over a range of fluxes.

For salt rejecting membranes such as used in NF and RO, both the hydraulic resistance of the cake layer and CEOP contribute to the overall increase in TMP during constant flux filtration and several studies have suggested that CEOP plays the dominant role [12, 27, 170, 191]. Based on Equation (7.4) the total pressure drop across the cake (ΔTMP) consists of contributions from the cake and due to CEOP:

$$\Delta\text{TMP} = \Delta P_{\text{cake}} + \Delta P_{\text{CEOP}} \quad (7.19)$$

In order to investigate the contributions of the hydraulic resistance of the cake layer and CEOP on RO fouling, the Δ TMP based on the predicted TMP profiles was plotted as a function of time. The pressure drop due to both the hydraulic cake resistance and CEOP was also compared with the predicted TMP. The hydraulic resistance of the cake layer was determined from the FFM. The contribution of CEOP was calculated based on cake layer porosity obtained from FFM and the cake layer thickness measured using UTDR.

Figure 7.12 shows the estimated contributions of the hydraulic cake resistance and CEOP on the TMP rise for the predicted TMP profiles.

Figure 7.12: Δ TMP as a function of time for RO fouling owing to a feed containing 200 mg/L of colloidal silica and 2000 mg/L of NaCl at a cross-flow velocity of 0.1 m/s at fluxes of a: 30 l/m².hr, b: 36.1 l/m².hr, c: 42.1 l/m².hr, d: 48.1 l/m².hr.

The TMP increases with time due to the increasing hydraulic resistance and the CEOP and the results confirm that CEOP is the major contributor to colloidal silica

fouling in this study. The contribution CEOP to TMP rise was in the range 89% to 94%.

According to equation (7.14), the concentration polarization increases exponentially with the flux and this implies that the CEOP also increases exponentially with the flux. The effect of flux on the rate of fouling is shown in Figure 7.13 that plots the slope of the TMP profiles versus time as a function of the flux.

Figure 7.13: Slope of the TMP profiles as a function of flux for RO fouling with a feed containing 200 mg/L or colloidal silica and 2000 mg/L of NaCl at a cross-flow velocity of 0.1m/s.

This figure indicates that the rate of increase in TMP due to the hydraulic cake resistance is approximately linear whereas the CEOP increases exponentially with increasing flux. These results agree well with those of Chong et al. (2007) [80] who showed that the CEOP is strongly influenced by the flux.

7.8 Conclusions

Effective prediction of RO colloidal fouling requires knowledge of the development

of fouling resistance and foulant height, where the latter determines the cake enhanced osmotic pressure (CEOP).

A fouling simulator described in this study, the Feed Fouling Monitor (FFM), can be used to provide online measurement of specific cake resistance of foulant and trends in foulant cake height can be measured by Ultrasonic Time Domain Reflectometry (UTDR). In this study it is shown that the measurements from FFM and UTDR can provide inputs to a RO fouling model that predicts the increase in transmembrane pressure (TMP) at constant flux. The predictions include the developing hydraulic resistance and the CEOP components. This approach effectively captures the trends of increasing fouling as flux increases for the system studied (colloidal silica with background salinity). Background salinity increases the specific cake resistance and decreases the effective porosity of the cake, and this was used to adjust FFM output data.

In addition to providing good predictions of the TMP rise the model shows that, for the system studied, the role of CEOP is more significant than the hydraulic resistance. Extension of this monitoring and modeling approach to real world foulants will be challenging, but may be addressed by use of a self-adapting model that estimates the effective foulant size.

CHAPTER 8

Prediction of RO Fouling by FFM and Salt Tracer Response Technique

8.1 Abstract

An on-line feed fouling monitor (FFM) combined with a salt tracer response technique was used in this chapter to predict RO fouling under constant flux filtration. The FFM was used to capture foulants loads using a small collection ultrafiltration membrane at the same cross-flow hydrodynamics as in the RO experiments. The obtained information from FFM was used to predict fouling behavior in RO. The salt pulse tracer technique was used to measure the development of concentration polarization which is important in the estimation of cake-enhanced osmotic pressure (CEOP). The developed mathematical model including both the cake resistance and the CEOP effect due to cake formation was used to predict RO fouling.

Colloidal silica (200 mg/L) and humic acid (20 mg/L) were used as inorganic and organic model fouling agents, respectively. 2000 mg/L sodium chloride (NaCl) was chosen as the ionic background in all experiments. RO and FFM fouling experiments were conducted at different constant fluxes using the same feed solutions and same cross-flow velocity (0.1 m/s). The results indicated that higher fluxes caused an increased fouling rate for both RO and the FFM. The concentration polarization estimated by the salt tracer response technique in the RO experiments was also higher at higher applied fluxes for filtration of both colloidal silica and

humic acid. Hence, the CEOP effect was strongly influenced by the flux.

The results indicated that combination of the FFM and the salt tracer response technique is a promising method to provide a good estimation RO fouling for both organic and inorganic foulants. The importance of CEOP in RO fouling is again highlighted in this study.

8.2 Introduction

In chapter 7, the information obtained from FFM combined with results from UTDR measurements were used to estimate the contribution of CEOP on RO fouling using colloidal silica as a foulant model. However, due to a small difference in acoustic properties of the organic cake layer/ membrane surface and organic cake layer/feed solution interface, the detection of organic cake layer on a membrane surface is a challenge for UTDR. An alternative method for estimation of CEOP was developed by Chong et al. [27, 80] who used a sodium chloride tracer response technique to measure directly the CEOP instead of employing a mathematical model with required knowledge of cake height. Hence in this chapter salt tracer response technique (STRT) was used to measure concentration polarization and the CEOP contribution during RO fouling experiments under constant flux using both organic and inorganic foulant models. The STRT information is combined with FFM results to predict RO fouling trends.

