Modelling and characterization of membrane fouling in osmotically-driven membrane processes (ODMPs)

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**MODELLING AND CHARACTERIZATION OF
MEMBRANE FOULING IN OSMOTICALLY-DRIVEN
MEMBRANE PROCESSES (ODMPs)**

**LAI LI
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
2020**

**MODELLING AND CHARACTERIZATION OF
MEMBRANE FOULING IN OSMOTICALLY-DRIVEN
MEMBRANE PROCESSES (ODMPs)**

LAI LI

School of Civil and Environmental Engineering

**A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy
2020**

Statement of Originality

I hereby certified the works embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other university and institution.

Mar 26th 2021

Date

Lai Li

Lai Li

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declared it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudices.

Mar 26th 2021

Date

Chong Tzyy Haur

Authorship Attribution Statement

This thesis contains material from 1 paper(s) published and 1 paper submitted in the following peer-reviewed journal(s) where I was the first author.

Chapter 4 is published as Lai, L., L. N. Sim, W. B. Krantz and T. H. Chong. Characterization of colloidal fouling in forward osmosis via ultrasonic time- (UTDR) and frequency-domain reflectometry (UFDR). *Journal of Membrane Science* **602**: 117969 (2020). DOI: 10.1016/j.memsci.2020.117969

The contributions of the co-authors are as follows:

- Prof. Chong Tzyy Haur: Supervision, Conceptualization, Writing - review & editing;
- Lai Li: Conceptualization, Investigation, Formal Analysis, Writing-original draft;
- Sim Lee Nuang: Writing - review & editing;
- Prof. William B. Krantz: Writing - review & editing.

Chapter 5 is submitted as Lai, L., T. H. Chong. Colloidal fouling in forward osmosis (FO) process in active-layer-facing-draw-solution (AL-DS) mode: Combination of optimization techniques and back-propagation neural networks (BPNN). Submitted.

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- Lai Li: Conceptualization, Investigation, Formal Analysis, Writing-original draft;

Mar 26th 2021

Date

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Lai Li

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LIST OF PUBLICATIONS

➤ Journals

Lai, L., L. N. Sim, W. B. Krantz and T. H. Chong. (2020). Characterization of colloidal fouling in forward osmosis via ultrasonic time- (UTDR) and frequency-domain reflectometry (UFDR). *Journal of Membrane Science* **602**: 117969.

Lai, L., T. H. Chong. Dynamic colloidal particle deposition in forward osmosis (FO) in active layer facing draw solution (AL-DS) mode: Quantitative interpretation by combination of optimization techniques and back-propagation neural networks (BPNNs). Submitted.

➤ Conference

Lai, L., L. N. Sim, W. B. Krantz and T. H. Chong. (2019). Characterization of external and internal fouling of forward osmosis through ultrasonic time reflectometry (UTDR) method, In: North American Membrane Society (NAMS 2019), Pittsburgh, USA

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LIST OF SYMBOLS

J_w	Water flux (L/(m ² ·h))
J_s	Back solute flux (mol/(m ² ·s))
D	Diffusivity of solute in the bulk (m ² /s)
D_u	Diffusivity of solute inside of support layer(m ² /s)
β	The Van't Hoff coefficient (e.g. $\beta=2$ for sodium chloride)
R_g	The universal gas constant (KPa/(M·K))
T	Absolute temperature (K)
μ	Solvent viscosity (Pa·s)
C_f	Concentration of bulk feed solution (mol/L)
C_s	Concentration on interface of feed side/support layer (mol/L)
C_i	Concentration on interface of support layer/active layer (mol/L)
C_a	Concentration on interface of active layer/draw side (mol/L)
C_d	Concentration of bulk draw solution (mol/L)
K_{ex}	External concentration polarization factor (m/s)
K_{exd}	External concentration polarization factor on draw side (m/s)
K_{exf}	External concentration polarization factor on feed side (m/s)
S	Structural parameter (m)
λ_m	Thickness of support layer (m)
ε	Porosity of support layer (-)
τ	Tortuosity of support layer (-)
Sh	Sherwood number (-)
d_H	The channel hydrodynamic parameter (m)
Re	Reynolds number
Sc	Schmidt number
ε_{sp}	Porosity (-) of spacer (m ² /m ³).
h_{sp}	Thickness (m) of spacer (m ² /m ³).
$S_{v.sp}$	Specific surface of spacer (m ² /m ³).
R_m	Membrane intrinsic resistance (1/m)
R_f	Additional resistance induced by blocked pores (1/m)
R_c	Additional resistance induced by cake layer (1/m)
B	Membrane permeate coefficient (m/s)
A	A: Water permeate coefficient (1/m)
R	Membrane apparent rejection rate (-)

E_{J_w}	The error produced by measured and predicted water flux (-)
E_{J_s}	The error produced by measured and predicted solute flux (-)
Q	Volumetric flow rate across the channel (m^3/s),
C_{sound}	Velocity of sound in media (m/s)
$J_{w,f}$	Water flux in fouled membrane ($\text{L}/(\text{m}^2 \cdot \text{h})$)
$J_{w, \text{limiting}}$	Limiting water flux in fouled membrane ($\text{L}/(\text{m}^2 \cdot \text{h})$)
$J_{s,f}$	Back solute flux in fouled membrane ($\text{mol}/(\text{m}^2 \cdot \text{s})$)
$F_{\text{cecp},f}$	Concentrative external concentration polarization factor (-)
$F_{\text{dec},f}$	Diluted external concentration polarization factor (-)
$F_{\text{ccp},f}$	Concentrative concentration polarization factor (-)
$F_{\text{dcp},f}$	Diluted concentration polarization factor (-)
Z	Acoustic impedance ($\text{kg}/(\text{m}^2 \cdot \text{s})$)
W	Weight (kg)
A_m	Surface area of membrane (m^2)
E_{global}	The cost function of determining R_m, B and S (-)
$\Delta C_{\text{active layer}}$	Concentration difference between active layer (mol/L)
M_d	Mass of foulants deposition (kg)
M_{dp}	Mass of foulants deposition on pores (kg)
M_{dc}	Mass of foulants deposition on membrane surface (kg)
$M_{dc, \text{fully-developed}}$	Mass of foulants deposition of fully-developed layer on surface (kg)
$M_{dc, \text{transitional}}$	Mass of foulants deposition of transitional fluid-cake layer on surface (kg)
K_p	Potential of particle deposition (-)
C_{foul}	Concentration of foulants in the bulk (kg/L)
$J_w(t_n)$	Water flux at sampling period [t_{n-1}, t_n];
V_p	Volume of pore (m^3)
V_T	Volume of total membrane (m^3)
A_m	Surface area of whole membrane sample (m^2)
A_p	Surface area occupied by a pore (m^2)
L_p	Effective pore length (m);
L_f	The tortuous length of pores being blocked by foulants (m);
L_{uf}	The tortuous length of pores being blocked by foulants (m);
S_c	Structural parameter of cake layer (m)
K_c	Mass transfer coefficient in cake layer (m/s)
S_f	Structural parameter of blocked pores (m)

K_f	Mass transfer coefficient in blocked pores (m/s)
S_{uf}	Structural parameter of unblocked pores (m)
K_{uf}	Mass transfer coefficient in unblocked pores (m/s)
b	The viscos permeability (m ²)
d_{sp}	diameter of colloidal particles (m)
$J_{w(i) modeling}$	The output of water flux in modeling algorithm at sampling time point as t_i (L/(m ² ·h))
$J_{w(i) experimental}$	The water flux value measured at sampling time point as t_i (L/(m ² ·h))
λ_m	Thickness of support layer (m)
μ	Solvent viscosity (Pa·s)
ε_m	Porosity of support layer (-)
ε_p	Porosity of colloidal particle deposition in pores (-)
ε_c	Porosity of colloidal particle deposition in cake layer (-)
$\varepsilon_{c fully-developed}$	Porosity of colloidal particle deposition in fully-developed cake layer (-)
$\varepsilon_{c transitional}$	Porosity of colloidal particle deposition in transitional fluid-cake interface layer (-)
ε_f	Porosity of blocked support layer (-)
ε_s	Support layer surface porosity (-)
τ_p	Tortuosity of colloidal particle deposition (-)
τ_c	Tortuosity of colloidal particle deposition in cake layer (-)
$\tau_{c fully-developed}$	Tortuosity of colloidal particle deposition in fully-developed cake layer (-)
$\tau_{c transitional}$	Tortuosity of colloidal particle deposition in transitional fluid-cake interface layer (-)
ρ_p	Density of colloidal particle (kg/m ³)
λ_c	Cake layer thickness (m)
$\lambda_{c fully-developed}$	Fully-developed cake layer thickness (m)
$\lambda_{c transitional}$	Transitional fluid-cake layer thickness (m)
λ_f	Vertical length of blocked pore (m)
λ_{uf}	Vertical length of un-blocked pore (m)
$\vec{F}_c$	Force vector representing convective drag force
$\vec{F}_{VDW}$	Force vector representing sum of Van-der- Waals force
$\vec{F}_{DL}$	Force vector representing electrostatic force
$\vec{F}_B$	Force vector representing random Brownian forces
E_{p-p}	Interaction energy between particles (J)
E_{p-m}	Interaction energy between particle and membrane (J)

F_{p-p}	Interaction force between particles (N)
F_{p-m}	Interaction force between particle and membrane (N)
ϵ_0	Dielectric permittivity of vacuum (F/m)
ϵ	Dielectric constant of the solvent (-)
κ	The inverse Debye screening length (1/m)
ψ	Surface potential (V)

LIST OF ABBREVAITONS

ODPMs	Osmotically-driven membrane processes
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse osmosis
FO	Forward osmosis
PRO	Pressure retarded osmosis
ICP	Internal concentration polarization
ECP	External concentration polarization
CECP	Concentrated concentration polarization
DECP	Diluted concentration polarization
RSD	Reverse solute diffusion
AL-DS mode	Active layer facing draw solution mode
AL-FS mode	Active layer facing feed solution mode
UTDR	Ultrasonic time domain reflectometry
UFDR	Ultrasonic frequency domain reflectometry
ANN	Artificial neural networks
GP	Genetic programming
CTA	Cellulose triacetate
TFC	Thin film composite
STFT	Short time Fourier transform
ICP-OES	Inductively coupled plasma optical emission spectrometry
FE-SEM	Field Emission Scanning Electron Microscope
BPNNs	Backpropagation neural networks
EPL	Effective pore length
DLVO	Derjaguin-Landau-Verwey-Overbeek

SUMMARY

With intensification of water scarcity, forward osmosis has been drawing increasing attention due to its low energy requirement and power of removing pollutants in wastewater treatment and desalination processes. Similar to other membrane processes, membrane fouling is still a big obstacle with respect to filtration effectiveness and membrane longevity in forward osmosis. To address this problem, this study focuses on two main part on investigation of membrane fouling: Characterization and Modelling.

In this first part of this study, a non-destructive real-time method, ultrasonic time domain reflectometry (UTDR), was for the first time applied to characterize colloidal fouling in osmotically-driven membrane process. In a dead-end forward osmosis setup, the ultrasonic signal is revealed to be much more sensitive to fouling than traditional fouling indicator water flux, especially when active layer was faced to feed side. From qualitative analysis to quantitative analysis, the location of peak raised by colloidal deposition is used to differentiate the deposition on surface of active layer and inside of support layer after being analyzed by arrival time shift and confirmed by statistical testing. Moreover, the further short-time Fourier transformation (STFT) was applied to transfer the original time domain data into time-frequency domain, which reveal a noticeable magnitude reduction on high frequency components when Rayleigh scattering was triggered by particle inside of membrane pores. By contrast, the frequency components are kept nearly unchanged on AL-FS mode in which no internal fouling occurs. Finally, the total reflected power (TRP) calculations for the arrival-times and principal peaks in the frequency-domain correlated well with the overall fouling and internal fouling, respectively.

In the second part of this study, the fouling model derived from mass balance equations in multiple boundary layers in forward osmosis membrane was studied and used to interpret colloidal particle deposition behavior in forward osmosis on AL-DS mode. Due to changing microscopic condition near concentration polarization layer of pollutants, particle deposition factor which characterizes the percentage of particle that attaches on membrane surface out of cross flow cannot be simply assumed as constant.

In order to connect this experimentally inaccessible parameter with model, the parameter was extracted from optimization through series layers model and fed into a backpropagation neural networks with various experimentally-accessible real time parameters. Correlating particle deposition factor with real-time experimental parameters through trained neural networks achieves high prediction accuracy with R squared and Pearson's coefficient as 0.938 and 0.970, respectively. Performance of neural networks bears strong relationship with learning rate, number of hidden layers and number of nodes in hidden layer. Finally, using gradient-based indices is able to identify the positive/ negative contributions of real-time parameters on particle deposition in different fouling stages: the most important factors promoting particle deposition on early stage include time and initial flux; the counterparts on late stage include solute flux and feed concentration. The result is in agreement with 'two-stage' fouling theory, which is characterized by transition from particle-membrane interaction energy dominative system to particle-particle interaction energy dominative system.

In the third part of this study, the focus was put on how deposited particles with different particle size affect deposition of new particles in fouling process on TFC forward osmosis membrane, from perspective of characterization and modelling. The result shows particle concentration and initial flux plays increasingly important role in early fouling stage with decreasing particle size. By modelling trajectories of particles, it's revealed that partition of particles on surface and inside of an ideal cylindrical pore is dominated by particle concentration at early fouling stage, in which nearly all particles transported from bulk ends up with blocking pore. By contrast, this relationship become less noticeable at late fouling stage due to strong repulsive effect from deposited particles. At late fouling stage, the status of blocked pore plays dominative role in determining the maximum flux in which no pore blocking occurs

1 CHAPTER 1. Introduction

2 1.1 Background

3 Water supply is facing increasing pressure due to exponential population growth and
4 stringent requirement of water quality standards. Water problem is so significant that it
5 nearly penetrates into all aspects of life, such as food, oil price, industrial and
6 manufacturing costs. Based on the prediction made by the United Nations Educational,
7 Scientific and Cultural Organization, nearly half of nations around the world will be
8 pushed to the edge of severe water shortage by 2025 (Hightower 2008). Membrane
9 technologies are playing critical role in addressing the water challenges in recent years.
10 The main advantages of membrane technologies include stable productivity, high
11 quality of permeate, easy to integrate with other treatment methods, smaller footprint
12 and lower operational costs etc. In water desalination and reclamation, the pressure-
13 driven membrane processes, where hydraulic pressure is applied to achieve separation,
14 are dominant. They can be classified into microfiltration (MF), ultrafiltration (UF),
15 nanofiltration (NF) and reverse osmosis (RO) based on the pore size of membrane.
16 Typically, MF and UF membranes are used for surface water treatment or as pre-
17 treatment for seawater desalination and water reclamation to remove turbidity and
18 microorganisms, while NF and RO membranes are used to remove dissolved
19 compounds in water. In particular the RO technology, despite its wide application in
20 seawater desalination, the high external pressure (i.e., energy) required to overcome the
21 high osmotic pressure has raised concern on the sustainability of the process (Elimelech
22 et al. 2011). Furthermore, increasing number of studies have pointed out that high
23 external pressure could compress the fouling layer on membrane, which caused negative
24 impact on the membrane performance and hindered the cleaning process (Tang et al.
25 2010; She et al. 2016). Thus, alternative membrane processes such as the osmotically-
26 driven membrane processes (ODMPs) developed to address the limitations of the
27 pressure-driven membrane processes are becoming attractive over the past decades.

28
29 ODMPs refer to membrane processes which are driven by concentration gradient
30 between a semi-permeable membrane, where solvent (water) will flow from low
31 concentration side (feed side) to high concentration side (draw side) (She et al. 2016).
32 The ODMPs include two main categories: forward osmosis (FO) and pressure retarded
33 osmosis (PRO). In FO process, no pressure is applied. In PRO process, hydraulic

pressure lower than the osmotic pressure difference across the membrane is applied on the high concentration side to ‘retard’ water flow; the increase in the volume of the pressurized draw solution can be used to generate electricity via a turbine. ODMPs have the advantages of low energy consumption, less compact fouling layer and ease of membrane cleaning compared to RO process, thus numerous lab-scale research work have been explored in wastewater reclamation (Cath et al. 2010), desalination (McGinnis et al. 2007; Quintanilla et al. 2011; Ling et al. 2011), osmotic membrane bioreactor (Lay et al. 2012; Cornelissen et al. 2011), active sludge dewatering (Cornelissen et al. 2008; Tung et al. 2015) and pharmaceutical applications (Santus et al. 1995; Nayak et al. 2010). This thesis mainly focuses on FO process and the fouling detection of FO process.

Forward osmosis membrane normally consists of two layers: (1) active layer and (2) support layer. The thin and dense active layer is the barrier to reject solutes between feed and draw solution, while the thick and porous layer is to provide mechanical strength for long-term stability in operation. There are two operation modes in FO process. When the active layer is facing the feed side, it is often known as AL-FS mode. While on the other hand, if the active layer is facing the draw side, it is referred as AL-DS mode, which is a more common mode that is used in PRO operation. Like RO process, ODMPs also suffer from the impact of concentration polarization effect. The existence of thick porous layer results in severe accumulation of solute molecules within the support layer, a phenomenon known as internal concentration polarization (ICP). Another adverse phenomenon occurring in FO process is the reverse solute diffusion (RSD). RSD refers to the diffusion of solute, i.e., osmotic agent, from draw solution side to feed solution side due to concentration difference, and the word ‘reverse’ is used to indicate the direction of solute flow which is opposite to water flux flow. Besides the osmotic agent, fouling species in the osmotic agent such as calcium ion may also diffuse from the draw solution to feed solution and may lead to more severe flux decline in FO process. Both ICP and RSD result in lower effective driving force across the membrane, i.e., osmotic pressure difference, thus compromised the FO flux. As such, a lot of studies have been looking for novel membranes to minimize the impact of inherent phenomena of ICP and RSD in the FO process.