8.3 Salt tracer response technique

Fouling in RO is related to concentration polarization (CP), a phenomena that occurs when solutes and rejected particles accumulate at the membrane surface. The

formation of a cake or deposit on RO membrane provides an unstirred layer that leads to hindered back diffusion of salt ions from the membrane surface to the bulk solution [12, 79]. This phenomenon is defined as cake-enhanced osmotic pressure (CEOP) so the concentration of salt near the membrane surface increases and local osmotic pressure rises.

The factors influencing CEOP can be seen in Equation (2.7). It is clear that there is an exponential relationship between flux, cake thickness and concentration polarization. Hence, it is important to characterize the build up of concentration polarization during filtration in RO to understand the fouling mechanism. Various in situ monitoring techniques for concentration polarization had been described which includes a light deflection technique [192], radio-isotope labeling [193, 194], electron diode array microscope (EDAM) [193, 194] and NMR micro-imaging [29, 195]. However, these techniques are not practical or economical due to requirements of special design for the membrane module or expensive monitoring facilities [196]. Therefore, a simple method is required to determine the concentration polarization for existing membrane systems.

Tracer tests are commonly applied to study the residence time distribution (RTD) of a reactor [197] and also successfully used to detect fouling in spiral wound reverse osmosis membranes [198]. This technique provides an analysis of the RTD in the feed and permeate side of the membrane and characterizes fouling and membrane aging. The selected tracer should not react with foulants or cake layer and provide immediate response when injected to the system.

Chong and co-workers (2007, 2008) [27, 80] proposed using a salt tracer response technique to determine the CEOP effect and fouling resistance in RO. In order to determine CP by this technique, transient in the flux, TMP and concentrations of both feed and permeate side should be monitored. When a spike of salt is injected into a clean RO system, the immediate response of TMP (in constant flux filtration) or flux (in constant pressure) can provide required information to estimate the concentration polarization of salt. Furthermore, the concentration polarization of a fouled system can be measured with same procedure as mentioned. Hence, the cake-enhanced osmotic pressure (CEOP) can also be determined. Chong et al. (2007, 2008) [27, 80] used sodium chloride as the tracer to inject into the RO system. Their experiments were conducted under constant flux filtration using mono-sized colloidal silica (20 nm) as a foulant agent. They reported that CEOP is more severe at low cross-flow velocity and high flux because of the thicker cake layer. This technique also has been successfully used for determination of enhanced osmotic effect in a biofilm; known as the biofilm enhanced osmotic pressure (BEOP) effect [199]. The theoretical background to the STRT is given in section 8.5.1.2.

8.4 Material and methods

8.4.1 Membranes and chemicals

Colloidal silica (Sigma Aldrich, Ludox TMA) as an inorganic and humic acid (Sigma-Aldrich) as an organic were used as a model foulants in this chapter. The desired concentration of NaCl (Sigma Aldrich) was also used in experiments as background ionic solution and for the salt tracer tests. All feed solutions were

prepared by Milli-Q water. UF regenerated cellulose (RC-30 kDa) membranes (Millipore - PLTK15005) were used for the FFM experiments to capture model foulants. The filtration tests were initiated with pure water (Milli-Q) to stabilize the membrane and to measure its intrinsic resistance (R_m). RO membranes (DOW FilmTecBW30) were also used in this study.

8.4.2 Experimental apparatus

8.4.2.1 RO setup

The schematic of RO set up is presented in Figure 8.1. The details of the RO set up is explained in chapter 4, section 4.3.3, but equipped with additional injection pump for the salt tracer response experiments.

Figure 8.1: Schematic diagram of reverse osmosis set-up for fouling studies

The permeate stream and concentrate were recycled back to the feed tank during the filtration. In the case of the salt pulsation experiments, a metering pump

(Pulsafeeder, model Pulsatron) was used to inject NaCl solution into the high pressure feed line of the RO cell. In order to keep the concentration of NaCl constant in the feed tank, the permeate stream and concentrate were drained out of the system during the tracer test while the feed tank was topped up to maintain a constant volume. Flux, pressures, cross-flow rate and conductivity of feed/permeate were monitored using a data acquisition system (National Instrument, Model PCI 6014).

8.4.2.2 Feed Fouling Monitor (FFM)

The feed fouling monitor (FFM) is an on-line flow simulator was designed for cross-flow. Description of the FFM setup is given in detail in chapter 4, section 4.3.2.

8.4.2.3 Dead-end setup

Since a UF membrane does not reject salt, the effect of salinity on the cake layer in both UF and RO systems was investigated. The dead-end set-up was used in this part to isolate the effect of the ion environment on the double layer. Description of the Dead-end setup is presented in detail in chapter 4, section 4.3.1.

8.4.3 Experiment Design Considerations

8.4.3.1 Fouling prediction model

The model for RO fouling prediction described in Chapter 7 (section 7.5) is used in this study to incorporate the CEOP effect for RO experiments. The contribution of the hydraulic cake resistance was estimated using information obtained from the

FFM while the salt tracer response technique was used to estimate the impact of CEOP in RO fouling tests.

8.4.3.2 Sodium chloride tracer response tests

A series of RO fouling experiments were conducted to assess the ability of FFM to predict RO fouling and compare the predicted profiles with actual RO performance. RO experiments were run using colloidal silica and humic acid over a range of different constant fluxes and the salt tracer response tests were conducted to determine CP and estimate the contribution of the CEOP effect.