Like pressure driven membrane processes, the performance of ODMPs can be impeded

by membrane fouling. Membrane fouling by definition is the deposition, accumulation and growth of undesirable substances on or inside the membrane during separation processes. Similar to other membrane processes, membrane fouling is highly unwanted for reasons such as severe flux decline, poor permeate quality, membrane damage due to long term exposure to cleaning chemicals and increase in operating costs due to membrane cleaning and replacement (She et al. 2016). In ODMPs, membrane fouling, ICP and RSD are inter-related. For instance, ICP and RSD determine the concentration of foulant at the membrane interface, thus play an important role in fouling (Wang et al. 2017; Park et al. 2013). Simultaneously, membrane fouling can impede the effective mass transfer of solutes through the fouling layers, thus have an impact on ICP and RSD. However, the interplay between ICP, RSD and membrane fouling in ODMPs are not well studied. The complexity involved in multiple parameters in ODMPs makes it necessary to combine both experimental observation and modeling approach for better understanding on the fouling behaviors in the ODMPs.

Typically, water flux is used as an indicator for the overall impact of ICP, RSD and membrane fouling phenomena in FO process. Although commonly used, it is insufficient to provide detailed information on the fouling behaviour especially the complex phenomena occurring in FO process. Another commonly used monitoring technique is through membrane autopsy performed on fouled membrane to investigate the root of fouling. Nevertheless, membrane autopsy is a destructive method where membrane has to be sacrificed. Therefore, in order to gain fundamental understanding of the fouling mechanism and fouling status in real-time manner in FO process, it is necessary to develop a non-destructive and real-time monitoring technique. In this study, the application of ultrasonic time domain reflectometry (UTDR) method for detection of colloidal deposition on FO membrane has been critically assessed.

Besides the development of UTDR method for FO fouling detection, this study also focus on developing and improving existing fouling models for FO process. Modelling tool in membrane fouling process has gained increasing attention since it provides interpretable and quantitative analysis on the interaction between foulants-foulants, foulants-fluid and foulants-membrane. Numerous modelling studies have been focusing on hydraulic-pressure driven membrane processes (Bagheri et al. 2019; Shokrkar et al. 2012; An et al. 2011; Bacchin et al. 2002), while modeling studies on ODPMs are

limited (Park et al. 2013; Tow et al. 2016; Siddiqui et al. 2018). Park *et al.* studied on the effect of RSD on colloidal fouling in forward osmosis on AL-FS mode through controlled-volume method with assumption that the percentage of colloidal deposited on the membrane in crossflow process is constant (Park et al. 2013). Tow *et al.* proposed the use of two variables, cake structural parameter (analogous to the support layer structural parameter in FO membranes) and pore hydraulic diameter, that can be extracted from flux measurements to estimate the foulant accumulation for both RO and FO process (Tow et al. 2016). A review paper from She *et al.* has summarized relatively complete mass transfer model in ODPMs, which took external concentration polarization (ECP), internal concentration polarization (ICP), cake layer growth and reverse solute diffusion (RSD) into consideration (She et al. 2016). She *et al.* further used the mass transfer model and cake structural parameter to illustrate that FO has higher fouling propensity as compared to RO process (Siddiqui et al. 2018). So far, most of the modelling work on ODPMs focused on AL-FS mode with several assumptions. However, these assumptions might not be valid for AL-DS mode of operation as more complicated phenomenon occurs during AL-DS mode. Firstly, both external and internal fouling are involved in membrane fouling in AL-DS mode when particle size is larger than pore size on surface of support layer. The partition of foulants in pores and outside of surface is governed by physical and chemical properties of foulants, properties of membrane, hydro-dynamic conditions as well as feed/draw components (Li et al. 2018; Agbangla et al. 2014; Aimar et al. 2010; Gassara et al. 2008). By contrast, these parameters are often not considered in AL-FS mode since there is no internal fouling in AL-FS mode. Moreover, varying conditions resulted from cake layer formation, draw dilution effect, feed concentration effect are expected to alter the foulants-foulants and foulants-membrane interaction thus altering particle deposition propensity (Tang et al. 2011; Boo et al. 2012). In colloidal fouling, it has been discovered that increasing ionic strength is one of main reasons contributing to colloidal destabilization and aggregation (Aimar et al. 2010). In organic fouling, diffusion of calcium cations is found to promote alginate adhesion on membrane surface (She et al. 2012). Without correlating these important parameters with different operation conditions in dynamic manner, the fouling prediction on AL-DS mode is difficult. Hence, in this study, model to incorporate the particle deposition at various operating conditions for AL-DS mode is developed.

Machine learning has gained increasingly attention in membrane processes due to its

capability in dealing with high-dimensional large dataset, especially when complex fouling mechanism cannot be fully understood. In recent studies, it has been applied in prediction of membrane fouling in microfiltration (Lee et al. 2009), adsorption of heavy metal on bio-chars (Zhu et al. 2019), fluidization (Chew et al. 2020) and even advanced system control in mitigation of membrane fouling after integrating with other algorithms (Bagheri et al. 2019; Aani et al. 2019). However, most of current studies are made in macroscale scope in which input parameters are fed into non-linear models which normally are treated as a black-box with little interpretability. Neural networks which are widely applied to capture the non-linear relationship between parameters are applied to correlate with the parameter in determinist model. This attempt is made to derive function of parameters whose mechanism is not fully understood while keeping the interpretability of determinist model. In this study, combination of the first principal models and machine learning algorithm was used to investigate the colloidal deposition in FO process.

1.2 Purpose and scope

The overall PhD study objectives are:

- (1) Assess the applicability of ultrasonic time domain reflectometry (UTDR) as a non-invasive, *in-situ* and real time monitoring method for FO membrane fouling;
- (2) Develop quantitative models to characterize osmotically-driven membrane process using machine-learning based algorithm and classical computational fluid dynamics.

More specifically, the breakdown of the thesis structure is outlined as follows:

- (1) Chapter 2: Review of available literature on ODMs, membrane fouling in ODMs, existing real time monitoring methods and various modeling approaches in membrane fouling process.
- (2) Chapter 3: Detailed information on the experimental setup and chemical used throughout this research.
- (3) Chapter 4: Investigate the applicability of ultrasonic time domain reflectometry in characterization of internal as well as external fouling in FO process;
- (4) Chapter 5: Develop a protocol of combining traditional mass transfer model and neural networks to interpreting impacts of varying parameters on particle deposition factor on forward osmosis on AL-DS mode in crossflow flow setup;

169 (5) Chapter 6: Investigate on the effects of particle size on fouling phenomenon on
170 forward osmosis on AL-DS mode based on experimental observation and modeling
171 approaches.
172

CHAPTER 2. Literature Review

2.1 Mass transfer in ODMPs

AL-DS Mode

AL-FS Mode

Fig. 2.1 Water flux and solute flux for two orientation FO process: (a) AL-FS; (b) AL-DS

As illustrated in Fig 2.1, four types of concentration polarization layers are considered in a FO. The two main categories are namely external concentration polarization (ECP) and internal concentration polarization (ICP), and the sub-categories are dilutive and concentrative. ECP is resulted from the solute accumulation or water loss outside of membrane when solute or water was retained by concentration gradient when transferring into the bulk. Similar to ECP, ICP is also related from same mechanism but inside of membrane. ECP takes places at the membrane surface, where ICP occurs in the porous support layer. For AL-FS mode, the solutes build up on the active layer, giving rise to concentrative ECP (CECP). As the water slowly permeate through the porous support layer and dilutes the draw solutes inside the support layer, dilutive ICP arise.

For AL-DS mode, the solutes inside the support are concentrated as water permeates through the membrane, giving rise to concentrative ICP (CICP). In this case the dilutive ECP (DECP) takes place on the active layer of the membrane. The first semi-empirical multiple-layers model based on mass balance in ODMPs could be traced back to the work from Loeb in 1976. It provided the basic concept to investigate the flux in ODMPs

even though reverse solute diffusion (RSD) and external concentration polarization (ECP; the concentration polarization on the external surface of active layer and support layer) were not taken into consideration (Loeb 1976; Loeb et al. 1976). In 1981, Lee. *et al.* further developed this model in PRO scenario by incorporating RSD and introducing solute resistivity K , which was widely used until structural parameter S was introduced to characterize solute transport in the support layer by Yip in 2010 (Lee et al. 1981; Yip et al. 2010). The first extension of this model from PRO process to FO process was accomplished by Loeb though no change was made on assumptions, i.e. ECP was not taken into account (Loeb et al. 1997). The effect of ECP was ignored in earlier studies since it was believed to have insignificant role as flux was quite low. The assumption was indeed valid if commercial RO membrane was tested in FO/PRO process. However, the availability of new type of FO/PRO membranes with optimized structural parameter, S , of the support layer that enabled high flux, had raised the awareness to consider the effect of ECP. McCutcheon et al. for the first time incorporated ECP on active layer side into mass transfer model in FO process in 2006 (McCutcheon et al. 2006). Similar modifications to PRO process were made by Achilli *et al.* and Yip *et al.* (Achilli et al. 2009; Yip et al. 2011). Navy et al. established a relatively comprehensive model for description of water flux in ODMPs by incorporating ICP, RSD and ECP on both sides in 2014 (Nagy 2014). This FO model on AL-DS mode was selected as the one derived in details in following section.

The concentration profile in each layer could be solved by integrating mass balance differential equation illustrated in (2.1) with various sets of boundary conditions:

$$J_s = -D \frac{dC}{dx} - J_w \cdot C \quad (2.1)$$

where: J_s is back solute flux ($\text{mol}/(\text{m}^2 \cdot \text{s})$); D is the diffusivity of solute (m^2/s), C is the solute concentration (mol/L). Positive direction is defined as the solute flux direction ($x=0$ at high concentration boundary). Negative sign was added in front of solute diffusion components to indicate positive water/solute flux for numerical consistency.

For a clean FO membrane system, water flux J_w is defined as:

$$J_w = \frac{(C_a - C_i) \beta R_g T}{\mu R_m} \quad (\text{FO process}) \quad (2.2)$$

where: β is the Van't Hoff coefficient (e.g. $\beta = 2$ for sodium chloride); R_g is the universal gas constant ($= 8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$); and T is the absolute temperature (K);

229 μ is the solvent viscosity (Pa·s).

230

231 The unknown parameters, C_a and C_i (in Equation 2.2) can be obtained through
 232 integrating Equation (2.1) in each side of active layer:

$$233 \quad \ln \frac{J_w \cdot C_i - J_s}{J_w \cdot C_f - J_s} = J_w \left(\frac{S}{D_u} + \frac{1}{K_{exf}} \right) \quad (2.3a)$$

$$234 \quad \ln \frac{J_w \cdot C_d - J_s}{J_w \cdot C_a - J_s} = J_w \left(\frac{1}{K_{exd}} \right) \quad (2.3b)$$

235

236 Substituting (2.3) into (2.2) gives the overall representation of water flux equation in
 237 AL-DS mode:

238

$$239 \quad J_w = \frac{\{[C_d + \left(\frac{J_s}{J_w}\right)] \exp\left(-\frac{J_w}{k_{exd}}\right) - [C_f + \left(\frac{J_s}{J_w}\right)] \exp\left[\frac{J_w}{\left(\frac{D_u}{S}\right)} + \frac{J_w}{k_{exf}}\right]\} \beta R g T}{\mu \cdot R m} \quad (2.4)$$

240

241 Similarly, water flux profile in FO on AL-FS mode can be derived:

$$242 \quad J_w = \frac{\{[C_d + \left(\frac{J_s}{J_w}\right)] \exp\left(-\frac{J_w}{k_{exd}} - \frac{J_w}{\left(\frac{D_u}{S}\right)}\right) - [C_f + \left(\frac{J_s}{J_w}\right)] \exp\left[\frac{J_w}{k_{exf}}\right]\} \beta R g T}{\mu \cdot R m} \quad (2.5)$$

243

244 where S and D_u correspond to the structural parameter and solute diffusivity inside of
 245 membrane support layer respectively. It should be noted that there are some
 246 controversies on definition of S . S and D_u are defined as follow in most of the studies:

$$247 \quad S = \frac{\lambda_m \cdot \tau}{\varepsilon} \quad (2.6a)$$

$$248 \quad D_u = \frac{D \cdot \varepsilon}{\tau} \quad (2.6b)$$

249 where λ_m is the thickness of the membrane support layer, ε is the porosity and, τ is the
 250 tortuosity.

251

252 For the phenomenon of ICP, in this study effective pore length (EPL) which is defined
 253 as the average length of route for solute transferring back to the bulk was calculated
 254 based on the definition defined in Eqn 2.6a and 2.6b. It is an important parameter that
 255 serves as the indicator to distinguish between pore-blocking and cake layer formation
 256 in FO process. The details are further discussed in Chapter 5.

257

k_{exd} and k_{exf} are mass transfer coefficient in vicinity of active layer surface and support layer surface respectively, calculated through following equations (She et al. 2013; Koutsou et al. 2009; Shakaib et al. 2009):

$$k_{ex} = D \cdot Sh/d_H \quad (2.7)$$

where Sh is Sherwood number presenting the ratio of convective to diffusive mass transport, and d_H is the channel hydrodynamic parameter (d_H varies based on the cell geometry and spacer configuration). In laminar flow regime, Sh are calculated through relating to Reynolds number Re , Schmidt number Sc as well as cell geometry (Koutsou et al. 2009; Kim et al. 2012) as:

$$Sh = 0.2Re^{0.57}Sc^{0.40} \quad (2.8)$$

where Re and Sc were given by (2.9) and (2.10):

$$Re = \frac{d_H u}{\mu} \quad (2.9)$$

$$Sc = \frac{\mu}{D_b} \quad (2.10)$$

where u is the average cross-flow velocity in channel (m/s), μ is kinematic viscosity (Pa·s), d_H is hydraulic diameter (m) and D_b is the diffusivity in bulk solution (m²/s).

For empty and spacer-filled flow channels, d_H is calculated through (11) and (12), respectively (She et al. 2013; Costa et al. 1994; Schock et al. 1987):

$$d_H = \frac{4 \times \text{Crosssection area}}{\text{wetted perimeter}} \quad (2.11)$$

$$d_H = \frac{4\varepsilon}{\left(\frac{2}{h_{sp}}\right) + (1-\varepsilon) \cdot S_{v.sp}} \quad (2.12)$$

where ε , h_{sp} and $S_{v.sp}$ are porosity (-), thickness (m) and specific surface of spacer (m²/m³).

In the case of rhombus mesh spacer, the ε and $S_{v.sp}$ can be determined through:

$$\varepsilon = 1 - \frac{\pi d_f^2}{2ah_{sp}\sin\theta} \quad (2.13)$$

$$S_{v.sp} = \frac{4}{d_f} \quad (2.14)$$

where d_f is the filament diameter (m), a is the mesh size (m), θ is the angle between adjacent filaments (°).

The average cross-flow velocity, u in empty channel and spacer-filled channel can be estimated by (2.15) (2.16), respectively (She et al. 2013):

$$u = \frac{Q}{W \cdot H} \quad (2.15)$$

$$u = \frac{Q}{W \cdot h_{sp} \cdot \varepsilon} \quad (2.16)$$

where Q is the volumetric flow rate across the channel (m^3/s), W (m) and H (m) are width and height of empty channel, respectively.

2.2 Membrane fouling in ODMPs

2.2.1 General aspects

Fig. 2.2 Two types of fouling (external fouling and internal fouling) in ODMPs

Membrane fouling in ODMPs is closely related to the membrane orientation in the process. As illustrated in Fig 2.2, both external fouling and internal fouling could occur in ODMPs. When active layer, i.e the selective layer or dense layer, is faced to the feed side (AL-FS mode), foulants in the feed water tend to deposit on the membrane surface leading to external fouling. This is a common phenomenon that was observed in pressurized membrane processes. Compared to cake layer experiencing high pressure in pressurized process, the cake layer in ODMPs was proved to be less compact and thus more vulnerable to cleaning processes such as flushing, air scouring and chemical cleaning (She et al. 2016). When support layer is faced to the feed side (AL-DS mode), small particles are prone to be either absorbed or blocked in the porous structure of support layer, known as internal fouling. External fouling could happen concurrently in AL-DS mode when the foulants have similar size range with the pore diameter of support layer. The mitigation of internal fouling is more difficult than that of external fouling as the particles that are trapped within the pores are unlikely to be removed by

typical physical cleaning methods such as increasing crossflow rate, air scouring and other strategies that aim to increase shear-force through creation of turbulence near membrane surface. In ODMPs, membrane fouling is associated with multiple parameters including feed concentration, draw concentration (Xie et al. 2014), membrane surface properties, structural geometry of support layer (Manickam et al. 2015), hydrodynamic conditions (Shakaib et al. 2009; Kim et al. 2012; She et al. 2013).

Fouling occurring in ODMPs can be mainly classified into four categories (She et al. 2016):

- Colloidal fouling: the deposition of colloidal particles either on membrane surface or inside of porous support layer;
- Organic fouling: the adsorption and transport of macromolecular substances on or inside of membrane;
- Inorganic fouling: the precipitation of dissolved inorganic compounds due to high concentration polarization in vicinity of membrane surface;
- Biofouling: the attachment and accumulation of microorganism, and continuous growth of biofilm.

The cleaning strategies vary in different situation when membranes are challenged by different types of foulants as well as interaction between multiple co-existing components. In lab scale, experiments focusing on specific type of fouling or combination of multiple types of fouling are normally conducted by using model foulants based on research interests. The most widely-investigated and simplest way to mitigate fouling in forward osmosis is physical cleaning by either applying cross-flow with high velocity on surface of membrane or switching between non-foulant feed/draw solution (i.e. osmotic backwashing). Despite some fouling cases in which the fouling is found to be reversible (Lee et al. 2010; Coday et al. 2014), the effectiveness of this method is also dependent on properties of foulants (e.g. concentration, diameter), properties of membrane, feed condition (e.g. ionic strength, cations concentration, co-existing ions) and hydrodynamic conditions (e.g. crossflow rate, hydraulic pressure, membrane orientation and use of spacers). Ngenyu studied a relatively universal fouling mitigation methods for both colloidal, inorganic and organic fouling in forward osmosis: operating water flux near or below critical flux. The result suggests that 92–98% and 98–100% of fouling is reversible after being fouled by combination of alginate and

gypsum near and below critical flux, respectively. The critical flux value is dependent on both foulants and membrane type after comparing values obtained from PA-TFC membrane and CTA membrane. It's also noteworthy that colloidal fouling leads to lower critical flux value than the alginate foulant does, in both two types of membrane investigated (Nguyen et al. 2019).

For colloidal fouling, the conclusion is found to be divergent when touching the point if full-developed cake is reversible, especially when different experimental conditions and model foulants with different properties (e.g., size, aggregation status and concentration) are investigated. Moreover, the situation is more complicated when other types of fouling is involved together. Mosta et al. studied the foulant-foulants interaction and effect of ionic strength on combination of sodium alginate and colloidal silica fouling. It's found that the main interaction force between foulants is non-electrostatic forces due to the sharp reduction of Debye length and suppression of electric double layer (EDL) under high ionic strength. Also, no evidence is found to show synergistic effects caused by addition of silica colloids compared to the alginate fouling alone (Motsa et al. 2015). Kim studied the roles played by cations, pH as well as applied pressure on fouling situation caused by silica colloidal fouling, alginate organic fouling and combination of both. The result shows the fouling is more favorable under high cations concentration, lower pH and higher applied pressure. Moreover, compared to the conclusion from Motsa (Motsa et al. 2015), Kim indicated it's indeed witnessed that more fouling on membrane challenged by combination of colloidal and organic fouling, compared to the fouling caused by either of them alone. It further validates the synergistic fouling behavior through the observation that less fouling occurred in neutral environment based on the claims that fouling will be otherwise promoted in acid condition and base condition by organic fouling and silica fouling, respectively. However, it's interesting to find that, in spite of synergist effect, all cake layers are still found to be removed easily through backwashing. Also, the ionic strength in Kim's environment is around 10 times less than Mosta's, which makes the effect of electrostatic force still hold (Kim et al. 2014). Choi proposed fouling mitigation method using ultrasound in a comparative study focusing on scaling and colloidal fouling in forward osmosis. As a result, scaling caused by saturated CaSO_4 solution is found to be fully reversible, while colloidal cake layer is found to be more challenging to remove. It's noteworthy that the silica concentration applied is relatively high (5000ppm) and

particle size is also relatively small (10-20nm). The study also pointed out application of pressure on feed side to increase initial flux in forward osmosis is found to be undesirable since it imposes more challenges on colloidal fouling mitigation. This result is in agreement with the conclusion related to effect of hydraulic pressure from Kim (Kim et al. 2014). There is a sperate study from Kim which also reported the ineffectiveness of backwashing in mitigation of colloidal fouling. It studied the different cleaning strategies for organic fouling, scaling and colloidal fouling. The result shows osmotic backwashing could achieve over 95% fouling removal for organic fouling and scaling, while no significant effect is observed on colloidal fouling due to polymerization of silica colloids. By contrast, air scouring was observed to be a feasible fouling mitigation option for colloidal fouling since CO₂ weakened interaction between membrane and fouling layer (Kim et al. 2020).

For organic fouling, the number of previous studies has shed light on this part: the key causes that are found to promote organic fouling are foulants concentration, back solute diffusion, cations concentration et al (Mi et al. 2008; Lee et al. 2010; She et al. 2012; Siddiqui et al. 2018). The interaction of foulants with membrane surface can be more influenced by effect of back solute diffusion which is found to alternate the ionic strength condition for organic matters on forward osmosis process when comparing to RO process. The increasing local concentration due to back solution is found to further promote concentration polarization. Moreover, the cake layer formed in forward osmosis can be easily removed after backwashing without using chemicals, while the cake layer formed during RO process is nearly unchanged after backwashing. The study proposed that cake layer in forward osmosis can be effectively mitigated by changing the feed components in upstream (Lee et al. 2010). Mi investigated the effect of various physical and chemical interactions on organic fouling in forward osmosis by comparing the fouling behaviors of Alginate, bovine serum albumin (BSA), and Aldrich humic acid (AHA). Despite combination of effects from cations, permeate flux drag and crossflow shear force, the results suggested rate of fouling is highly dependent on intermolecular adhesion forces between foulants and membrane. Although there is no further study on cleaning strategies, this study showed difference of fouling rate is unnoticeable once cake layers are formed by 3 model foulants (Mi et al. 2008). The study from She et al. is also in agreement with the promoting effect of back solute diffusion and cations concentration on forward osmosis. They further investigated which cations as draw

solution promote membrane fouling most and obtained the order as $\text{Ca}(\text{NO}_3)_2 > \text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl}$ (She et al. 2012). Arkhangelsky et al. studied the impact of organic matters including serum albumin (BSA), dextran, sodium alginate and xanthan gum on AL-FS mode. The results indicate the addition of calcium ions plays a dominative role in exacerbating membrane fouling for any feed solution containing alginate due to intermolecular bridging effect among alginate molecules. Also, synergistic effect was overserved when BSA are combined with sodium alginate (Arkhangelsky et al. 2016). In this regard, tailoring components of draw solution and decreasing back solute diffusion are suggested as an effective method to mitigate organic fouling. Moreover, physical cleaning by using high velocity of crossflow is also found useful in most of published studies mentioned before. Finally, based on significance of interactive force between membrane and organic matters (Mi et al. 2008), modification on membrane surface in fabrication process is also promising. A recent study from Balkenov et al. showed the effectiveness of doping silver nano-particles in alternating properties of forward osmosis membrane including zeta potential, contact angle, roughness, and antimicrobial resistance. After doping silver nano-particles, the flux decline at the 1st run was limited to 10% and can be almost 100% recovered through physical cleaning, while the pristine membrane is found to experience over 50% flux loss (Balkenov et al. 2020).

For bio-fouling, the main methods for fouling mitigation can be summarised as chemical cleaning, alternating feed component to limit nutrient supply for biofilm, controlling bio-precursors like TEP, controlling co-existing ions, membrane surface modification et al (Yoon et al. 2013; Meng et al. 2017; Valladares et al. 2014). Compared to colloidal or organic fouling caused by non-living substances, bio-fouling is caused by bi-organism which capture nutrients in feed, propagate and finally colonize in membrane surface/substate. Hongsik compared the bio-fouling caused by *Pseudomonas aeruginosa* PA01 GFP in forward osmosis and reverse osmosis suggesting that bio-fouling in forward osmosis is less severe than it's in reverse osmosis under same permeate drag force. It also revealed that, in order to recovered fouled membrane, it's required to add chloride in backwashing process to effectively remove bio-fouling layer, while physical cleaning using water alone is revealed to be ineffective (Yoon et al. 2013). Controlling bio-fouling is found share some similarity with controlling colloidal/organic fouling in aspect of effect of cations. Zou et al investigate the fouling caused by

microalgae *Chlorella sorokiniana* in forward osmosis and pressure retarded osmosis. The result showed that existence of Mg^{2+} in feed solution promoted the bio-fouling significantly. Moreover, even though there is no Mg^{2+} in feed solution, Mg^{2+} -based draw solution is revealed to promote bio-fouling through back solute diffusion (Zou et al. 2011). The results are in agreement with the results obtained from study in organic fouling from She et al (She et al. 2012). However, more studies are focused on the unique behaviours of biofouling. Based on three stages theory of micro-organism growth from Flemming: the first stage (induction) is controlled by micro-organism concentration, and the last 2 stages (logarithmical growth and plateau phases) are controlled by nutrient concentration. Controlling nutrients supply in bulk solution is identified as a key point in bio-fouling mitigation (Flemming 1997). The sources of nutrients can be classified as following three categories: feed solution, membrane and substance back diffused from draw solution (She et al. 2016). Chen et al. found that CTA membrane was more vulnerable to fouling in an anaerobic OMBR system since micro-organism are found to consume CTA material as nutrient for growth (Chen et al. 2014). As a practical solution, the interaction between membrane surface and micro-organism should be considered during membrane selection. Furthermore, draw solution components is also a key point effecting bio-fouling since nutrients and salt can be transferred into feed side through back solution diffusion process (Nawaz et al. 2013). There are also some studies addressing effect of extracellular polymeric substances (EPS) and Transparent exopolymer particles (TEP) in bio-fouling. The study from Zhang et al. investigated the bio-fouling in a forward osmosis integrated bioreactor. This study revealed the key role played by micro-organism and EPS in decline of mass transfer coefficient and increasing of hydraulic resistance. As a practical solution, the study proposed that bio-fouling can be mitigated by switching membrane orientation from AL-DS mode to AL-FS mode and applying intermittent tap water flushing to remove EPS on membrane surface (Zhang et al. 2012). Meng et al. did a critical review to address the importance of Transparent exopolymer particles (TEP), which is closely related to the cations determining the cross-linking degree of precursor materials. How the TEP level determines the bio-fouling is suggested to follow the steps including formation of TEP-associated gel layer and biofilm formation together with microorganism. Moreover, trapping deformable TEP in support layer is another cause of decline of driven pressure. In this regard, decreasing ETP level is addressed as a key to mitigate bio-fouling potential (Meng et al. 2020). As for the practical method to

decrease the level of TEP, Meng pointed out in a separate study that increasing Na^+ is found to decrease TEP level as well as TEP-associated membrane fouling, which is validated by severer fouling in experiment using seawater compared to the one using freshwater (Meng et al. 2017). Apart from feed conditions, hydrodynamic condition is found to be another important factor in determining bio-fouling degree in forward osmosis. Valladares investigated the role of feed apace thickness on bio-fouling potential and results based on studies on flux development, biomass accumulation and fouling localization and composition analysis. The result shows water flux decline is found to decrease with increasing thickness of spacer (Valladares et al. 2014).

In this study, the research topic focuses on colloidal fouling detection and modelling using silica colloidal particle as model foulant. Rather than providing a practical suggestion for fouling detection/mitigation in industrial scale where complex co-existing ions are involved, this fundamental study focuses on quantitative analysis of signal and model development in a relatively controllable testing condition in lab scale. In this regard, the effect on signal and cake layer acoustic impedance caused by any other foulants (e.g. organic foulants or bio-foulants) was not addressed. Analysis and interpretation of signal generated through UTDR is typically associated with foulants properties and media in which ultrasound propagates. This characteristic makes it's necessary to perform signal validation of known fouling layer caused by single foulant before applying it to more complicated feed. More studies using complex feed are still necessary before generalizing UTDR as a universal real-time membrane fouling characterization technique in osmotic driven processes involving complex feed components.

2.2.2 Membrane fouling and associated phenomenon

Reverse solute diffusion (RSD) is typically used to describe the transport of solute molecules in the direction opposite to water flux in ODMPs due to the high chemical gradient of solute on the draw side. In ODMPs, RSD was reported to be closely associated with fouling by Tang and his coworkers (Zou et al. 2011). The main mechanisms can be classified as follows: (1) The solute molecules or ions that diffuse from high concentration will eventually accumulate near the active layer thus increasing concentration polarization. The enhanced concentration polarization further leads to

destabilization and deposition of colloidal particles on the membrane surface; (2) The solutes diffusing from draw side changes the solution chemistry of feed side (ionic strength, pH and specific ion concentration). In this regard, She *et al.* revealed that the fouling potential induced by RSD is related to (1) type of draw solute diffusing to FS; (2) the ability of draw solute to interact with solute on FS; (3) the rate of RSD (She et al. 2012).

Diffused solute acts as fouling-promotor when it is able to destabilize and react with components in feed side. For example, Tang and his coworkers observed noticeable enhancement of microalgae fouling during the process of microalgae separation through FO process when calcium ions was added into draw solution (Zou et al. 2011). Similar phenomenon was reported by She *et al.*, who revealed that alginate fouling and humic acid fouling could be both promoted by reverse diffusion of $\text{Ca}^{2+}/\text{Mg}^{2+}$ (She et al. 2012) (She et al. 2013). The effects of divalent ions on organic fouling is attributed to their strong ability of forming complex with carboxylic groups with macromolecules and of bridging adjacent molecules together (Mi et al. 2008; Hong et al. 1997). Comparing the role of Ca^{2+} in fouling process initiated by alginate, bovine serum albumin (BSA), and humic acid in FO processes, Mi and Elimelech reported that severe flux decline was observed when the feed water contain alginate (Mi et al. 2008). This is most likely due to the interaction between carboxylate functional groups of alginates with and calcium ions to form complexes. Furthermore, the special structural characteristics of alginate also promoted the formation of cross-linked network of alginate gel with the presence of calcium ions. In some cases, the fouling behavior enhanced by RSD also associated with the type of counter-ions in draw solution. It is reported that $\text{Ca}(\text{NO}_3)_2$ resulted in more flux decline than CaCl_2 in organic fouling even though both have the same cation. This could be to the different diffusion rate of Cl^- and NO_3^- . Apart from the effects of specific ions discussed, Na^+ diffused from draw side also influence the water flux adversely. The accumulation of Na^{2+} inside or on the membrane surface reduce water flux mainly by: (1) enhancing CP inside of microscale fouling layer structure, (2) increasing feed osmotic pressure of bulk feed through concentrative effect. In inorganic fouling, the enhanced ion species such as Ca^{2+} , SO_4^{2-} etc on the membrane surface may eventually form scale if exceeding its solubility (Xie et al. 2013; Zhang et al. 2014; (Wang et al. 2010). Sometimes the permeation of fouling precursors of foulants from draw side could lead to more severe fouling potential (Zhang et al. 2014; McCutcheon

et al. 2005; How et al. 2006). Due to the critical role of RSD in ODMPs performance, selection of proper draw solution which reduces the RSD to the specific degree is of great insignificance in maintaining stable water productivity in ODMPs.

Another main challenge in FO/PRO process is the internal concentration polarization (ICP). Unlike ECP, ICP cannot be easily alleviated by optimizing the hydrodynamic across the membrane surface. It occurs when the diffusion rate of the ions to/from the active layer are hindered by the material and the structure of the membrane substrate and hence ICP is very much depend on the s parameter (Eqn 2.6) of the membrane substrate. ICP becomes less severe for membranes with thinner and more porous layers.

Furthermore, the membrane orientation in the ODMPs determine the degree of ICP in the process. Generally, it was observed that AL-FS mode has higher flux stability as compare to AL-DS mode even though AL-FS has lower initial flux when using same feed and draw solution (Tang et al. 2010; Wang et al. 2010; Parida et al. 2013). A unique phenomenon occur during FO fouling is the ICP-self compensation effect. ICP-self compensation causes the effective driving force in FO to increase progressively due to the fouling. The decrease in water flux due to membrane fouling results in the decrease in ICP, which in turn leads to the increase in the effective osmotic driving force. On AL-FS mode, particles are prone to deposit on membrane surface and thus act as additional filtration layer. Apart from additional hydraulic resistance, fouling layer hinders the transport of the solute and leads to cake enhanced external concentration polarization (CE-ECP) (Hoek 2003). In this case, support layer on draw sides are free from foulants and retains its original properties. With the flux decline, less water permeates into draw side contributing to reduction of diluted ICP. For AL-DS mode of operation, as the support layer is facing the feed side it suffers from pore-blocking, a phenomenon known as in pore blocking enhanced ICP (PCE-ICP) (Tang et al. 2010; She et al. 2012). The ICP compensation effects on AL-DS mode is much weaker than on AL-FS mode due to two reasons. On the one hand, the initial diluted ICP is much severer than concentrative ICP, thus effect of flux reduction can be enlarged on AL-FS mode. Moreover, pore-blocking support layer increases the tortuosity and reduces the porosity of routes for solute transport thus retaining solute inside of support layer. The blocked support layer acts as an unhindered layer filling with solutes, which offset a part of benefits brought by flux decline (She et al. 2012).