8.4.3.3 FFM experiments

Since most RO systems are conducted at constant flux, FFM using UF membrane was designed to capture foulants load under constant flux and cross-flow to simulate hydrodynamic condition in RO tests. Foulants captured by FFM are potential RO foulants, and as described earlier (Chapter 6, section 6.2) using UF instead of RO membrane for FFM can provide a rapid assessment of the fouling potential. The information obtained from FFM can be used to estimate hydraulic resistant of cake layer in RO.

8.4.3.4 Critical flux measurements

As discussed in chapter 6 and chapter 7, FFM experiments using UF membranes were conducted at similar net flux to the RO tests. Therefore it was necessary to measure critical fluxes for both UF and RO tests to be sure experiments were run at comparable net fluxes. The critical flux for these experiments was determined by the step-by-step method [31].

8.4.3.5 Effect of salt concentration on the cake porosity

Due to the different nature of the RO and UF membranes, the effect of salinity in the UF and RO filtration systems should be taken into account for prediction purposes. The salt concentration can change the charge of particles and influence the cake porosity. Therefore it is essential to investigate the effect of salinity on the cake layer properties such as specific cake resistance.

In order to isolate the effect of the salinity on the double layer, these experiments were conducted using a dead-end setup to eliminate the complications introduced by cross-flow. The effect of salt concentration on the specific cake resistance was investigated by monitoring the TMP as a function of time during constant flux filtration.

8.4.3.6 RO fouling prediction

Information obtained from the FFM, salt tracer response experiments and the dead-end tests were used to predict RO performance by the fouling model adapted for CEOP (see equation 7.4). The predicted TMP profiles were compared against the actual RO performance.

8.5 Theory

8.5.1 Model development

8.5.1.1 Cross-flow RO filtration

According to the developed RO fouling prediction model (Equation 7.4), the TMP rise in RO is based on both hydraulic cake resistance and CEOP effect. In this chapter the contribution of cake resistance is estimated using FFM while the salt

tracer response technique is used to determine the CP and estimate the contribution of CEOP to RO fouling.

8.5.1.2 Salt tracer response technique

A schematic representation of salt tracer response technique is presented in Figure 8.2. This technique is based on the ability of RO membranes to reject salts such as sodium chloride.

Figure 8.2: Schematic of the STRT to determine the concentration polarization and CEOP in an RO membrane system operated at contact flux: (a) Feed concentration showing increase to $Cond_s$ during salt injection; (b) Permeate concentration showing increase to $Cond_s$ during salt injection; (c) TMP versus time showing increase to TMP_s owing to concentration polarization during salt injection

As seen in Figure 8.2, the conductivity and osmotic pressure of the RO system are increased during the injection of NaCl into the system. As a result, in order to maintain a constant flux filtration, the TMP of the system has to be increased.

Before the injection of sodium chloride into the system, flux can be measure by the following equation:

$$J = \frac{(\text{TMP} - \text{CP} \cdot \Delta\Pi_b)}{\mu(R_m + R_f)} \quad (8.1)$$

Where R_m , is the membrane resistance and R_f is the fouling resistance, μ is the viscosity of permeate solution, $\Delta\Pi_b$ is the osmotic pressure difference of between the permeate and feed solutions and CP is the concentration polarization.

The concentration polarization, CP, is linked to the flux and mass transfer of the membrane system via a boundary layer film model [200]. When no fouling is present:

$$\text{CP} = \frac{C_w - C_p}{C_b - C_p} = \exp\left(\frac{J}{k_m}\right) \quad (8.2)$$

where C_w , C_p , and C_b are the membrane surface, local and bulk salt concentrations, respectively and k_m is the mass-transfer coefficient. However, after particle deposition and the presence of a cake layer, the salt concentration near the membrane wall C_w is increased due to the hindered back transport, so:

$$\text{CP} = \frac{C_w - C_p}{C_b - C_p} = \exp\left(\frac{J}{k_{eff}}\right) \quad (8.3)$$

k_{eff} is the effective mass transport coefficient. As explained in chapter 7, k_{eff} decreases as the thickness of cake layer increases (Equation 7.12).

The osmotic pressure of the RO system would be increased as a pulse of NaCl introduced into the system. Hence, the TMP of the system has to be increased to TMP_s in order to maintain constant flux filtration. Therefore:

$$J = \frac{(TMP_s - CP \cdot \Delta\Pi_{bs})}{\mu(R_m + R_f)} \quad (8.4)$$

where TMP_s is the trans-membrane pressure of the system during the salt pulsation while $\Delta\Pi_{bs}$ is the difference between osmotic the feed and permeate stream. By combining Equation (8.3) and Equation (8.4), CP can be related to the TMP of the system as well as conductivities of feed and permeate before and during the NaCl pulsation. Hence, CP can be determined using following equation:

$$CP = \frac{TMP_s - TMP}{\Delta\Pi_{bs} - \Delta\Pi_b} \quad (8.5)$$

As can be seen form Equation (8.5), by monitoring the TMP and conductivity of the system before and during salt injection, CP can be estimated [80].

The salt concentration in the feed solution and the peremate stream can be calculated from conductivity (k) using Equation (8.6) as follows [201]:

$$\log(k) = 0.9856 \log(C) + 0.3444 \quad (8.6)$$

where C is the concentration of NaCl in mg/L.

The osmotic pressure of the NaCl can be determined as follows:

$$= 2C R_g T \phi \quad (8.7)$$

R_g is the universal gas constant ($8.314 \frac{J}{Kmol}$) and ϕ is the molar osmotic coefficient [202]:

$$\log(1-\phi) = -1.09373 - 0.08101(C) - 0.17492\{\log(C)\}^2 - 0.01785\{(C)\}^2 \quad (8.8)$$

Equation (8.8) is valid for NaCl concentrations ranging from 5.85 mg/L to 17,880 mg/L.