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585 More specifically, colloidal fouling is a tricky problem which underscores the
586 importance of early detection. Although the number of related cost-balance analysis in
587 industrial scale is quite limited, increasing number of papers in lab scale pointed out the
588 transitional characteristics of colloidal fouling from concentration polarization to dense
589 gel. With respect to fouling mechanism, the study from Sim on ultrafiltration
590 revealed that, before formation of foulant cake layer with constant thickness, some
591 transitional phases are observed including concentration polarization phase which
592 results in rapid TMP increase as well as a meta-stable phase with nonconstant increasing
593 rate of TMP. Simply switching from fouling to non-fouling feed solution, nevertheless,
594 cannot completely remove all cake layer of foulants, when a thick cake layer is fully
595 developed (Sim et al. 2012). A further follow-up study pointed out the transition from
596 such meta-stable phase to a dense-gel cake layer was witnessed to be shortened with
597 lower crossflow velocity, higher water flux, increasing salinity and higher silica
598 concentration (Sim et al. 2014). Boo et al. expanded focus of studying colloidal fouling
599 from hydraulic pressure driven process to forward osmosis by also using suspended
600 silica nanoparticles as model foulants. The results shared some similarity with
601 conclusion from Sim, which underscored the promotion of formation of gel layer under
602 high salinity condition. Also, in forward osmosis high reverse salt diffusion is found to
603 be the main cause that makes the dense gel fouling cake layer uncovered at later fouling
604 stage (Boo et al. 2012). Choi et al. further studies the application of ultrasound in fouling
605 mitigation in a comparative study on colloidal fouling and scaling in forward osmosis.
606 The study shows that, when silica colloidal (diameter: 10-20nm) concentration is as high
607 as 5000ppm, it's much harder to remove the colloidal cake layer than to remove scaling.
608 The application of hydraulic pressure on feed side (i.e. PAO mode) is found to make
609 cake layer more irreversible (Choi et al. 2014). Moreover, a recent paper from Kim et
610 al. did a comprehensive comparative study on fouling removal strategies for fouling
611 including organic fouling, scaling and inorganic fouling. The result shows that,
612 compared to organic fouling and scaling, it's more difficult to remove silica gel-like
613 cake layer by using either intense physical cleanings, which includes air scouring and
614 the combination of various physical cleaning, or chemical cleanings. The challenge of
615 moving silica cake layer is attributed to the polymerization of silica colloids (Kim et al.
616 2020).

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2.3 Real-time fouling monitoring

2.3.1 General aspects

Early-stage detection of membrane fouling allows mitigation measures to be carried out promptly to save on chemical costs and plant downtime (Zhao et al. 2017; Alizadeh et al. 2014; Al-Juboori et al. 2012). The study on fouling behavior detection involves consideration of phenomenon in three regions: 1) the membrane, 2) the fluid boundary layer including the membrane–fluid interface and the possible presence of a cake or fouling layer and 3) the bulk fluid in the membrane module (Chen et al. 2004). Many non-destructive approaches have been developed such as direct observation through membrane (DOTM) (Wang et al. 2010; Zou et al. 2013), shadowgraph refractometry (Eggen et al. 2010), fluorescence (Zeng et al. 2011), impedance spectroscopy (Ho et al. 2016; Ho et al. 2017; Sim et al. 2013), ultrasonic reflectometry (Sim et al. 2012; Sim et al. 2013; An et al. 2011; Hou et al. 2010; Li et al. 2006; Zhang et al. 2003), nuclear magnetic resonance (NMR) (Culfaz et al. 2011), x-ray computed tomography (Haaksman et al. 2017), small angled neutron scattering (SANS) (Jadav et al. and so on. The comparison between these methods was well organized in (Chen et al. 2004). Non-destructive methods allow real-time fouling behaviors without disturbing the filtration process.

The classification of various real-time characterization can be based on multiple standards including characterization mechanism (optical, ultrasound, electrical impedance et al.), region specific (membrane, membrane-fluid interface, bulk feed solution, cake layer build-up et al.), responsiveness, detection limits, non-destructive characteristics (non-destructive or slightly destructive), data presentation methods (direct fouling visualization or specific interpretation model/metric), potential of application in industrial scale, requirement of specialization in analysis methods et al. (Chen et al. 2004). Real-time fouling characterization aims to provide information for the ‘State of membrane’ through on-line non-destructive techniques. Sim et al classified the real-time characterization methods in reverse osmosis into two basic categories (Sim et al. 2018):

1. The ‘in-situ’ methods which uses sensors to detect early-stage membrane fouling situation. One of examples is installation of sensors directly in spiral wound module.

2. The ‘ex-situ’ methods which simulate similar hydrodynamic condition and fouling situation of cell by building an independent cell, such as ‘canary cell’ in RO module.

The details in-situ and ex-situ real-time methods are extended based on summary from Sim (Sim et al. 2018):

Table 2.1 The summary of real-time membrane fouling characterization methods (Sim et al. 2018)

Methods	Working principle	Non-invasive ¹	Response time ²	Complexity ³	On-line ¹	Approximate resolution	Applied to FO ¹
Ex-situ scale observation detector	optical magnification /combination of bright and low angle dark field illumination	Y	R, P	M	Y	> 100 µm	N
UTDR	propagation /reflective characteristics of ultrasound in matters	Y	R	L	Y	~ 1 µm	N
Electrical impedance spectroscopy (EIS)	conductance and capacitance of matters	Q	M, P	H	Y	1 nm	N
Salt-tracer response technique (STRT)	development of equations using Injection of tracers to solve concentration polarisation and resistance	Q	M	M	Y	N.A	N

Optical coherence tomography (OCT)	light interference properties of backscattered beam from different depths	Y	R, P	H	Y	10 μm	Y
Nuclear magnetic resonance (NMR)	magnetic moment of NMR active nuclei using electromagnetic pulses and applied magnetic fields.	Y	R	H	Y	10 μm	N
Direct observation over the membrane (DOTM)	optical microscopy	Y	R	L	Y	$\sim 3 \mu\text{m}$	Y

¹ Y = Yes, N = No, Q = Quasi non-invasive.

² Response time R = Rapid; S = Relatively slow; P = the obtained data required software processing.

³Complexity H = High complexity; M = moderate; L = low.

Despite summary of real-time characterization methods in membrane fouling studies, their application in forward osmosis is quite limited. To our best of knowledge, only DOTM and OCT has been studied in characterization of membrane fouling in forward osmosis before:

- Direct observation over the membrane (DOTM) utilizes optical microscopy to monitor even a slight amount of fouling directly over membrane surface directly before such fouling impacts water flux. The first attempt was made by Wang et al. in characterization of fouling caused by latex in CTA forward osmosis

membrane (Wang et al. 2010). Zou et al. further investigate the possibility of application of DOTM on characterization of membrane fouling caused by microalgae. In this study, it's further confirmed that DOTM is of high potential in early-stage microalgae fouling detection when initial flux is higher than critical flux (Zou et al. 2013). The advantage of DOTM is its ability to present fouling status directly without much model or metrics calculation involved (Haupt et al. 2018).

- Optical coherence tomography (OCT) is an advanced optical imaging technique which is of ability of performing 'optical slicing' at relatively high resolution ($\sim 2 \mu\text{m}$) and providing a powerful tool to non-invasively detect the 3D structure of a semi-transparent foulant layer (Liu et al. 2017). The first attempt of application of OCT on forward osmosis-related study was made by Pathak et al. at 2018. In this study, OCT was applied to monitor growth of biofilm in CTA forward osmosis membrane integrated in an osmotic and microfiltration membrane bioreactor over 21 days. Through OCT, combination of qualitative and quantitative analysis was applied to identify the promoting effects from back solute diffusion on bio-film growth is well identified in complex feed condition of such a bioreactor (Pathak et al. 2018). A more recent study from Liu et al. used OCT to characterize fouling caused by clay suspensions in a special type of forward osmosis membrane with relatively loose actively layer (Liu et al. 2020). With real-time data collected through OCT, the step should be using this real-time information to do effective fouling or flux decline prediction, which is what has been done by a recent study from Im et al. who use OCT to extract images of cake layer in time series and fed into a deep learning convolutional neural network model for fouling prediction (Im et al. 2021).

2.3.2 Ultrasonic Time Domain Reflectometry: Basic Principle

The term 'Ultrasonic Time Domain Reflectometry' was first proposed in 1998 by Bond L. J. *et al.* UTDR measurement and analysis are based on the principle that the wave is affected by the media through which it travels (Krantz 2008), which include wave generation, wave propagation in media, wave impinging at boundary, wave receiving and signal presentation. Changes in transmit time, attenuation, scattering and frequency content in such a cycle give information on the properties of the media the wave travels

(Krantz 2008). When ultrasonic wave encounters an interface between media with different acoustic impedance, the wave may be reflected or transmitted through the media. Typically, arrival time and amplitude changes of peaks from the waveform are analyzed. Based on relationship between time and velocity of ultrasound through the media, the thickness of the media (Δd) can be calculated through Equation (2.17).

$$\Delta d = \frac{t \cdot C}{2} \quad (2.17)$$

where t is the time required for a wave to travel from a reflecting interface to the receiver; C is the velocity of ultrasound through the media.

To perform UTDR measurement on a membrane filtration setup, an ultrasonic sonic transducer is attached on a filtration cell as illustrated in Fig 2.3. (a) For a clean membrane system, peak 1 and peak 2 representing the top plate/feed water and membrane top/support layer can be observed. When fouling occurred on the membrane surface and reached the detectable limit of the UTDR, a separate peak 3 will be raised in front of peak 2. With the movement of peak 3 towards to the stationary peak 1, the growth of fouling layer can be detected and recorded in real time manner. The difference of arrival time between peak 2 and peak 3 is can be used to calculate the foulant thickness using Eqn 2.17.

Fig. 2.3 (a) Cross section of a liquid-filled membrane cell showing a UTDR transducer and reflected waveforms from the top plate (1), membrane (2), and fouling layer (3). (b) Reflected waveform amplitude. (Krantz 2008)

UTDR is a non-destructive and on-line characterization method that can potentially be

integrated in an existing process control system in membrane desalination process (Bond. 2011). Compared to the traditional fouling detection methods which are based on flux analysis and membrane autopsy, UTDR is able to measure fouling layer growth in real-time style with theoretical resolution down to 2.5λ (λ equals to the wavelength of ultrasound applied) (Chang et al. 1974). The precision can even be further improved through signal analysis methods like Fourier wavelet transform, differential signals, acoustic signature and sound intensity calculation, which has been made and attested in the literatures (Sanderson et al. 2005; Chai et al. 2007; Zhang et al. 2003; An et al. 2011). Unlike flux/TMP analysis, UTDR can be used to quantify the growth of fouling layer but quite insensitive to other causes which also contribute to flux decline/ TMP increase such as concentration polarization. Moreover, compared to other non-destructive methods such as nuclear magnetic resonance (NMR), small angled neutron scattering (SANS), UTDR is not device-specific, and this trait make it possible to install UTDR in various RO modules even industrial tests. Within last few decades, the number of exploration has been made by applying UTDR in fouling layer detection in variety of modules including flat sheet (Sanderson 2005; Chong et al. 2007), spiral wound (Chai et al. 2007; Zhang et al. 2003; An et al. 2011), hollow fibers (Li et al. 2014) and so on. Despite robustness in pressurized processes, UTDR still have not yet been extended into fouling detection in ODMPs

2.3.3 Ultrasonic Time Domain Reflectometry: Signal processing and presentation

The ultrasonic data in non-destructive characterization can be presented in multiples ways. The three common ways are A-scan, B-scan, C-scan (Lin et al. 2013). All three types of data presentation methods have been applied in membrane fouling characterization. A-scan presentation shows the amplitude of signal as a function of time. The waveform presented in Fig 2.3(b) is an example of A-scan, which is also the most common presentation method in membrane characterization. In this way, arrival time constitutes horizontal axis, amplitude of signal constitutes vertical axis. One waveform presents the real-time situation of a particular point. Data procurement in A-scan is straightforward, while interpretation of this data requires specific model and calculation. B-scan presents the cross-section profile of sample along the linear direction the transducer moves, as shown in Fig.2.4 (A,C,D). In B-scan, arrival time of sample in particular point is display in vertical axis, and the linear position of transducer was

presented in horizontal axis. B-scan is easier to be visualized than A-scan, while more effort should be put in enabling automatic movement of transducer with additional trigger gate. Compared to A-scan and B-scan, C-scan is able to provide a more straightforward plane-type profile of the sample by moving transducer in the plane parallel to surface of sample, as shown in Fig.2.4 (B,E,F). The data in C-scan was obtained through automatic data acquisition system with regular interval during scanning process, and the amplitude or arrival time in each point was presented by shade of grey or different colours.

Fig. 2.4 The schematic graph of scan mode (B-scan (A), C-scan (B)) and data presentation (B-scan (D), C-scan (E)) (NDT Education Resource Center); the actual experimental result of B-scan (C) and C-scan (F) presenting fouling layer (Lin et al. 2013).

In this study, the UTDR signal is presented in time domain, that is, A-scan. As mentioned before, the process of data collection in A-scan is easy. Nevertheless, due to the resolution of the transducer, wave overlapping and variation of hydro-dynamic conditions, the perfect separate fouling cake peak cannot be obtained in some cases. Under such cases, multiple transform methods can be utilized to extract more information from

time-domain waveform. To give readers an overall perspective, the presentative methods and mathematic equations behind them (if any) were summarized here.

Fourier transform method: For ultrasonic data that is presented in time-domain, Fourier transform is applied to extract frequency content from original waveform. However, standard Fourier transform treat signal sample as a continuous function and generate frequency domain data without quantified time resolution. Thus, the relationship between local magnitude in frequency domain and arrival time is still unclear. This information is of great significance for non-destructive characterization of inhomogeneous materials such as fouling layer.

One method is windowed Fourier transform (WFT), which utilizes a scalable modulated window to select a time slot and then applies Fourier transform in this period of time (Sanderson et al. 2005a). Gaussian window $w(t)$ was adopted in this study:

$$w(t - \tau) = \exp[-(t - \tau)^2/\sigma^2] \quad (2.18)$$

where $w(t-\tau)$ is the window function around time slot τ ; σ is constant. The transform with σ is called Gabor transform.

When this window is shifted along the arrival time axis by predetermined step, Fourier transform was applied using Equation 2.19:

$$[WFTs](\omega, \tau) = \int_{-\infty}^{\infty} s(t)w(t - \tau) \exp(i\omega t) dt \quad (2.19)$$

where $s(t)$ is the signal function in time-domain, $w(t-\tau)\exp(i\omega t)$ is the time-shifted and modulated version of the window function $w(t)$.

With movement of window function by changing τ over the whole signal and application of Fourier transform in each point, the signal can be re-presented in both time and frequency domains through a three-dimensional graph. The frequency spectra in a particular arrival time could be obtained by through three-dimensional wavelet at the point of interest.

Acoustic signature: To cope with ultrasonic signal reflected from module with multiple layers, such as spiral wound, signal overlapping is a big challenge in data interpretation. Some studies preferred selecting the peak from outmost layer in the module due to the

ease of detection and convolution (Chai et al. 2007). Considering signal amplitude throughout whole layers inside of module, a new protocol called amplitude shift factor was developed to cope with the dilemma in spiral wound module (Z.-X. Zhang et al. 2003). In this method, amplitude shift factor and arrival time shift factor were defined as follows:

$$\text{Amplitude shift factor: } Q_A = \sqrt{\frac{\sum_{j=1}^{j=N} (V_{ju} - V_{jr})^2}{N}} \quad (2.20)$$

$$\text{Arrival time shift factor: } Q_T = \sqrt{\frac{\sum_{j=1}^{j=N} (T_{ju} - T_{jr})^2}{N}} \quad (2.21)$$

The method starts with the selection of peaks of interest as peak j , the V_{ju} and T_{ju} are amplitude and arrival time of peak j during fouling process; V_{jr} and T_{jr} are counterparts in reference peak j , which is usually obtained from signal from unfouled membrane. When membrane was fouled, changes in signal of peak j can be observed. It is suggested that more changes occur on membrane surface when the increase in acoustic amplitude was observed. With increasing value of acoustic signature, the growth of fouling layer could be detected, especially when observation of a separate fouling peak is hindered by overlapping reflections from multiple layers inside of module.

Ultrasonic intensity calculation: The method was developed to deal with multiple superimposed reflections in a module with multiple layers such as outer and inner surfaces of module housing, element wrapping materials, membrane layers, support layers and channel spacers. The protocol bridges the acoustic pressure with the acoustic intensity and takes all reflections inside of module into consideration (An et al. 2011). The method started with selecting a range with multiple peaks in acoustic pressure amplitude spectra and modelled it as a continuous function. When semi-sinusoidal function was selected as modelling function, real-time acoustic pressure could be expressed as:

$$P_i = A_i \sin \left[\frac{2\pi}{T_a} (t - t_0) \right] \quad (2.22)$$

where A_i is the amplitude of peaks selected; T_a is the average period of each range; t_0 is the phase angle determined by the arrival time of peaks.

When original ultrasonic wave was given, the simulated spectra can be obtained. Then, the sound pressure at interval of T can be calculated based on the simulated spectra using equation:

$$P_e = \sqrt{\frac{\int_0^T P^2 dt}{T}} \quad (2.23)$$

The ultrasonic intensity in any arrival time period T can be calculated through equation:

$$I = \frac{P_e^2}{\rho_0 C_0} \quad (2.24)$$

By combining equation. and equation, obtains:

$$I = \frac{\int_0^T P^2 dt}{T \rho_0 C_0} \quad (2.25)$$

where ρ_0 is the density of media ultrasonic wave propagates; C_0 is the ultrasonic velocity in the media.

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Ultrasonic intensity was defined as the amount of energy flowing per unit area per unit time and proportional to the square of the acoustic amplitude. The intensity of any range with T can be calculated and whole acoustic intensity is the sum of multiples range divided at beginning. Similar to acoustic signature, a reference obtained from unfouled membrane is required for comparison in this method. Changes in acoustic intensity value during fouling process was used to identify fouling in particular layers or whole module. When particular layers are under investigation, the corresponding arrival time range would be selected in advance.

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2.3.4 Ultrasonic Time Domain Reflectometry: Current research status in membrane process

Mairal *et al.* were the first group of researchers who applied UTDR for RO (Mairal et al. 1999). The study has shown the possibility to distinguish between the concentration polarization and formation cake layer behind flux decline behaviours. After year 2000, the increasing number of research about UTDR application in membrane process was spurred and mainly focused on three fields: membrane fouling characterization, membrane compaction and membrane fabrication process monitoring, which are presented in Table.2.2 comprehensively (Wang et al. 2018; An et al. 2011; Hou et al. 2010; Krantz et al. 2008).

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Table 2.2 The summary of research on the application of UDTR in membrane process

Type of membrane and configuration	Type of foulant	Key findings	Reference
RO, flatsheet	Scaling	UTDR signal can be used to distinguish between CP and cake layer formation	(Mairal et al. 1999)
RO, flatsheet	Scaling	UDTR signal reveals two types of morphologies of scaling	(Mairal et al. 2000)
RO, flatsheet	Scaling	UTDR signal detects scaling at different axial velocities and cleaning process.	(Sanderson et al. 2002)
MF, flatsheet	Paper mill wastewater	UTDR differential signal increase the detection sensitivity to $h/\lambda \geq 0.25$. Wavelet transform is firstly applied.	(Sanderson et al. 2005b)
RO, spiral wound modules	Scaling	UTDR was for the first time applied in spiral wound modules with entire acoustic spectrum presented.	(Zh.-X. Zhang et al. 2003)
Pore size characterization	N.A.	UFDR was applied for differentiating membranes with different pore diameters.	(Ramaswamy et al. 2004)
UF, tubular module	Organic foulants	UTDR was revealed to recognize the acoustic response signals from the various curve surfaces of the housing holder, steel support and membrane.	(Li et al. 2006)
MF/NF, flatsheet	Bio-fouling	UTDR and total reflected power were applied to differentiate biofouling on different membrane surfaces.	(Kujundzic et al. 2007)

MF, hollow fiber	Organic fouling	UTDR and wavelet methods are applied to visualize fouling and cleaning process of oil wastewater.	(Xu et al. 2009)
MF, flatsheet	Organic fouling	UTDR was applied to differentiate two types of fouling mechanism induced by oil with different sizes.	(Silalahi et al. 2009)
RO, flatsheet	Colloidal fouling	UTDR was applied to monitor the growth of cake layer thickness of silica fouling, which was compared to other non-destructive tracer techniques.	(Chong et al. 2007b)
UF, flatsheet	Scaling	UTDR was applied for monitoring different deposition behavior of scaling on membrane with and without bio-film.	(Hou et al. 2010)
NF, flatsheet	Scaling	Internal transducer was fabricated and integrated with membrane increasing the detection sensitivity.	(Cobry et al. 2011)
RO, flatsheet	Scaling	Sound intensity calculation was applied to provide direct metric for quantifying scaling process in RO.	(An et al. 2011)
NF, flatsheet	Colloidal fouling	UTDR was applied to reveal four types of colloidal fouling stages and metastability characteristics of colloids.	(Sim et al. 2012)
UF/RO, flatsheet	Bio-fouling	UTDR was applied to detect bio-fouling growth with addition of silica was ‘acoustic enhancer’ from a canary cell.	(Sim et al. 2013)
MF/UF, flatsheet	Colloidal fouling	UTDR was further applied in comprehensive investigation of effect of crossflow velocity, flux,	(Sim et al. 2014)

salinity and colloid concentration
on colloidal metastability.

RO, fiber	hollow	Organic fouling	UTDR was successfully applied to monitor sub-critical flux fouling induced by yeast under different aeration rate, fiber length and operating flux. (Li et al. 2014)
Bio-carrier		Bio-fouling	UTDR, differential signal, wavelet methods were applied to differentiate distinguish the initial adherence, reversible adhesion and irreversible adhesion of bio-fouling on membrane challenged by two types of wastewater. (Wang et al. 2018)

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876 Since this thesis focused on colloidal fouling, the progress of application UTDR on
877 colloidal and inorganic fouling was expanded in details as below. UTDR was firstly
878 applied to characterize high concentration calcium sulfate fouling process on flat-sheet
879 RO membrane by Mairal *et al.* in 1999 (Mairal et al. 1999). UTDR responses were used
880 to demonstrate the two stages of flux decline: the first stage with constant amplitude
881 (caused by sudden concentration polarization) and the second stage with reducing
882 amplitude (caused by gradual membrane fouling). UTDR was found to be more
883 sensitive than flux measurement when hydrodynamic exit effect was investigated
884 among different fouling locations. A good correlation between flux decline and UTDR
885 responses of membrane surface was also confirmed by Sanderson *et al.* who applied
886 UTDR to study the fouling growth and cleaning process of a filtration system
887 (Sanderson et al. 2002). Based on the successful attempt, Mairal *et al.* made a
888 progressive research to differentiate sequential two-mode growth mechanisms of
889 calcium sulfate during long-term fouling under two different crossflow velocities
890 (Mairal et al. 2000). The application of UTDR on colloidal deposition was investigated
891 in 2007. Chong *et al.* compared the UTDR response with a salt tracer technique which
892 was developed to characterize both concentration polarization and cake layer resistance
893 in RO process and succeeded in characterizing concentration polarisation factor and

cake layer separately (Chong et al. 2007). Sim *et al.* used UTDR to study the effect of crossflow velocity, flux, salinity concentrations on colloidal metastability in real time. The abnormal flux drifts or TMP jumps were found to be caused by the metastability of silica which was evidenced by observing the recovery of signal amplitude when feed solution without foulants was flushed into the system (Sim et al. 2012). The fouling layer thickness obtained from UTDR measurement was comparable to the measurement obtained from scanning electron microscope analysis (SEM) on fouled membrane (Sim et al. 2012). In the investigation of the effect of hydraulic and feed solution parameters on silica metastability, it was observed that low crossflow velocity, higher flux, increased salinity and high colloidal silica concentration in the feed could decrease the time required for the transition from metastable phase into more immobile gel-like phase. The result obtained through responsive UTDR signals can be used to propose the operating strategies that delay the occurrence of gel-like cake-layer which is hard to be removed by conventional cleaning process (Sim et al. 2014).

2.4 Modeling approaches in membrane fouling process

2.4.1 General introduction

There are numerous of studies related to membrane fouling process in hydraulic pressure-driven membrane processes, while the related works on osmotically-pressure driven membrane processes are quite limited in research field. Based on results obtained from searching ‘*Modelling*’ and ‘*membrane fouling*’ and ‘*microfiltration*’/ ‘*nanofiltration*’/ ‘*ultrafiltration*’/ ‘*reverse osmosis*’ as key words compared to the results obtained from searching ‘*Modelling*’ and ‘*membrane fouling*’ and ‘*forward osmosis*’/ ‘*pressure retarded osmosis*’ in Scopus Database, the trend of number of papers published in recent 10 years is presented in Fig. 2.5. It is noticeable that only 7 publication focus on model development of membrane fouling in osmotically-driven membrane processes. Despite limited numbers of research in ODPs, it is undeniable that most of the work which has been done on hydraulic-driven membrane processes can be applied to model development in ODPs.

Fig. 2.5 The comparison of number of papers focusing on modeling hydraulic-pressure driven membrane process and on osmotically-driven membrane process

2.4.2 Mass-transfer equation-based models

The classic mathematical models which model the membrane and its adjacent boundary layers are presented in Section 2.1 Eqn. (2.1) to Eqn. (2.5). The advantage of this type of model is its simplicity. Since there are no particle trajectories are involved in modelling process, the key parameters such as specific fouling resistance and cake layer structure parameters are obtained through curve fitting using experimental data. The disadvantages of this model include: (1) assumptions made on properties of fouling layer may not be true as the properties of the fouling layer may vary under different hydraulic dynamic conditions, feed components and filtration time. (2) it is difficult to model membrane fouling in dynamic manner without considering particle deposition propensity.

As reviewed by She *et al.*, the general form of water flux equation in ODMPs fouling process are derived as (She et al. 2016):

$$J_{w,f} = \frac{(\pi_d - \pi_f) - F_{cep,f} \left(\pi_f + \frac{J_{s,f}}{J_{w,f}} \beta R_g T \right) - F_{dcp,f} \left(\pi_d + \frac{J_{s,f}}{J_{w,f}} \beta R_g T \right)}{\mu(R_m + R_f)} \quad (\text{AL-FS mode})$$

$$J_{w,f} = \frac{(\pi_d - \pi_f) - F_{ccp,f} \left(\pi_f + \frac{J_{s,f}}{J_{w,f}} \beta R g T \right) - F_{dec,f} \left(\pi_d + \frac{J_{s,f}}{J_{w,f}} \beta R g T \right)}{\mu (R_m + R_f)} \quad (\text{AL-DS mode})$$

(2.26)

where $F_{ccp,f}$, $F_{dec,f}$, $F_{ccp,f}$, $F_{dcp,f}$ indicate external concentrative concentration polarisation, external dilutive concentration polarization, total concentrative concentration polarisation, total dilutive concentration polarisation of fouled membrane respectively. R_f indicates hydraulic resistance of the cake layer and pore-blocking (in AL-DS mode). In this model, fouling-induced resistance and concentration polarization, in ODPMs are considered in model. Furthermore, She *et al.* summarized four phenomena which should be considered in ODPMs model development:

(1) Hydraulic resistance due to fouling: Similar to hydraulic-pressure driven osmotic process, formation of cake layer or pore-blocking results in higher resistance even at same bulk concentration difference. This phenomenon is model are presented by term R_f .

(2) Fouling-induced concentration polarisation: Accumulation of cake layer or blocking pore lead to prolongment of path, which may hinder solute to back diffuse to the bulk. Furthermore, pore-blocking process accelerates the internal concentration polarisation and form an unhindered layer, which cannot be mitigated through alternating hydro-dynamic conditions. In the model, these terms are represented through $F_{ccp,f}$, $F_{dec,f}$, $F_{ccp,f}$, $F_{dcp,f}$.

(3) Dynamic membrane rejection: As fouling proceeds, both water flux and solute flux would be affected. Thus, the apparent membrane permeability, which is presented through the ratio of solute flux to water flux would change over time. Sometimes, the pore-blocking would mitigate fouling propensity through reducing solute flux from draw side into feed bulk. In the model, this term was presented through $\frac{J_{s,f}}{J_{w,f}}$.

(4) ICP-self compensation effects: This phenomenon is unique in ODPMs and widely discussed in several recent literatures (She et al. 2016; Tow et al. 2016; Siddiqui et al. 2018). It is widely observed that the water flux under AL-FS mode are more stable than counterpart in AL-DS mode, which is attributed by ICP-

compensation effect (Tang et al. 2010). In this model, this term was presented by $F_{cecp,f}$, $F_{dec,p,f}$, $F_{ccp,f}$, $F_{dcp,f}$, in which water flux are placed in the exponential term. Besides membrane fouling, other attempts including increasing feed concentration or reducing draw concentration could also induce ICP-compensation effect (She et al. 2013).

Due to the difference between hydraulic-pressure driven membrane process and osmotically-driven membrane process, mass transfer models are applied to make quantifiable comparison between them. Tow *et al.* compared effects of foulants accumulation on reverse osmosis and forward osmosis with respect to membrane types, driving forces and feed solution (Tow et al. 2016). Based on mass-transfer governing equations in multiples layers, two variables consisting of cake structural parameter and hydraulic diameter. The results indicated that FO exhibits more foulants accumulation due to much more stable water flux than its counterpart in RO, and it is characterized by more rapid enhancement of cake structural parameter as fouling proceeds. The cake structural parameter trend is found to be independent on both ionic strength and hydraulic pressures. The same group further explored the effects of fouling on FO and PRO based on the mass-transfer model (Nagy et al. 2018). The foulants accumulation rate was evaluated as function of feed concentration, cross-flow velocity and membrane orientation. Under AL-DS mode, the foulants accumulation rate is found to decrease with enhancement of feed salinity and cross-flow velocity. Despite validation based on fouling experiment, the whole model assumes that mass transfer inside of support layer is constant even at AL-DS mode. This assumption might not be always true especially when the foulants tend to clog in the membrane pores and consequently lead to severe pore-blocking enhanced internal concentration polarisation. The study from Siddiqui *et al.* who compared FO fouling and RO fouling through experiments and mass-transfer models also pointed out the FO indeed has higher fouling propensity than RO process does (Siddiqui et al. 2018). Moreover, the study cast doubt on the positive effect of hydraulic pressure on fouling layer compaction, which was in agreement with the conclusion drawn by (Tow et al. 2016). The model they used was based on mass-transfer equations on multiple layers. The main method they used to decrease the dimensionality of unknown variables was by extracting fouling-induced cake layer resistance under multiple assumed scenarios, where the cake layer structural

parameter was developed from (Tow et al. 2016) was applied and assumed to be multiple values. As a result, in comprehensive assumptive scenarios FO is found to have more fouling propensity than RO. Nevertheless, the mass-transfer model proposed by these two studies cannot be used to dynamically model forward osmosis due to lack on consideration on microscopic particle deposition factor, the factor used to quantify mass deposition as function of time. Park *et al.* used a controlled volume method to simplify the boundary layer adjacent to membrane under colloidal fouling. Rather than considering the sophisticated interactions between multiple forces including Van der Waals forces, electrostatic double layer forces and Brownian forces, they just lumped them into a simple parameter called particle deposition factor. The particle deposition factor was used to specify the percentage that particle depositing on membrane out of the total particle brought through cross flow during crossflow filtration. The results showed good agreement between the model and experimental data, while the way they obtained particle deposition factor is not mentioned in paper (Park et al. 2013). In a more recent work by Liu and co-workers, a novel collision-attachment approach for modelling dynamics of colloidal fouling was proposed. The model considered the colloidal fouling in two steps: the colloidal particles would first collide with a membrane surface and attached on the membrane surface if the energy barrier between colloidal and surface can be overcome. The model shows excellent agreement with the flux and foulant mass deposition data and pointed out that the water flux and energy barrier is the governing factor colloidal fouling. (Liu et al. 2018).

2.4.3 Machine-learning algorithm-based models

With the development of computational capacity and reduction of computational cost, the availability of numerous data drives the application of artificial intelligence in field of membrane processes. In research focusing on membrane fouling, multiple algorithm including fuzzy-logic model (Altunkaynak et al. 2010), particle swarm optimization (Fan et al. 2018), neural networks (Roehl et al. 2018; Cabrera et al. 2017; Veerapaneni et al. 2010), genetic algorithms (Zhang et al. 2019) haven been utilized. Instead of exploring the sophisticated fouling mechanisms, the main purpose of machine learning algorithm-based model is to trigger automatic response with small or little delay. This self-adaptive characteristic decreases the demands of manual control and provides a bridge between real-time monitoring and smart controlling system. Furthermore,

without exploring the complicated relationship between foulants in membrane fouling process, high prediction accuracy can be still achieved with optimized algorithm structures and integration of multiple algorithms together. Based on these advantages, application of machine learning in membrane fouling prediction and subsequent process control are blooming in areas such as modelling contaminant removal, cost optimization and generation of optimal conditions in membrane fouling process (Fan et al. 2018).

As reviewed by a recent paper from Majid *et al.*, the detailed classification of application of machine-learning based models in membrane fouling control can be presented as Fig 2.6 (Bagheri et al. 2019).

Fig. 2.6 The classification of machine learning algorithm used in simulation of membrane fouling (Bagheri et al. 2019)

2.4.3.1 Artificial Neural Networks (ANNs)

Machine Learning techniques, such as artificial neural networks (ANN), have been increasingly used to model membrane fouling and performance. The advantage of ANN over traditional knowledge-based model is its capability of handling non-linear multivariate problem and when the internal coupling mechanisms are not fully understood. Through training sets of data with several experimentally accessible parameters, such as run time, feed flow rate, pressure, temperature, feed components, pH and turbidity, supervised learning has been proved as a potential tool in lab-scale predicting water flux decline (Teodosiu et al. 2000), total hydraulic resistance (Dornier et al. 1995), chemical oxygen demand (Giwa et al. 2016) and feed pressure (Cabrera et al. 2017) in membrane processes. With respect to optimizing network structure, Chen compared the prediction performance of the back-propagation neural network (BPNN) and radial basis function neural networks (RBFN) in predictability of water flux challenged by colloidal suspension (Cheng et al. 2008). Despite the superiority of RBFN found over BPNN in their study, Sahoo and Ray pointed out the advantages of two methods are incomparable unless the structures of each layer are optimized (Sahoo et al. 2006). Cheng proposed an overlapped type neural network to construct layers through considering the data distribution of flux decline (Cheng et al. 2008). Sahoo *et al.* integrated genetic algorithm with neural networks for providing optimized parameters of network before any data was input and trained inside of system (Sahoo et al. 2006). The success achieved in lab scale investigation has initiated the attempts to integrate the learning algorithm to a full-scale membrane system (Shetty et al. 2003; Veerapaneni et al. 2010; Peleato et al. 2017). In a recently published study, artificial networks were developed to quantify membrane fouling in a three-stage RO system and to identify the main predictive water quality parameters through training six-year of process data (Roehl et al. 2018). Neural networks can be constructed in multiple ways, forward propagation and back-propagation neural networks (BPNN) were widely used due to their well-defined and explicit equations for weights correction (Cheng et al. 2008). The detailed and deep discussion of BPNN can be found (Monica et al. 1998), here basic of

neural networks with one hidden layer was outlined. The process of obtaining weights matrix in each layer consist of two processes: forward propagation and back propagation.