8.5.1.3 FFM experiments

The FFM was developed and used to incorporate the cross-flow condition and also capture foulants under constant flux using UF membrane. Since UF membrane does not reject NaCl, the fouling index and the specific cake resistance of the FFM experiments can be calculated using Equation (6.6). The obtained information was used to determine the contribution of cake hydraulic cake resistance in RO.

8.5.1.4 Dead-end filtration

The fouling index for dead-end and constant flux experiments can also be measured using the simplified form of Equation (7.16). The specific cake resistance can be calculated by combining equations (7.16) and (6.3) from a plot of the TMP as a function of time for dead-end experiments under constant flux filtration.

8.6 Experimental procedure

The RO experiments were conducted for a range of constant fluxes using humic acid and colloidal silica as model foulants. The sodium chloride tracer response technique was used periodically to estimate the development of concentration

polarization in the RO experiments. The specific cake resistances were measured by FFM using the adapted model for RO (Equation 6.6) under the same hydraulic conditions and comparable net fluxes. These results were used to predict RO fouling potential performance.

The effect of salinity on the specific cake resistance of humic acid and colloidal silica was also investigated. The dead-end apparatus was used under constant flux for this part to avoid the complications of a cross-flow velocity on the particle deposition and isolate the effect of salt on cake properties. The results from the dead-end filtration tests were used to study how the salt would affect the specific cake resistance in the FFM and RO.

Finally, the TMP profiles were predicted using FFM and salt pulsation data and compared with actual RO performance.

Figure 8.3 is a flow diagram to summarise the method to estimate RO TMP profile from the information obtained from the FFM and salt tracer response technique.

Figure 8.3: Experimental procedure to predict RO performance

8.7 Discussion

8.7.1 RO experiments

RO fouling experiments were conducted at different fluxes using colloidal silica (200 mg/L) and humic acid (20 mg/L) as an inorganic and organic model foulant, respectively. 2000 mg/L NaCl was also used in all experiments as an ionic background. The TMP of the system as well as the feed and permeate conductivity were measured during filtration. The information obtained was used to estimate concentration polarization, which is discussed in section (8.7.2).

The TMP profiles of fouling tests using colloidal silica and humic acid as a function of time for a range of constant fluxes are plotted in Figure 8.4 and Figure 8.5, respectively.

Figure 8.4: TMP versus time for different fluxes under a cross-flow velocity of 0.1 m/s, Feed: 200 mg/L SiO₂ and 2000 mg/L NaCl

Figure 8.5: TMP as a function of time for different fluxes, cross-flow velocity of 0.1 m/s, Feed: 20 mg/L HA, 2000 mg/L NaCl

As shown in Figure 8.4 and Figure 8.5, the TMP profiles and fouling rates ($dTMP/dt$) increased with increasing flux for both colloidal silica and humic acid. As discussed earlier, TMP rise for RO can be due to both hydraulic cake resistance and CEOEP. However, CEOEP is often the major fouling mechanism with salt rejecting membranes such as RO [12, 27, 163, 170].

For RO prediction purposes, the critical flux was also measured using the step by step method and was found to be $J_{cr-RO} = 20 \pm 2$ LMH and $J_{cr-RO} = 16 \pm 2$ LMH for colloidal silica and humic acid, respectively.

8.7.2 Determination of concentration polarization

The RO fouling experiments started with filtration of Mili-Q water (~24 h) at high pressure (~20 bar) to compact the membrane and stabilize the system. Afterwards, the system was equilibrated with the desired ionic background (2000 mg/L NaCl), cross-flow rate (0.1 m/s) and flux level for around 3 hours. Before introducing the model foulant into the system, tracer tests were conducted for the clean membrane and the value obtained (CP at $t=0$) was taken as a reference point for the fouling tests. During the tracer tests, high concentrated NaCl (200 g/L) was introduced to the feed solution (before entering the RO cell) using the injection pump (rate of 1 mL/min) to increase the concentration of salt by 500-1000 mg/L. The concentration of injected salt and duration of pulsation was chosen to obtain a condition of stable detection [80]. When the salt pulse was stopped, the TMP and conductivity of both feed and permeate returned to the initial value while the system was operated for a further 2 hours to stabilize. Afterwards the model foulant was introduced to the feed tank and the fouling experiments were started. The same procedure was used for

tracer tests for estimation of CP during the fouling experiments. According to Equation (8.5), the TMP and feed/permeate conductivity values can be used to estimate the CP during filtration.

Figure 8.6 presents TMP, feed/permeate conductivity and measured CP during one of the sodium chloride spikes for the clean system (without foulants). The measured CP can be used as a reference point at time zero $t=0$.

Figure 8.6: (a) TMP, (b) feed and permeate conductivity, (c) CP profile during one of the NaCl pulsations, Feed: without fouling agent, NaCl background: 2000 mg/L
Flux= 36.1 l/m².hr, Cross-flow: 0.1 m/s

As can be seen, before the injection of NaCl into the system, the TMP was 13.2 bar at a flux of $36.1 \text{ l/m}^2\cdot\text{hr}$ (Figure 8.6 a). When NaCl was injected into the system, the conductivity of the feed increased from 3.65 to 5.28 ms/cm (Figure 8.6 b). Since the osmotic pressure of the system increased, the TMP was also increased to 14.8 bar in order to maintain constant flux filtration. At the same time, the conductivity of the permeate stream increased from 0.24 to 0.33 ms/cm due to higher salts passage (Figure 8.6 b). Equation (8.5) was then used to estimate the CP value from the obtained information, such as TMP and feed/permeate conductivity (Figure 8.6 c). Note that CP values reached a steady value during the salt pulsation and did not continue to increase since there was no foulant in the system.