The basic forward propagation process in neural network was illustrated as follows. The first layer is input layer, which feeds the neural networks with data after normalization. The main purpose of normalising the data is to prevent the input with large values from dominating the training (Sahoo et al. 2006; Maier et al. 2000). The normalized data then acts as the inputs and the final layer is assigned as final outputs. Between input layer and output layer are hidden layer with number of neurons with pre-determined or stochastically optimized number. One hidden layer was used here for illustration, while sometimes more than one is applied if necessary. Forward propagation processes the incoming inputs through outputs in current layer, which are then fed into subsequent layer as inputs until the last layer is reached. The transformation was made through weights matrix connecting neurons in either two successive layers (shown as $\Theta^{(l)}$ and $\Theta^{(2)}$ in Fig.4.). In hidden layer, the activation function connecting output of last layer and input of next layer are often subject to optimization. Consequently, the process of whole forward propagation is as follows:

From inputs to hidden layer:

$$\vec{a}^{(2)} = \vec{x} \Theta^{(1)T} \quad (2.27)$$

$$\vec{z}^{(2)} = g(\vec{a}^{(2)}) \quad (2.28)$$

From hidden layer to output layer:

$$h_{\theta(\vec{x})} = \vec{z}^{(2)} \Theta^{(2)T} \quad (2.29)$$

where $g(x)$ is sigmoid function and defined as

$$g(x) = \frac{1}{1 + \exp(-x)} \quad (2.30)$$

At end of forward-propagation, the performance of prediction was evaluated based on the cost function formulated as

$$J_{(\theta)} = \frac{1}{m} \sum_{i=1}^m (h_{\theta(\frac{\vec{x}}{x^{(i)}})} - y^{(i)})^2 + \frac{\lambda}{2m} (\sum_{j=1}^h \sum_{k=1}^{n+1} \theta_{j,k}^{(1)2} + \sum_{j=1}^l \sum_{k=1}^{h+1} \theta_{j,k}^{(2)2}) \quad (2.31)$$

The first term of function above is the square of errors between predicted results and actual data based on current weights matrixes, the second term is the regularization term, which is designed to prevent the algorithm from overfitting problem (Ornato et al. 2001). m is the number of total n -dimensional data used in this study, n is the number of dimension of data, h is the number of neurons in hidden layer, l is the dimension of output (for a single value output, $l=1$). λ is the coefficient in regularization term.

In back-propagation (BP) process, the error between output and actual y is utilized to correct weight matrix and update all weights simultaneously. Multiple BP training algorithms are available including Levenberg-Marquardt, steepest-descent and gradient-descent algorithms, and gradient-descent was selected in this study. The whole weights were updated simultaneously after each iteration, and the iterations are repeated until either the smallest partial derivatives of cost function to each weight or maximum iteration number was reached. The gradient descent method was based on correction of errors of predicted values in each layer:

$$\delta^{(l)} = h_{\theta(\vec{x})} - \vec{Y} \quad \text{for layer } l \text{ as output layer}$$

$$\delta_{j,k}^{(l)} = \delta_j^{(l+1)} \theta_k^{(l)} \frac{\partial g}{\partial z_{j,k}^{(l)}} \quad \text{for layer } l \text{ as hidden layer}$$

(2.32)

The error was utilized to minimize the partial derivative of cost function to every weight in every layer:

$$\Delta^{(l)} = \Delta^{(l)} + \delta^{(l+1)T} a^{(l)}$$

$$\frac{\partial J}{\partial \theta_{j,k}^{(l)}} = \frac{1}{m} \Delta_{j,k}^{(l)} \quad \text{for } k=1$$

$$\frac{\partial J}{\partial \theta_{j,k}^{(l)}} = \frac{1}{m} \Delta_{j,k}^{(l)} + \frac{\lambda}{m} \theta_{j,k}^{(l)} \quad \text{for } k \neq 1$$

(2.33)

The number of cross validation data and that of test data were dependent on the data size and study purpose. The effects of number of neurons in hidden layer and selection

of input dimension on prediction performance are also hyperparameters which should be considered in structure optimization.

2.4.3.2 Genetic programming (GP)

Genetic programming (GP) is evolutionary rule-based algorithm by which candidate programs in pool are selected generation by generation through selecting the most fit candidates at each generation, producing offspring and triggering stochastic mutation till the selection standard or maximum number of generation was reached (Grosman et al. 2002; Muttill et al. 2005). Rather than generating a random candidate, GP starts with generating a set of candidates and refined them in stepwise manner based on the pre-defined fitness function. The main advantages of GP, compared to normally gradient-based algorithm such as ANNs, is the unnecessary that the function should be differentiable everywhere. Moreover, traditional optimization method sometimes is manipulated by random selection of initial value, which results in the dilemma of local optimum. By contrast, the random generation of a set of candidates in GP normally decrease the possibility of local optimum through considering a wider range of results. Similar to genetic programming, genetic algorithm (GA) also produces results through comparing the fitness of candidates and eliminating unfit one generation-by-generation. The main difference between them is their algorithm presentations: GP is often presented as a nest of data structure; while GA is often presented as a list of actions or values (Bagheri et al. 2019).

In the field of modelling membrane process, GP was applied in numerous studies, especially when the links between the input parameters were so complicated that the numerical expression between them cannot be fully understood. Cho *et al.* applied GP to simulate scaling formation and subsequent resistance growth in RO process (Cho et al. 2010). The resultant model that linked resistance growth with input parameters such as time, feed concentration, humid acid concentration, applied pressure, was able to give high accuracy of prediction. Based on the final GP model humic acid concentration, feed concentration and applied pressure were the most important parameters that determine scale formation on membrane. Lee *et al.* used GP to explore the relationship between membrane fouling rate on microfiltration and several operating parameters

(crossflow flowrate, filtration time) as well as feed water quality (turbidity, temperature, algae pH) (Lee et al. 2009). The generated GP model can achieve prediction accuracy as high as 92% through experimental validation. GP also applied by Shokrkar *et al.* to reach a mathematical expression of membrane flux during microfiltration process for oil wastewater (Shokrkar et al. 2012). The model which used input parameters including filtration time, oil concentration, temperature, transmembrane pressure, crossflow rate showed excellent agreement with experimental data. The overall residual error between experimental data and modeling results was as low as 5%. Compared to traditional mass transfer equation-based model, the GP also proved to have higher applicability. Furthermore, GP modeling does not require underlying description of the physical process. Fouladitajar *et al.* compared the power of GP and traditional pore-blocking model in modeling pore-blocking process in microfiltration of oil-in-water emulsions (Fouladitajar et al. 2013). It was observed that individual pore-blocking models and five combined blocking models were unable to fit for all cases in dataset, while GP was proved to have better fit of experimental data in dataset. Despite high prediction accuracy, GP was also weakened by its poor interpretability since the resultant expression are produced through revolution of random combination of operators and parameters. In this regard, the determinist model, either continuous or discrete, is indispensable in shedding light on basic fouling mechanism.

2.5 Research gap and novelty of this study

The previous studies have made great breakthroughs in exploration of membrane fouling-related studies in forward osmosis, while there are some research gaps which deserve further investigation. As a brief summary of this literature review, the current status of research on forward osmosis and membrane fouling in forward osmosis are presented as follows:

- The fouling behaviors caused by various types of fouling (colloidal fouling, organic fouling, bio-fouling, combined fouling) are widely investigated in lab-scale. Moreover, the influence of multiple operating conditions including foulants concentration, feed components, draw components, membrane orientations are studied through using different model foulants in lab scale (Cath et al. 2006; Ibrar et al. 2019; Im et al. 2020; Kim et al. 2014; Mazlan et al. 2016;

1196 Mi et al. 2008; Nagy et al. 2018; Nawaz et al. 2013; Parida et al. 2013; Xie et al.
 1197 2013; Xie et al. 2014; Yoon et al. 2013; Zhang et al. 2012);

- 1198 • Also, several important phenomena including back solute diffusion, co-existing
 1199 cations, membrane orientation are well investigated from the perspectives of
 1200 how they are inter-connected with foulant-foulant interactions and foulant-
 1201 membrane interaction (Arkhangelsky et al. 2016; She et al. 2012; Siddiqui et al.
 1202 2018);
- 1203 • Moreover, several studies focus on difference between hydraulic pressure driven
 1204 membrane processes and osmotic pressure driven process in regard to fouling
 1205 propensity and fouling mitigation strategies (Tow et al. 2016; Lee et al. 2010).
 1206 Some studies suggest it's easier to remove cake layer in forward osmosis
 1207 compared to the one in reverse osmosis due to non-existence of cake layer
 1208 compaction effect in environment which is free of hydraulic pressure. There are
 1209 some studies pointed out forward osmosis actually has higher fouling propensity
 1210 compared to reverse osmosis because there is ICP-compensation effect which
 1211 makes flux decline less significant in forward osmosis (Siddiqui et al. 2018).
- 1212 • In the field of membrane fouling characterization in forward osmosis, off-line
 1213 characterization methods like membrane autopsy are still in the mainstream. The
 1214 development of real-time characterization methods, even in lab scale, is still
 1215 limited. In the paper published, to our best of knowledge, the attempt made on
 1216 real-time fouling characterization in forward osmosis are Still DOTM and OCT.
 1217 In the field of membrane fouling growth modelling in forward osmosis, the study
 1218 method which has been tried and published is still limited in traditional
 1219 determinist mass transfer model (Park et al. 2013). Also, the experimental
 1220 condition is selected as AL-FS side, in which both external fouling and external
 1221 fouling-enhanced concentration polarisation is involved. Correspondingly, the
 1222 particle deposition factor is assumed as a constant throughout a long fouling
 1223 period. In this regard, transference of the modelling study from AL-FS mode to
 1224 AL-DS mode has still not been investigated yet, in which both external and
 1225 internal fouling, cake-layer enhanced concentration polarisation and pore-
 1226 logging enhanced concentration polarisation are involved together.

1227 The purpose of this study is to detect the fouling process in forward osmosis process
 1228 through either real-time membrane characterization or multiple modelling approaches.

From the perspective of real-time characterization, most of current works are focused on hydraulic-pressure driven membrane processes like RO (Ho et al. 2016; Ho et al. 2017; Sim et al. 2013; Sim et al. 2012; Sim et al. 2014). However, there are certain difference of operating conditions and fouling behaviours between RO and FO processes (She et al. 2016; Siddiqui et al. 2018). Such differences includes operating conditions, effect of back solute diffusion and the implication of internal concentration polarization. Furthermore, the application of UTDR has always been focused on external fouling by placing transducer on the top of fouling layer (An et al. 2011; An et al. 2011; Sim et al. 2012; Sim et al. 2014). Characterization of internal fouling is often neglected. To further address the characterization of fouling behavior in forward osmosis, in this study the transducer was placed on the bottom of membrane to enable a simultaneous characterization of internal fouling through analysis on signal in both time domain and frequency domain. This study further extends the application of UTDR from hydraulic-pressure driven process to osmotic-pressure driven process, from characterization of external fouling alone to characterization of both external fouling and internal fouling. From perspective of membrane modelling, there is limited study adopting machine learning techniques in FO membrane process. Most of the studies so far have focused on flux performance without further exploration on how the trained model can be used to explain contributions of different operating parameters (Suh et al. 2011; Lim et al. 2019; Zhang et al. 2020) such as cake layer resistance, degree of concentration polarization and feed components. This study at the first time addresses how BPNNs can be applied to train and predict experimentally non-accessible parameters in forward osmosis.

CHAPTER 3. Materials and Methods

3.1 Experimental setup

3.1.1 Cross-flow forward osmosis setup

Fig. 3.1 Schematic diagram of a crossflow forward osmosis setup

The crossflow FO apparatus was presented in Fig.3.1. Two parallel units of FO cells were used in this study. The two FO cells have the same active membrane area of 0.0034 m² (dimension 85 mm x 40 mm). The channel height for the feed and draw side were 3 mm. Variable speed gear pumps (Micropump, INC., model GJ-N23.PF1S.A) were used to pump the feed and draw solution counter-currently to the FO cell. The temperature of system was kept at 25±0.5 °C by a chiller (Polyscience). To maintain constant weight/mass, DI water was added through a digital pump. The flux was measured through weight change of dosing DI water.

The water flux J_w during period of T :

$$J_{w(T)} = \frac{(W_{DI(t_0)} - W_{DI(t_1)})}{\rho_w A_m T} \quad (3.1)$$

where $W_{DI(t_0)}$, $W_{DI(t_1)}$ represent the weight of DI water at the beginning of observation ($t=t_0$) and at the end of observation ($t=t_1$), T equals to $t_1 - t_0$ (s), ρ_w is the density of pure water ($\rho_w=1000\text{kg/m}^3$) and A_m is the effective membrane area (m^2).

The change in concentration of feed solution as a function of time was used to calculate the solute back diffusion flux:

$$J_{s(T)} = \frac{(C_{f(t_1)} - C_{f(t_0)})V}{A_m T} \quad (3.2)$$

where $C_{f(t_0)}$, $C_{f(t_1)}$ represent the concentration of feed side at the beginning of observation ($t=t_0$) and at the end of observation ($t=t_1$) respectively. V is the volume of feed solution (m^3), which was maintained at constant level.

3.1.2 Dead-end forward osmosis setup

Fig. 3.2 The dead-up setup with UTDR system used in this thesis

As shown in Fig. 3.2, a cylindrical filtration cell made of acrylic with effective membrane area of 0.00196 m^2 . The filtration cell has top and bottom compartments separated by the FO membrane: the draw solution side (bottom) has a flow channel with a height of $0.7\text{-}0.8 \text{ mm}$, fitted with a commercial diamond-patterned spacer ($h_{sp} = 0.71 \text{ mm}$, $\varepsilon_{sp} = 0.858$, $\theta = 90^\circ$) and was operated in crossflow mode; the feed side (top) has a volume capacity of 150 mL and was operated in dead-end mode. The rationale of operating at dead-end mode on the feed side was that the amount of particles depositing

onto the membrane could be easily estimated by the mass-balance method. This provided an independent measurement to cross-check the data obtained from UTDR, i.e., cake-layer thickness. A digital gear pump (Micropump, INC., model GJ-N23.PF1S.A) was used to recirculate the draw solution, which was prepared from sodium chloride (EMSURE, ACS grade), at 250 mL/min between the draw solution tank and filtration cell.

3.2 Membranes

3.2.1 CTA membranes

The FO membrane used in this thesis was a commercial cellulose triacetate (CTA) FO membrane purchased from HTI (HTI, Albany, OR). The SEM images of the support-layer surface, active-layer surface and cross-section of the CTA FO membrane are shown in Fig.3.3. The CTA FO membrane has tube-like woven meshes with a diameter of 40~50 μm near the surface of the support-layer, which is relatively homogeneous throughout the membrane thickness. On the support-layer surface, as shown in Fig. 3.3b, the pores having diameters ranging from 20 to 50 nm are distributed randomly with some being connected to form a bifurcated structure. A smooth texture is observed on the active-layer surface (Fig. 3.3c). The distance between the lowest point (Fig. 3.3d) of the mesh and the active layer is 10~20 μm , which results in the membrane thickness ranging from 40 μm to 80 μm . The clean membrane and the fouled membrane were observed by field-emission scanning electron microscopy (JEOL, JSM-7200F) and energy-dispersive X-ray spectroscopy (Oxford, X-Max 80).

Fig. 3.3 SEM images of the CTA FO membrane used in this study. (a,b) support-layer surface; (c) active-layer surface; and (d) cross-section.

3.2.2 TFC membranes

Fig. 3.4 SEM images of the TFC FO membrane used in this study. (a,b) support-layer surface; (c) active-layer surface; and (d) cross-section.

The TFC membrane used in this thesis is cut from FO4040 spiral wound element from Toray Korea. As shown in Fig 3.4, the woven mesh is less obvious on the support layer surface of a TFC membrane, and small pores with diameter ranging from 20 to 40 nm are observable. The active layer surface of TFC membrane is rougher than CTA membrane, and no discernible pores can be observed, as shown in Fig. 3.4a. Furthermore, the walls of pores are connected with each other to form highly porous and connecting spatial structure, which is more obvious in the cross-section view (as shown in Fig. 3.4d). Compared to CTA cross-section image, the TFC membrane exhibits less homogeneity throughout the support layer. The support layer surface (Fig. 3.4d) consists of a layer of finger-like pores with 10 μm in length and diameter of ~5 μm. These relatively straight pores start to expand into larger pores and become increasingly connected, which consist of porous structure with diameter of ~80 μm at the middle section of support layer. The layer near active skin layer is composed of small finger-like pores with diameter ~10 μm. The tube-like woven meshes with diameter of 40-80 μm can be seen at the center of TFC membrane. The thickness of TFC membrane is ~120 μm, which is not affected by the location of mesh.

3.3 Chemicals

The feed solution and draw solution are synthesised using NaCl (Merch, USA) with analytical grade.

Two types of silica colloids are used as model foulants: The smaller silica colloids stock solution was synthesized through diluting colloidal silica 34% solution (Sigma Aldrich, LUDOX® SM-30, specific surface area of 320-440 m²/g, diameter = 7 nm). The larger silica colloids stock solution was synthesized through dispersing silica microspheres with 0.3 µm diameter (ITS science& medical PTE. LTD) into deionized water and placing the stock solution into ultrasonic bath to disperse particles into mono-dispersed system.

3.4 Characterization methods

3.4.1 Ultrasonic Time Domain Reflectometry (UTDR) and signal analysis

An innovative feature of this study is fixing an ultrasonic transducer on the bottom plate of the filtration cell to detect the pore-blocking process within the support-layer of the FO membrane, which was closed to the transducer for reducing the signal attenuation. A transducer with a peak frequency of 10 MHz (Olympus, model V611-RB) was held tightly to the bottom plate by a holder; silicon oil (Olympus, couplant C) was used as the coupling agent between the filtration cell and transducer. The UTDR system consists of a pulsar-receiver (GE Panametrics, model 5800) and an oscilloscope (Tektronix, model MDO3034). The sampling rate of the oscilloscope was set at 1 point/4 ns, and 10000 points in total were recorded in the time-domain. The oscilloscope was connected to a computer for real-time data logging using the WaterMon Version 1.3.4.0 software. The interval between two consecutive signal recordings was set at 5 min.

The raw UTDR signal obtained via the real-time data-logging system was obtained in the time-domain. The analysis of the arrival-time shifts and amplitude changes of the principal peaks that associated with the draw solution/membrane/feed solution interfaces were performed using the '*locatepeaks*' function in MATLAB. To increase the sensitivity or signal response, the data in the time-domain were transferred into the time-frequency-domain using the Short-Time-Fourier-Transform (STFT) technique. The equation governing this transformation is given by the following:

$$\mathbf{STFT}\{x[n]\}(m, \omega) \equiv X(m, \omega) = \sum_{n=-\infty}^{\infty} x[n]w[n-m]e^{-j\omega m} \quad (3.3)$$

where STFT $\{x[n]\}$ presents the STFT transformation of n discrete data in the time-domain, m stands for each time point at which the Fourier transform is conducted, ω is the frequency component ranging from 0 to $\pi/\text{sampling rate}$, $w[n-m]$ stands for a sliding window centered at $n = m$. Through STFT, the window gives different weights to N data in the time-domain as it slides from $t = 0$ to $t = N$. Fourier transformation is performed on every set of N data weighted by window centring at $t = m$ resulting in $N/2$ normalised magnitude frequency components at every arrival-time point. Finally, an $N/2$ by N matrix is obtained in the form of the normalised magnitude in the time-frequency-domain.

3.4.2 Inductively coupled plasma optical emission spectrometry (ICP-OES)

In the study, the in-situ monitoring method was validated through measuring silica accumulation on the surface of membrane. The silica concentration measurement was conducted using Inductively coupled plasma optical emission spectrometry (ICP-OES, optima 8000, Perkin Elmer, USA).

3.4.3 Field Emission Scanning Electron Microscope (FE-SEM)

The surface and cross-section of either clean or fouled membrane was identified through Field Emission Scanning Electron Microscope (FE-SEM, Jeol JSM-7600F) at acceleration voltage of 5kv. Before measurement, the membranes are totally dried in freeze drier. The images are captured at more than 3 positions to ensure repeatability.

3.5 Programming languages

In Chapter 4, UTDR signal are analysed by a code developed in-house using the *Signal Processing Toolbox*TM available in MATLAB. More specifically, the process of locating specific peaks in time domain is accomplished by '*locatepeaks*' function, which returns the array containing the information of arrival time of the peaks with amplitude higher than the pre-defined threshold. The results are further used in time domain analysis. In the section of Short-Time Fourier Transform, the process is achieved by a code developed in-house using the *Signal Processing Toolbox*TM. The main function used is

1406 'Spectrogram' function, which is able to return a 2-dimensional magnitude matrix in
1407 both time and frequency domain after providing defined inputs including time domain
1408 data, type of sliding window, number of points included in the window and number of
1409 points in overlap. In this algorithm a Gaussian window with a length consisting of 512
1410 points was applied after pre-testing. The more detailed analysis is shown in Chapter
1411 4.2.2.

1412
1413 In Chapter 5, the modelling algorithm was programmed in *Visual Basic of Application*
1414 (*VBA*) environment, and iterative process as well as regression analysis are
1415 accomplished by *Microsoft. Solver* with evolutionary method. The training of neural
1416 networks and calculation of gradient-based interpretable indices are accomplished by
1417 code developed mainly using *TensorFlow* open source platform based on *Python*. In the
1418 section of extracting particle deposition factor, the classical mass transfer models are
1419 applied to calculate the theoretical flux in which cake layer resistance, cake layer-
1420 enhanced concentration polarisation factors, pore-clogging resistance, pore-clogging
1421 enhanced concentration polarisation are calculated based on an initial input of particle
1422 deposition factor. Then, the evolutionary method is applied to minimize difference
1423 between theoretical flux and experimental flux and to repeat this process recursively.
1424 After this process, the result of particle deposition factors is obtained in time series of
1425 fouling period. The evolutionary optimization method is determined after trying three
1426 available optimization methods in *Microsoft. Solver*, and this method is of ability to find
1427 local minimum when target function is highly non-linear. The more detailed will be
1428 presented in Chapter 5.2.4.1. In the section of optimization of BPNNs, the particle
1429 deposition factor in time series is combined with multiple experimental condition
1430 parameters in certain time point, which are fed into an in-house developed optimization
1431 framework built on *TensorFlow*. Through this framework, key hyper-parameters
1432 involved in this BPNNs can be optimized after providing a list of parameter candidates.
1433 The detailed information is provided in Chapter 5.2.4.2.

1434
1435 In Chapter 6, all models as well as object-oriented programming are all coded based on
1436 *Python*. The packages used in code development include *sklearn*, *numpy*, *scipy*, *math*,
1437 *matplotlib* et al. The class called 'particle' is defined with instance properties for each

1438 particle including positional information (x,y) , velocity information (V_x, V_y) ,
1439 acceleration information (a_x, a_y) , particle mass (m) , radius (r) and unique particle id.
1440 Then a list containing all information of all particles was created as class variable, to
1441 which any new particle will be added. The move of particles is dependent on
1442 combination of multiple types of driving forces from other particles in a very short time
1443 step and visualized through package *pyplot* module in *matplotlib* package. The
1444 decomposition of different types of forces and how they drive particle movement are
1445 illustrated in details in chapter 6.2.1 and 6.2.2.

1446

CHAPTER 4. Characterization of fouling in forward osmosis via Ultrasonic Time and Frequency Domain Reflectometry

4.1 Introduction

The pressure-driven reverse osmosis (RO) process has been widely applied in the water reclamation and desalination industries to produce potable water. However, RO requires high external pressure (i.e., energy) to overcome the osmotic pressure of the feed water, which has raised concern on the sustainability of the technology (Wang et al. 2009). In addition, several studies have pointed out that the application of high external pressure compresses the fouling layer on the membrane surface, which significantly impacts the membrane performance and fouling-mitigation (Tang et al. 2010; She et al. 2016). As an emerging alternative to RO technology, the non-pressure-driven forward osmosis (FO) process has been drawing wide attention in wastewater reclamation (Cath et al. 2010), desalination (McGinnis et al. 2007), osmotic membrane bioreactors (Lay et al. 2012), activated sludge dewatering (Cornelissen et al. 2008), as well as in pharmaceutical (Santus et al. 1995) and many other industrial applications. By definition, FO process is based on a spontaneous process in which the solvent (i.e., water) permeates through a semi-permeable membrane from the low-solute-concentration side (i.e., feed solution) to the high-solute-concentration side (i.e., draw solution), which is driven by an osmotic pressure difference (She et al. 2016). It only requires a small pressure-energy consumption (i.e., for the crossflow of the feed and draw solutions) and has great flexibility for integrating with other processes to recover the solvent (i.e., water) or draw solute (note the recovery process requires energy input). However, membrane fouling in FO remains a major challenge, which results in a performance loss that includes water flux decline, change of membrane properties and membrane replacement (She et al. 2016; Mazlan et al. 2016; Parida et al. 2013).

Compared to the RO process, membrane fouling in FO exhibits some unique traits, which makes early detection in real-time important but challenging. The water flux, the most frequently used fouling indicator in a pressure-driven process, was not adequate to tell the condition of a membrane in FO process. Flux decline can be influenced by several factors apart from membrane fouling such as changing operating parameters (e.g., temperature, concentrations, recovery, etc.), membrane orientation (i.e., active-layer facing the draw solution (AL-DS) and active-layer facing the feed solution (AL-FS)), internal concentration

polarization (ICP) (i.e., concentrative ICP and dilutive ICP), reversed solute diffusion (RSD), feed-concentration effect, and draw-dilution effect (McCutcheon et al. 2006). Thus, unlike the RO process, sustaining membrane performance is more complicated in the FO process since all these factors are interrelated. Moreover, the ‘ICP-compensation effect’, which is manifest by mitigation of concentration polarization when the flux declines, has been reported to be the main reason why the water flux in FO process was observed to be stable in several studies in which membrane fouling occurred (Tang et al. 2010; She et al. 2016). In this regard, a recent study points out that indeed FO has a higher fouling propensity than RO even though less water-flux decline is observed in FO (Siddiqui et al. 2018). The common practice in lab studies is to compare the flux profile against the baseline flux obtained from a ‘foulant-free’ feed solution; however, this is impractical in industrial applications. Moreover, the water flux profile does not provide information on the fouling mechanisms. As in all membrane processes, real-time monitoring of FO fouling is critical for plant operators to act in a timely manner to implement appropriate countermeasures before fouling becomes too serious.

This study is the first to apply a real-time monitoring technique, Ultrasonic Time Domain Reflectometry (UTDR), for fouling detection in the FO process. UTDR is a non-destructive technique to detect the thickness and physical properties of a fouling layer through transmitting the ultrasound waveform, into multiple layers of interest and recording the reflections from different interfaces it encounters (Krantz et al. 2008). The detailed introduction of UTDR system and principle are outlined in Chapter 2 and Chapter 3. The fouling progress can be measured in real-time by monitoring the changes in the amplitude of peak 2 and peak 3. In addition, the thickness of the fouling layer, l_f , can be determined from the difference between the arrival-times of peak 2 and peak 3, t , if the sound velocity in the fouling layer, C , is known:

$$l_f = \frac{t \cdot C}{2} \quad (4.1)$$

The velocity of the sound wave, C , is a property of the medium and increases with increasing medium density, ρ . The magnitude of the reflected and transmitted waves is determined by the difference between the acoustic impedance of the media, $Z_2 - Z_1$, where $Z_i = \rho_i \cdot C_i$; the subscripts 1 and 2 denote the subsequent media through which 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 a function of the acoustic impedance difference between the media and the topography of the interface, and is given by (Krantz and Greenberg 2008):

$$A = \frac{Z_1 - Z_2}{Z_1 + Z_2} \quad (4.2)$$

The UTDR technique has been widely applied in the membrane field for fouling (e.g., particulate, colloidal, inorganic, organic) detection in several hydraulic pressure-driven processes such as microfiltration (Silalahi et al. 2009), ultrafiltration (Li et al. 2006), reverse osmosis (An et al. 2011) and in a variety of modules including flat sheet (Sanderson et al. 2005a), spiral wound (Chai et al. 2007), and hollow fiber (Li et al. 2014). However, several challenges when applying UTDR for fouling detection in FO applications warrant investigation due to the unique characteristics of FO membranes and the FO process:

- a. The amplitude of the reflected signal is proportional to the density difference between two media on either side of the interface of interest (Krantz et al. 2008). The thickness and compactness of the cake-layer in FO is significantly different from that for the cake-layer in RO (Valladares et al. 2014). The cake-layer in FO, which has been shown to be removed by backwashing more easily than the cake-layer in the RO process (Lee et al. 2010), implies a less compacted structure. This presents a new challenge to UTDR since the signal response is proportional to the density of the medium.
- b. The existence of a mesh inside the support-layer of an FO membrane, which is designed to increase the mechanical strength, impacts the membrane overall thickness, particle deposition, and proportion of ultrasonic energy reflected from the interfaces. In contrast to RO, for which the peak corresponding to the thin membrane is easy to identify, the reflected signal from an FO membrane consists of multiple peaks spread over a relatively wide range of response times. For this reason, quantitative analysis needs to be performed to identify the location of the fouling layer and its evolution during the FO fouling process.
- c. The FO process can be operated in the AL-FS mode or the AL-DS mode, for which external fouling and mixed fouling (external and internal) are likely to occur, respectively. External fouling refers to the formation of cake-layer on the active-layer surface or support-layer surface, whereas internal fouling refers to the pore-blocking by particles that are trapped within the support-layer (She et al. 2016). Based on the membrane autopsy data, deposition inside the support-layer was reported as the main reason for the observed enhanced internal concentration polarization (Kim et al. 2016; Wang et al. 2017). The mechanism and severity of internal fouling varied owing to factors that include the hydrodynamic conditions, particle size and foulant-membrane interaction, which were

elucidated by prior membrane autopsy studies (Kim et al. 2016; Mi et al. 2008). The possibility of differentiating between external and internal fouling mechanisms via UTDR signal changes and fouling behaviour in real-time style has not been explored.

To explore the possibility of detecting the early-stage of fouling and to illustrate external and internal fouling in the FO process, this study employed UTDR to investigate the signal changes caused by a model foulant, colloidal silica, in both the AL-FS mode and AL-DS mode. To increase the sensitivity of the signal, the data in the time-domain were transferred to the time-frequency-domain by applying the Short-Time-Fourier-Transform (STFT) technique. The results are presented in both 2-D and 3-D formats. The organization of this paper is the following. The materials and methods are described in Section 2. The peak assignment and signal stability test are discussed in Section 3.1. The water flux indicator is discussed in Section 3.2.1. The features of the UTDR signal in the time-domain for the AL-FS mode and AL-DS mode are presented in Section 3.2.2. The features extracted from the STFT and frequency-domain are discussed in Section 3.2.3. The corroboration of the cake-layer thickness and total reflected power (TRP) with the mass-balance data in the AL-FS mode and AL-DS mode are presented in Section 3.2.4. The conclusions are summarized in Section 4.

4.2 Materials and Methods

4.2.1 FO system

The dead-end FO system are illustrated in details in Chapter 3. The rationale for applying dead-end operation on the feed side in this study was that the number of particles depositing onto the membrane could be easily estimated by the mass-balance method. This provided an independent measurement to cross-check the data obtained by UTDR, i.e., cake-layer thickness. On the draw side, the draw solution concentration was adjusted to achieve same initial flux under AL-DS mode and AL-FS mode: under flux around 10LMH condition, the draw concentration was 1.25M and 3M for AL-DS mode and AL-FS mode, respectively; under flux around 15LMH condition, the draw concentration was 3M and 5.5M for AL-DS mode and AL-FS mode, respectively. The driving force given by bulk osmotic pressure under AL-DS mode and AL-FS mode are: 61.93 bar and 148.65 bar (under 10 LMH initial flux condition); 148.65 bar and 272.53 bar (under 15LMH initial flux condition), respectively. A digital gear pump (Micropump, INC., model GJ-N23.PF1S.A) was used to recirculate the draw solution, which

was prepared from sodium chloride (EMSURE, ACS grade), at 250 mL/min between the draw solution tank and filtration cell. On the feed side, 100 mL of DI water was added into the filtration cell for membrane conditioning. After 30 min of membrane conditioning, to initiate the fouling process, colloidal silica (Sigma Aldrich, LUDOX® SM-30, specific surface area of 320-440 m²/g, diameter = 7 nm) stock solution was added into DI water to obtain a concentration of 2000 mg/L (the inductively coupled plasma (ICP) measurement of total silica concentration during the experiment is provided in the Appendix A.1). Since there is no crossflow applied in feed side, the particles are assumed to 100% deposited on membrane. The duration of fouling process lasted for 120 min. After the fouling experiment, the membrane was turned over and the draw solution side was switched to DI water for membrane cleaning at a flow rate of 2250 mL/min. After 30 min of cleaning, the membrane was turned back to the same orientation used in the fouling experiment; then draw solution at the same concentration used in the fouling experiment was used to measure the flux recovery. During the membrane conditioning, fouling and recovery stages, DI water, feed solution and DI water were added periodically on the feed side to maintain constant volume (i.e., constant water level), respectively. This procedure minimized membrane displacement caused by the change in weight of the feed solution above the membrane in the filtration cell and minimized the effect of variations in the feed concentration (i.e., feed-concentration effect). The water flux, $J_{w(t')}$, calculated from the mass difference recorded by a digital balance (Mettler-Toledo, model PB3002-L) at the n^{th} addition of DI water or feed solution is given by the following:

$$J_{w(t')} = \frac{(W'_{(n)} - W_{(n)})}{\rho_w A_m \Delta t'} \quad (4.3)$$

where $W'_{(n)}$ and $W_{(n)}$ represent the weight of solution after and before DI water or feed addition at time t' , respectively; $\Delta t'$ is the time interval between two consecutive DI water or feed additions; ρ_w is the density of water ($\rho_w = 1000 \text{ kg/m}^3$); and A_m is the effective membrane area (m²).

In order to do the cross-validation of external and internal fouling through mass balance, ICP-OES (ICP-OES, optima 8000, Perkin Elmer, USA) was used in 2 sections for determining silica deposited on membrane surface and in feed solution. For measurement of silica deposited on surface of membrane (i.e. external fouling), the sperate experiment was conducted on AL-DS mode. In this experiment, the fouling observation periods are 30mins, 60mins, 90 mins and 120mins in each batch, respectively. After membrane was fouled

continuously after each period, the fouled membrane was taken from cell immediately. The silica deposited on membrane surface are washed carefully from membrane surface, dissolved into deionized water and collected into 50mL centrifuge tube. The tubes are treated in ultrasonic bath to fully dissolve silica into solution. Before testing, the sample are diluted with different times (based on fouling period) using deionized water to make concentration of sample fall into testable range of ICP-OES (0.5ppm- 500ppm in this study) in 45mL centrifuge tubes. Secondly, the sample was put in ultrasonic bath again and then passed through 0.45 μm filters before analysis. Finally, the solution was filled with 5mL 1% HNO_3 to make sure the samples are in acid condition. During testing, standard solutions are diluted with 1% HNO_3 for calibration. ICE -OES is also used in process of determining silica concentration in feed solution during fouling period, for which the detailed experimental processes and result are presented in Appendix A.1.

4.2.2 UTDR System

An innovative feature of this study is fixing an ultrasonic transducer on the bottom plate of the filtration cell to detect the pore-blocking process within the support-layer of the FO membrane, which was closed to the transducer for reducing the signal attenuation. A transducer with a peak frequency of 5 MHz (Olympus, model V611-RB) was held tightly to the bottom plate by a holder; silicon oil (Olympus, couplant C) was used as the coupling agent between the filtration cell and transducer. The UTDR system consists of a pulsar-receiver (GE Panametrics, model 5800) and an oscilloscope (Tektronix, model MDO3034). The sampling rate of the oscilloscope was set at 1 point/4 ns, and 10000 points in total were recorded in the time-domain to 20 μs . The beam width of the ultrasonic transducer used in this study is ~ 13 mm, which makes it's difficult to present the lateral thickness variability of membrane (i.e., micron size range). The oscilloscope was connected to a computer for real-time data logging using the WaterMon Version 1.3.4.0 software. The interval between two consecutive signal recordings was set at 5 min.