Figure 8.7 shows TMP, feed/permeate conductivity and measured CP during sodium chloride spikes after introducing the foulants into the system. The tracer tests were conducted after around 16 hours with 20 mg/L HA and 2000 mg/L NaCl in the background running at a constant flux of $36.1 \text{ l/m}^2\cdot\text{hr}$. The TMP was around 14.2 bar at a flux of $36.1 \text{ l/m}^2\cdot\text{hr}$ before the salt spike (Figure 8.7 a). When NaCl was injected into the system, the TMP was increased to 15.3 bar in order to maintain constant flux filtration due to an increase in osmotic pressure of the system (Figure 8.6 b). As shown in Figure 8.7 a, the TMP profile slowly continued to increase to 15.8 bar during the spike instead of reaching a steady value.

Figure 8.7: (a) TMP, (b) feed and permeate conductivity, (c) CP profile during one of the NaCl spikes, Feed: 20 mg/L HA, NaCl background: 2000 mg/L
Flux= 36.1 l/m².hr, Cross-flow: 0.1 m/s

Equation (8.5) was used to estimate the CP value from the TMP and feed/permeate conductivity (Figure 8.7 c). The measured CP value also slowly increased as a function of time from almost 2.8 to around 3.2. A possible explanation for this was the suppression of the electrostatic double layer repulsion and creation of more compact fouling layer under higher ionic strength as discussed in section 5.4.4 and section 5.5.3.

The variation of CP values over time obtained by the salt response technique for constant flux filtration of colloidal silica and humic acid are presented in Figure 8.8 and Figure 8.9, respectively.

Figure 8.8: Concentration polarization as a function of time, Feed: 200 mg/L SiO₂, 2000 mg/L NaCl, Cross-flow: 0.1 m/s

Figure 8.9: Concentration polarization as a function of time, Feed: 20 mg/L HA, 2000 mg/L NaCl, Cross-flow: 0.1 m/s

During the filtration under constant flux, the cake layer slowly built up and consequently transmembrane pressure (TMP) increased (Figure 8.4, Figure 8.5). The variations in CP values in Figure 8.8 and Figure 8.9 confirmed the existence of cake-enhanced osmotic pressure in colloidal RO fouling. In another word, the back transport of NaCl is hindered by the presence of the cake layer and the concentration of NaCl is increased near the membrane surface [12, 80, 203].

8.7.3 FFM experiments

RO membrane processes are usually operated under constant flux filtration with an increasing TMP due to fouling. Since both the pressure and flux can cause cake compression, conducting the FFM experiments under the constant flux mode and cross-flow can simulate RO fouling behaviour. In order to find a suitable flux for predicting RO fouling behaviour from the FFM simulator, the effect of flux in the range of 95-155 l/m².hr on the fouling was investigated using 200 mg/L SiO₂ and

20 mg/L HA as the model foulant and 2000 mg/L NaCl as the ionic buffer. The cross-flow velocity was kept constant at 0.1 m/s for all experiments.

It should be noted that the critical flux for FFM experiments was measured using the step-by-step method and found to be higher than the critical flux measured for RO membrane under the same conditions ($J_{cr.FFM.SiO_2} = 83 \pm 5$ LMH, $J_{cr.FFM.HA} = 80 \pm 5$ LMH). The possible reasons for difference in J_{crit} for RO and UF are discussed in Chapter 6 (section 6.6.1.1)3. The effect of applied flux on FFM fouling behaviour using colloidal silica and humic acid was investigated and discussed in detail in 6.6.1.4.

These results obtained from the FFM are used in combination with those from the dead-end filtration to modify the specific cake resistance (section 8.7.4.2). The final results are to predict RO fouling potential performance (section 8.7.5).

8.7.4 Dead-end filtration

8.7.4.1 Effect of salt concentration

As discussed earlier, the effect of salt concentration on specific cake resistance of colloidal silica (200 mg/L) and humic acid (20 mg/L) were studied using the dead-end setup under constant flux filtration in order to isolate the effect of the ion environment on the double layer.

Detail of experiments and the effect of salt concentration on both silica and humic acid are discussed in Section 5.5.3. The specific cake resistance of the silica cake layer was observed to increase over a broad range of NaCl concentrations (2000 to

16000 mg/L) and can be explained by a decrease in the particle-particle repulsion as the salt concentration increased. Similarly, the specific cake resistance of humic acid increased as the salt concentration increased.

8.7.4.2 Correction for specific cake resistance

Since RO membranes reject salt, the effect of different salinities in RO and UF systems should be taken into account for prediction purposes. Hence, the specific cake resistance at different salt concentrations (C_c) was compared with the specific cake resistance at the reference salinity (C_0 at 2000 mg/L NaCl) for both colloidal silica and humic acid. For retentive membranes, equation (8.2) can be simplified as follows:

$$CP = \frac{C_w}{C_b} \quad \text{if} \quad C_p \ll C_w \quad (8.9)$$

The correction factor for specific cake resistance of colloidal silica as a function of concentration polarization is given in section 7.7.4.2. The ratio of specific cake resistance for humic acid normalized with respect to the reference value (α/α_0) as a function of concentration polarization is presented in Figure 8.10.

Figure 8.10: Correction factor for specific cake resistance as a function of concentration polarization, Constant flux: 95 l/m².hr, 20 mg/L HA

The specific cake resistance of humic in RO (α_r) can be estimated at any concentration polarization by the specific cake resistance obtained from FFM measurements using equation (8.10) as follows:

$$\alpha_r = \alpha_0 \times (0.0236CP^2 + 0.0927CP + 0.8613) \quad (8.10)$$

Since $CP > 1$, equation (8.10) indicates that the specific cake resistance increases as CP increases.

8.7.5 RO fouling prediction

The major aim of this chapter is to combine information obtained from the online FFM, tracer tests and dead-end experiments to predict RO fouling. Hence, the fouling trend of the RO for both colloidal silica and humic acid are predicted using equation 7.4 which contributes cake resistance and the CEOP effect. The contribution of hydraulic cake resistance on RO fouling was determined from the

specific cake resistance at an equivalent net flux for the same flow conditions in FFM (section 8.7.3). The specific cake resistance obtained was then modified for the effect of salt concentration (section 8.7.4). The initial trends of CP (10 to 20 hrs) were used to estimate the contribution of CEOP over the duration of the tests.

The two predicted trends for filtration of colloidal silica are compared against the actual RO fouling behaviour in Figure 8.11.

Figure 8.11: TMP as a function of time for a range of RO fluxes showing the measured (solid lines) and predicted values (dashed lines) based on FFM running a same net flux with RO, cross-flow velocity of 0.1m/s and feed containing 200mg/L of colloidal silica and 2000 mg/L NaCl

The predicted trends based on online FFM shows good agreement with the experimental data. As mentioned earlier, the predicted trends are determined based on the hydraulic cake resistance and the CEOP effect. The contribution of the hydraulic cake resistance and CEOP on the predicted TMP profiles is presented in Figure 8.12.

Figure 8.12: $\hat{e}$ TMP versus time for RO fouling owing to a feed containing 200 mg/L of colloidal silica and 2000 mg/L of NaCl at a cross-flow velocity of 0.1 m/s at fluxes of a: 30 $\text{l/m}^2\cdot\text{hr}$, b: 36.1 $\text{l/m}^2\cdot\text{hr}$

As it is clear from the graph above, the contribution of CEOP is higher than cake resistance in colloidal fouling of silica in RO filtration. The contribution of CEOP to predicted TMP was in the range of 87-97% which is similar to that observed for the UTDR based prediction (see section 7.7.5).

The RO fouling prediction approach was also conducted using 20 mg/L humic acid as an organic foulant. Figure 8.13 compares a range of experimental RO fouling trends at different fluxes and those predicted by the model using the FFM. Note that

for prediction purposes, the FFM experiments were conducted at the same net flux as the RO experiments. Figure 8.13 compares the predicted RO fouling trends for 200 mg/L humic acid against the actual RO fouling behaviour.

Figure 8.13: TMP versus for a range of RO fluxes, measured trends (solid lines) and predicted values (dashed lines) based on FFM running a same net flux with RO, cross-flow velocity of 0.1m/s Feed: 20 mg/L of HA and 2000 mg/L NaCl

As can be seen from Figure 8.13, the predicted trends show excellent agreement with actual RO performance. The results confirm that the model in combination with the FFM and STRT measurements provides a good estimate of the TMP profile for RO fouling over a range of fluxes using humic acid as an organic foulant.

The pressure drop due to the hydraulic cake resistance and CEOP was compared with the predicted TMP in Figure 8.14. The FFM was used to estimate the hydraulic resistance of the cake layer while the contribution of CEOP was calculated from salt tracer tests.

Figure 8.14: $\hat{e}$ TMP as a function of time, Feed: 20 mg/L of HA and 2000 mg/L of NaCl, Conditions: cross-flow velocity of 0.1 m/s at fluxes of a: 30 l/m².hr, b: 36.1 l/m².hr, c: 42.1 l/m².hr

Figure 8.14 indicates that the TMP increases in time due to the increasing hydraulic resistance and the CEOP. An elevated osmotic pressure due to hindered back-

diffusion of solutes leads to an increase in the effective TMP and thereby a decrease the overall performance of RO filtration.

8.8 Conclusions

By using a feed fouling monitor (FFM) employing a UF membrane the RO performance in the presence of organic fouling can be characterized in a much shorter time. However, it is necessary to characterize the concentration-enhanced osmotic pressure (CEOP) using a different technique than used to predict RO performance in the presence of inorganic fouling using the FFM. In this study the salt-tracer-response technique (STRT) was used to determine the CEOP.

The online feed-fouling monitor (FFM) employing a UF membrane was applied to predict RO fouling under the same net flux (flux minus the critical flux) and flow conditions. The salt-tracer-response technique was used to determine the CEOP component of the TMP. Fouling was studied using humic acid as the model foulant using an aqueous solution of sodium chloride as an ionic buffer for both the FFM and RO experiments.

The effect of flux on the fouling rate and cake properties was investigated for both RO and the FFM. The results showed that higher fluxes caused an increased fouling rate for both RO and the FFM. In contrast with the FFM experiments for which

the CEOP effect does not exist, in RO systems CEOP plays a more significant role than cake resistance in determining the TMP rise during filtration. The concentration polarization measured by the salt-tracer tests in the RO experiments also increased at higher applied fluxes.

The effect of salt concentration on the specific cake resistance was investigated using dead-end filtration. The specific cake resistance of the cake layer was observed to increase over a broad range of NaCl concentration (2000 to 16000 mg/l) for humic acid that can be explained by a decrease in the particle-particle repulsion and a change in the foulant layer packing as the salt concentration increased.

The results indicate that RO performance data in the absence of fouling, in combination with the FFM and the STRT, can provide a reasonable estimate of the TMP rise during RO fouling over a broad range of effective fluxes for an organic foulant. The predicted TMP profiles also underscore the significant contribution of CEOP to RO fouling.

CHAPTER 9

Conclusions and Recommendations

9.1 Summary and conclusions

Reverse osmosis (RO) is widely used for water reclamation and desalination. The efficient operation of RO plant requires effective control of membrane fouling, which can decrease productivity and increase energy usage per unit of water. RO foulants include components that form “cake deposits”, such as particulates, colloids and macrosolutes, and components that form “growing films”, such as inorganic scale or biofilms. This project deals with the deposition foulants and methods for characterization of their fouling propensity in RO feed waters. In the first part of the project conventional fouling indices such as SDI, MFI, MFI-UF (under constant pressure and constant flux) are evaluated for a range of feed and operating conditions (Chapter 5). The second part of the project involves evaluation and optimization of a novel feed fouling monitor (FFM) (Chapter 6) combined with the ultrasonic time domain reflectometry (UTDR) (Chapter 7) and salt tracer response technique (STRT) method (Chapter 8) to predict likely RO fouling. The major finding and conclusions in this thesis are summarized as follows:

- An extensive literature review on membrane, membrane fouling and available fouling indices were summarized in Chapter 2 and Chapter 3, respectively. The needs for an alternative approach were identified.
- In Chapter 5, the influences of several parameters on conventional fouling indices were investigated. In contrast with SDI which showed non-linear response

to bentonite concentration, MFI results confirmed a more linear behavior. A linear relationship between the $\text{MFI-UF}_{\text{const.pressure}}$ and humic acid and colloidal silica was also observed, except at low concentrations. The initial low value of the specific cake resistance of low concentration colloidal silica under constant pressure filtration is assumed to be due to dispersed cake formation while the subsequent decline presumably was related to inhomogeneous deposition of particles on the membrane surface at higher concentration. The performance of $\text{MFI-UF}_{\text{const.pressure}}$ was also investigated using mixed feed at different mixture ratios. In a mixture of humic acid and colloidal silica the $\text{MFI-UF}_{\text{const.pressure}}$ value increased with increasing humic acid concentration at a constant concentration of colloidal silica. The $\text{MFI-UF}_{\text{const.pressure}}$ of the combined foulants at low concentrations of humic acid was less than that silica alone presumably due to repulsion of humic acid and silica which creates a more porous cake layer. At higher concentrations of humic the $\text{MFI-UF}_{\text{const.pressure}}$ of the combined foulants was found to be higher than silica alone due to infiltration of humic acid into the silica cake layer. Furthermore, the effect of salinity on $\text{MFI-UF}_{\text{const.pressure}}$ was also studied. $\text{MFI-UF}_{\text{const.pressure}}$ of the colloidal silica was observed to pass through a maximum over a broad range of NaCl (0 to 25,000 mg/L) while for humic acid $\text{MFI-UF}_{\text{const.pressure}}$ increased monotonically. The specific cake resistance obtained from constant flux and constant pressure for humic acid and colloidal silica were also compared. The results indicate that during constant pressure filtration of colloidal silica, the specific cake resistance was found to be greater than that obtained during constant flux experiment. This could be due to the initial high flux in constant pressure operation leading to a more compact cake structure, especially for feeds like silica with high compressibility properties.

However, the specific cake resistance of humic acid was found to be independent of applied flux. This may be probably due to the lower compressibility value and aggregation of the foulants at higher flux.

➤ A novel feed fouling monitor (FFM) which uses a UF membrane to predict RO fouling at the same flow conditions was introduced in Chapter 6. Fouling experiments were conducted using colloidal silica and humic acid to investigate the effect of several parameters such as foulants concentration, cross-flow velocity and applied flux on the FFM. The specific cake resistance obtained from the FFM was used to predict RO fouling profiles at the same hydrodynamic conditions and net flux when the effect of CEOP was not been considered. The results indicated that the predicted TMP starts to deviate from the actual RO fouling trend as flux increases, presumably because the CEOP effect is becoming more dominant at higher fluxes. As a result, CEOP should be taken into consideration in the model to predict RO fouling.

➤ In order to quantify the CEOP effect, in Chapter 7, UTDR was employed to determine the cake growth rate on the RO membrane. The measurement of FFM from Chapter 6 was combined with UTDR to predict RO colloidal fouling under constant flux filtration. The UTDR was applied to estimate the CEOP by monitoring the rate of cake thickness increase. The RO fouling profile was predicted using the estimated cake resistance (obtained from FFM) and the CEOP effect (estimated using data from FFM and UTDR) due to cake formation. The results indicated that the new model (FFM combined with UTDR) provided a good estimation of the RO fouling profile over a period of 50 hours for different applied fluxes. The importance of CEOP in RO fouling was also highlighted in this chapter.

➤ Another technique to quantify CEOP effect, known as salt tracer response technique (STRT), was investigated and discussed in Chapter 8. STRT aims to estimate the contribution of CEOP in TMP rise during RO filtration. As STRT only provides information on CEOP, this technique was combined with an on-line FFM to predict RO fouling under the same net flux and flow conditions. The foulants used in this study were humic acid and colloidal silica. The predicted RO fouling trends obtained from combination of FFM and STRT provides a reasonable estimate of the TMP rise during RO fouling over a broad range of effective fluxes.

9.2 Recommendations

The following are recommended as potential future research directions:

- The RO fouling predictions using FFM were only conducted with organic (humic acid) and inorganic foulants (colloidal silica). Therefore it is recommended to further validate the prediction model with mixture of foulants and real feed water from a water treatment plant.
- The RO prediction trends based on FFM have been examined using a lab scale RO device. Hence, it is suggested to extend this work in a pilot scale RO.
- Long term experiments (at least a week) are recommended to validate the ability of FFM to predict RO fouling. A self-adjusting model may be required for prediction of long term trends.
- Further experiments need to be done to obtain a correlation between FFM (using a small flat sheet membrane) and spiral wound modules for RO prediction purposes.

- The experimental results highlighted the significant contribution of CEOP in RO fouling which was estimated using UTDR or STRT method. It would be interesting to modify FFM as stand-alone device which can estimate the CEOP effect independently.
- Regeneration of the FFM during long term use may be required. The relaxation strategy introduced in Appendix A could be optimized for this ask.

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APPENDIX A

Preliminary Observation of Membrane Regeneration by Relaxation

A.1 Introduction

A novel fouling simulator (Feed Fouling Monitor or FFM) was developed in this study to provide high quality information for process monitoring and predict likely RO fouling. However, one of the challenges with the FFM is the need for occasional regeneration to improve sensitivity [1].

Membrane cleaning could significantly increase the performance of the sensor and exhibit longer lifetime. Cleaning methods for membrane regeneration can be generally divided into two main groups: physical and chemical methods. In order to maintain an efficient process and reduce energy consumption, various physical membrane cleaning strategies are applied, based on backwash, bubbling or intermittent filtration with membrane relaxation [2-6]. Of these three strategies membrane relaxation is the most benign, requiring less energy imposing less stress on the membranes and avoiding chemical cleaning. It is also readily automated.

This appendix reports a preliminary evaluation of intermittent filtration and relaxation as a means of fouling control in the FFM for retentive UF membranes with different types of foulant. The system operates with constant flux (except during relaxation) and modest crossflow velocity.

This appendix is based on "A.H. Taheri, S.T.V. Sim, L.N. Sim, T.H. Chong, W.B. Krantz, A.G. Fane, Benign foulant control in crossflow ultrafiltration by intermittent filtration and relaxation: the effect of foulant type, Oral presentation at Euromembrane 2012 conference, 23-27 September 2012, London, UK".

A.2 Experimental

A cross-flow filtration setup was used for the membrane relaxation experiments. The description of the low pressure cross-flow filtration setup is presented in Chapter 4, section 4.3.2.

A.3 Materials and Methods

Ultrafiltration membranes (regenerated cellulose (RC)) with molecular weight cut off (MWCO) of 30kDa were used in this study. Colloidal silica (Sigma Aldrich, Ludox TMA) and humic acid (Sigma-Aldrich) were used as fouling agents in the experiments. These materials were chosen as they are well-characterized and represent colloidal/particulate foulants and organic macromolecules commonly found in feed waters. The colloidal silica was supplied in the form of 34 wt% suspension in deionised water at pH 7.0. The particle size of the colloidal silica was 20 nm as reported by the manufacturer. All suspensions were prepared using Milli-Q water.

A.3 Results and Discussion

Three different intermittent filtration modes as well as continuous filtration were conducted to investigate the effect of membrane relaxation to control fouling under constant flux filtration. During 9 hours of filtration, the TMP was continuously monitored and the fouling rate ($dTMP/dt$) and final TMP were compared to assess the performance of relaxation. The cross flow velocity was kept unchanged during relaxation (five minutes duration) for all experiments.

Normalized TMP (TMP/TMP_0) and fouling rate ($dTMP/dt$) are depicted in figures

A.1 and A.2 as a function of time for different filtration modes using colloidal silica and humic acid as model foulants.

Figure A. 1: Normalized TMP vs. Time, (a) 400 mg/L SiO₂, 2000 mg/L NaCl, applied flux: 125 LMH, (b) 20 mg/L HA, 2000 mg/L NaCl, applied flux: 125 l/m².hr, cross-flow velocity: 0.16 m/s

Figure A. 2: Fouling rate, (a) 400 mg/L SiO_2 , 2000 mg/L NaCl, applied flux: 125 LMH, (b) 20 mg/L HA, 2000 mg/L NaCl, applied flux: 125 $\text{l/m}^2\text{.hr}$, crossflow velocity: 0.16 m/s

It can be seen from the Figure A.1 that intermittent filtration with relaxation can limit the membrane fouling and has a significant effect on final TMP especially by applying periodical relaxation every 1 hour. However, 3 and 4.5 hours intermittent filtration show less positive effects on final TMP and fouling control. This implies the importance of relaxation interval which should be carefully selected to prevent more consolidated fouling and provide positive benefits for fouling control. During relaxation, concentration polarization and reversible fouling layers can diffuse away and detach from the membrane surface which leads to reduction of TMP. However we observe that the response depends on the foulant properties.

Results show that for colloidal silica the normalized TMP and the fouling rate are responsive to membrane relaxation, and initially the 1 hr interval maintains a low $dTMP/dt$. However this does not last and after about 8 hours the $dTMP/dt$ rises rapidly. This may be due to the metastability of colloidal silica which we have observed to gradually coalesce over time during ultrafiltration [7]. The dynamics of the TMP profile for silica (Figure A.1) are interesting and show, after several cycles, a more rapid build up of foulant resistance. We have tentatively attributed this to a patchy removal process during relaxation that creates conditions for local variations in flux and convection of foulant. Further surface layer characterization is required to test this hypothesis. For the humic foulant the TMP dynamics are much more reproducible and at the 1 hr relaxation interval the $dTMP/dt$ remains relatively stable over many cycles.

A.3 Conclusions

Relaxation could provide a benign method for fouling control. However the response to intermittent filtration and relaxation depends on the characteristics of the foulant. For metastable species, such as colloidal silica, the removal during relaxation may not be homogeneous and this could eventually lead to local rapid fouling and accelerating $dTMP/dt$. Shorter filtration intervals may be required. For less aggregative species, such as humic acid, the relaxation process appears to be more effective, although the strategy requires optimization. Overall, the benign fouling control provided by membrane relaxation deserves consideration in the quest for more sustainable membrane processing.

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