The raw UTDR signal obtained via the real-time data-logging system was obtained in the time-domain. The analysis in the time-domain included arrival-time shifts and amplitude changes of the principal peaks associated with the draw solution/membrane/feed solution interfaces; these were analysed automatically using the '*locatepeaks*' function in MATLAB. To increase the

sensitivity or signal response, the data in the time-domain were transferred into the time-frequency-domain using the Short-Time-Fourier-Transform (STFT) technique. The equation governing this transformation is given by the following:

$$\mathbf{STFT}\{x[n]\}(m, \omega) \equiv X(m, \omega) = \sum_{n=-\infty}^{\infty} x[n]w[n-m]e^{-j\omega n} \quad (4.4)$$

Where: STFT $\{x[n]\}$ presents the STFT transformation of n discrete data in the time-domain, m stands for each time point at which the Fourier transform is conducted, ω is the frequency component ranging from 0 to $\pi/\text{sampling rate}$, $w[n-m]$ stands for a sliding window centered at $n = m$. Through STFT, the window gives different weights to N data in the time-domain as it slides from $t = 0$ to $t = N$. Fourier transformation is performed on every set of N data weighted by window centring at $t = m$ resulting in $N/2$ normalised magnitude frequency components at every arrival-time point. Finally, an $N/2$ by N matrix is obtained in the form of the normalised magnitude in the time-frequency-domain. In this study, this process was achieved by a code developed in-house using the *Signal Processing Toolbox*TM available in MATLAB. In this algorithm a Gaussian window with a length consisting of 512 points was applied. The signal analysis scheme is summarised in Fig. 4.1. Qualitative comparisons of the arrival-time and amplitude of the peaks were made to differentiate the onset and growth of fouling in different membrane orientations. For quantitative analysis in characterising fouling layer thickness build-up, peak assignment and key fouling indicator selection were made on the differential signal in the time-domain, and validated via the mass-balance method. The pore-blocking and external fouling characterisations were made in the frequency-domain via the STFT technique and total reflected power (TRP) calculations.

Time-Domain Analysis	Frequency-Domain Analysis
<ul style="list-style-type: none"> • Fouling Detection: Arrival-time & amplitude • Thickness Calculation: Differential signal Statistical test Validation with mass-balance data • Pore-Clogging Characterisation: Differential signal 	<ul style="list-style-type: none"> • Pore-Clogging Characterisation: Short-Time-Fourier-Transform (STFT) Total reflected power (TRP)

Fig. 4.1 Signal analysis scheme applied in this study.

4.2.3 FO Membrane

The FO membrane used in this study was a commercial cellulose triacetate (CTA) FO membrane (HTI, Albany, OR). The details of membrane characteristics are presented in Chapter 3.

4.3 Results and discussion

4.3.1 UTDR peak assignment and signal stability

Fig. 4.2 (a) Schematic of UTDR signals of (i) only spacer; (ii) spacer and membrane in AL-FS mode, and (iii) channel with spacer and membrane in AL-DS mode. (b) Schematic of membrane orientations and corresponding reflected signals (red arrows are used to indicate membrane thickness and corresponding arrival time delay in UTDR signal).

The UTDR signals of channel fitted with only the spacer and the channel fitted with the spacer and CTA FO membrane in the AL-FS mode and AL-DS mode are shown in Fig. 4.2a. For the

clarity in displaying the signals, the waveforms are shifted vertically by 0.02 V apart from one another. The measurements were conducted using deionised (DI) water for both the draw and feed solutions. The reflected peaks denoted by X (arrival-time at 3.64 μ s) corresponded to the bottom plate/draw solution interface, and the signal denoted by X' was the echo of the peaks X (arrival-time at 7.28 μ s), which was exactly 2 times the arrival-time of peak X. The sound velocity in the acrylic bottom plate was 2730 m/s, which gave a calculated thickness of 4.97 mm that agreed with the design specification of 5 mm. When a membrane was fitted into the filtration cell, the clean membrane exhibited two major peaks that were labelled as peaks A and B. Peak A, which was closest to the transducer, corresponded to the interface of the draw solution/bottom surface of the membrane; i.e., the interface of the draw solution/support-layer surface in AL-FS mode and the interface of the draw solution/active-layer surface in the AL-DS mode, respectively. In the AL-FS mode the arrival-time of peak A was 4.60 μ s, the arrival-time difference between peak X and A could be converted to distance by using the sound velocity in water (1500 m/s) as 720 μ m, which agreed with the channel height of 0.7-0.8 mm in the design specification. Likewise, in the AL-DS mode, the arrival-time of peak A was 4.68 μ s, the height of draw side flow channel given by UTDR measurement was 780 μ m. In principle, based on the thickness of membrane determined from SEM images in Chapter 3 (i.e., 40-80 μ m), the second peak that corresponded to the interface of the membrane top surface/feed solution should appear at $\sim$ 0.05-0.11 μ s after peak A (assuming the sound velocity in water and the membrane were both 1500 m/s); i.e., 4.65-4.71 μ s in the AL-FS mode and 4.73-4.79 μ s in the AL-DS mode, depending on the location of the transducer. As shown in Fig. 5, the arrival-time of peak B was 4.69 μ s and 4.80 μ s in the AL-FS mode and the AL-DS mode, respectively, which meant the mesh was detected by the transducer that gave a membrane thickness of $\sim$ 80 μ m. The slightly higher amplitude in the AL-FS mode was attributed to the polyester mesh, which has higher density (1.40 g/cm³) than cellulose triacetate (1.28-1.32 g/cm³), as shown in Fig. 4.2b.

In addition, in order to address the challenge presented by the absence of hydraulic pressure to hold the membrane tightly in the filtration cell that could result in inaccuracy in identifying the fouling layer growth, the average changes with respect to the arrival-time and amplitude under fouling-free conditions were determined as 0.14% and 1.48% for peak A, and 0.08% and 0.89% for peak B, respectively, as shown in Fig. 4.3.

Fig. 4.3 Amplitude change and arrival-time shift during membrane conditioning stage.

4.3.2 Flux measurement

Fig. 4.4 Water flux as a function of time for a feed containing 2000 mg/L silica in (a) AL-FS mode, and (b) AL-DS mode. (c) Normalised water flux at the end of fouling and after cleaning. Feed replenishment was done every 10 min; DI water is used as the feed solution; 1.25M and 3M, 3M and 5.5M were used to achieve different initial flux conditions in the AL-DS mode and AL-FS mode, respectively; the crossflow rate of the draw solution was fixed at 250 mL/min. After 2h of fouling, membrane cleaning was performed using DI water, and the flux during this period is shown after the dash line. Error bar indicates the deviation of results obtained from 3 replicate measurements.

In order to compare the effect of initial flux on membrane fouling, both high and low initial fluxes were tested in the AL-FS mode and AL-DS mode, respectively. DI water with 2000 mg/L colloidal silica was used as the feed solution for all experiments; the initial flux in each test was controlled by adjusting the draw solution concentration. Note that the feed side had a dead-end configuration, which caused complete deposition of particles, i.e., particle deposition of 100%, caused by the water flux passing through the membrane. As shown in Fig. 4.4, the water flux remained stable in the AL-FS mode for both high and low initial flux conditions, where at the end of fouling, 90.3% and 93.6% of the initial flux was retained, respectively; the near overlap with the baseline flux profile implied the decline was nearly entirely attributed to the feed-concentration effect; that is, the coverage of colloidal silica on the surface of the membrane resulted in negligible cake-layer resistance and cake-enhanced osmotic pressure (CEOP) effect. After cleaning, approximately 96.9% and 99.8% of the initial flux was recovered, respectively. These results in combination with the SEM images suggested that the cake-layer could be easily removed by increasing the back-flushing and that nearly all the initial flux could be recovered for fouling that occurred in AL-FS mode. In contrast, the water flux decline in the AL-DS mode was more pronounced for both initial flux conditions; after fouling the water flux for the initial high flux condition was reduced to 61.8% of the initial flux, which was significantly lower than observed for the low initial flux condition, i.e., 79.8%. The much more stable water flux profile in the AL-FS mode than in the AL-DS mode was due to the strong ICP-self-mitigation effect, which agreed with prior studies. The lower stable flux also meant that fewer particles were brought to and deposited on or in the membrane in the AL-DS mode. The slight decline of the baseline water flux in the AL-DS mode suggested that the feed-concentration effect was also minor. In view of all these effects, the explanation for the severe water flux decline in AL-DS mode was due to internal fouling that caused blocking-enhanced internal concentration polarization (CEICP) effect. The conclusion was consistent with the SEM images of the fouled membrane in Fig. 4.5. The normalised fluxes after cleaning in the AL-DS mode were 90.6% and 84.5% at the low and high initial flux conditions, respectively, which suggested an irremovable portion of the colloidal particles inside the pores. The effect of fouling on the water flux in the AL-DS mode was dominated by the physical properties of the support-layer of the CTA membrane and size of the foulant particles. Nearly the same water flux profile was observed for both AL-FS mode and AL-DS mode when calcium alginate fouling was investigated for the same CTA membrane, which was due to the highly structured gel formation upon aggregation and relatively dense support-layer that made fouling a surface phenomenon even in the AL-DS mode (Mazlan et al. 2016). A similar study

using colloidal foulants such as bovine serum albumin (BSA) and Aldrich humic acid (AHA) that had a smaller size relative to the pore size of the CTA support-layer caused more severe fouling in the AL-DS mode than that in the AL-FS mode(Mi et al. 2008).

Fig. 4.5 SEM images of (a) surface, and (b) cross-section of the support-layer of a fouled membrane; and (c) surface, and (d) cross-section of the support-layer of the membrane after cleaning for the AL-FS mode; (e) surface, and (f) cross-section of the membrane after cleaning for the AL-FS mode; (g) surface, and (h) cross-section of the active-layer of a fouled membrane; and (g) surface, and (h) cross-section of the active-layer of the membrane after cleaning in the AL-DS mode. The EDX image shows the location of silica deposition.

4.3.3 UTDR analysis on time domain

Fig. 4.6 Membrane fouling at high initial flux conditions (a) in AL-FS mode, and (b) in AL-DS mode; (i) UTDR responses of a fouled membrane at $t' = 0, 30, 60$ and 120 min (time before $t' = 0$ min is for membrane conditioning), (ii) profile of amplitude of peaks, (iii) profile of arrival-time of peaks. Error bar indicates the deviation of results obtained from 3 replicate measurements.

Fig. 4.7 The arrival-time shift and amplitude change in the (a, b) AL-FS mode, and (c, d) AL-DS mode at low initial flux conditions.

Fig. 4.6 shows the UTDR responses in the time-domain (only for those peaks shown in window ‘M’ in Fig. 5) at times $t' = 0, 30, 60, 90$ and 120 min; the amplitude and arrival-time vs. fouling time of peaks A, B and F in the AL-FS mode and peaks A and B in the AL-DS mode at the high initial water flux condition are shown in Fig. 4.6 (the data for the low initial water flux condition are shown in Fig. 4.7). Note that the UTDR responses exhibited much higher sensitivity to fouling than the water flux profile shown in Fig. 6. In the AL-FS mode, during which the water flux remained unchanged throughout the entire fouling period, a new peak F (on the right of peak B) corresponding to the fouling-layer/feed solution interface, appeared after 5 min of fouling. The amplitude of peak B and peak F increased by $165.7 \pm 8.9\%$ and $611.3 \pm 44.5\%$, respectively at the end of the fouling process. At the same time, the arrival-time of peak F shifted to the right, from 4.75 ± 0.02 to $4.80 \pm 0.02 \mu\text{s}$, as fouling proceeded (note that the UTDR transducer was located under the bottom plate of the filtration cell, which meant that

the arrival-time shifted to the right corresponding to longer arrival-time as the fouling layer became thicker). However, the arrival-time and amplitude of peak A remained unchanged since peak A was unaffected by external fouling in which the silica particles only deposited on the top surface of the membrane (active-layer). In contrast, in the AL-DS mode, there was no appearance of a separate peak F, although there were increases in the amplitude ($127.5 \pm 21.2\%$ and $245.2 \pm 39.8\%$, respectively) and a shift in the arrival-time for peaks A and B. This meant the cake-layer formed on the external top surface of the membrane (support-layer) was inconsequential; hence, the UTDR only detected a change in the acoustic properties of the top surface of the membrane since the cake-layer was not sufficiently thick to detect (i.e., no peak F). On the other hand, the slow movement to a slightly longer arrival-time of peak A, from 4.68 ± 0.00 to $4.71 \pm 0.02 \mu\text{s}$, indicated the accumulation of particles inside the support-layer of the membrane, within which denser silica particles increased the acoustic impedance of the reflected signal. The changes in amplitude and arrival-time shifts in the time-domain gave qualitative insight into the fouling process. However, because the membrane was very thin, there could be overlapping peaks in window 'M' that complicated quantitative analysis. As such, the arrival-time shifts were analysed via the differential signal in the time-domain to obtain information on the cake-layer thickness increase. The changes in amplitude also were analysed in more detail via STFT and total reflected power, whereby peak A provided a specific characteristic for identifying the internal pore-blocking process.

Fig. 4.8 Differential signal of the fouled membrane at $t' = 0, 30$ and 120 min in (a) AL-FS mode, and (b) AL-DS mode at high initial flux conditions. The original clean

membrane signal is indicated by the waveform in black colour. The red dashed lines indicate the location of peak A and peak B of the original signal.

In order to extract information from the arrival-time shifts, a statistical-based comparative analysis was applied (Kujundzic et al. 2007). To increase the resolution, differential signals were obtained by subtracting the signals at t' from the signals at $t' = 0$. For an RO application, with the transducer positioned above the membrane, the movements of the largest peak in the differential signal mode were used to estimate the cake-layer thickness build-up (Sim et al. 2012; Sim et al. 2013). In the AL-FS mode, peak A in the original signal disappeared in the differential signal since the interface of the draw solution/support-layer was not affected by external fouling; while peak D1 in the differential signal appeared at the same arrival-time as peak B in the original signal (i.e., interface of the active-layer/feed solution); moreover, the arrival-times of peaks D2 and D3 in the differential signal shifted to the right (i.e., increase in arrival-time) as fouling progressed; this suggested that peaks D1, D2 and D3 represented external fouling on the active-layer. Thus, peak A was selected as the reference peak in the statistical test. In contrast, in the AL-DS mode, peak D1 appeared at a location corresponding to the arrival-time between peak A (interface between the draw solution/active-layer) and peak B (interface between the support-layer/feed solution) in the original signal, which suggested a possible change in the acoustic impedance properties (i.e., sound velocity) of the support-layer due to pore-blocking by the silica particles. Meanwhile peaks D2 and D3 were also affected by internal and external fouling since a signal reflected from the external fouling layer was propagated through the support-layer with increasing pore-blocking. In addition, the non-smooth support-layer surface can influence the particle deposition or cause uneven distribution of the deposits (Kim et al. 2016), thus influencing peaks D2 and D3. Statistical analysis was performed to test if the arrival-time shifts observed between peaks D1 and D2 and between peaks D1 and D3 were significant at the beginning and end of fouling.

Before hypothesis testing the arrival time-shift data, a normality test was done to ensure proper parametric and non-parametric test methods. The D'Agostino's K^2 test was applied in this study to test the normality of the arrival-time shift data. The quantile-quantile-plot of the data obtained from different experimental conditions are shown in Fig. 4.9, in which being closer to the diagonal implies a higher possibility of being a normal distribution. Given significance level of 0.05, the data set was classified as a normal distribution if the P-value resulted from the test

was larger than 0.05. The student t-test was applied for the data set following a normal distribution, while the non-parametric Mann-Whitney U test was applied to the data set not following a normal distribution. Based on the normality test in Tab.4.1(a), in the AL-FS mode, the arrival-time differences between peak D1 & peak A, peak D2 & peak A, peak D3 & peak A are with a P-value of 0.149, 0.410 and 0.356, respectively, which both failed to reject the null hypothesis that they followed a normal distribution. In the AL-DS mode, the arrival-time difference between peaks D1 & D3 met the criteria with a P-value of 0.210, while the arrival-time difference of peaks D1 & D2 was not normally distributed with a P-value of 0.002. To investigate the evolution of fouling, a t-test was applied to compare the arrival-time difference of specific pairs of peaks arising from the differential signal at the beginning and end of fouling for the dataset that failed to reject it was not normally distributed. For the arrival-time difference between peaks D1 & D2 in AL-DS mode, the non-parametric Mann-Whitney U test was applied, since the distribution of variables were proven to be not normally distributed.

The P-values of the arrival-time shift via the hypothesis test are given in Table 4.1(b). In the AL-FS mode, the arrival-time difference between peak D1 and peak A as well as between peak D2 and peak A when comparing before and after fouling was significant at a confidence level of 0.99. The result suggested that a reliable cake-layer thickness can be obtained from the arrival time shift in the AL-FS mode when peak D2 or peak D3 was chosen as the fouling indicator (i.e., the thickness of the cake-layer build-up is shown in Figure 4.12). On the other hand, in the AL-DS mode, the results suggest that peak D2 and peak D3 were not suitable as a reliable indicator; thus, the thickness parameter was not used to characterize external fouling.

Fig. 4.9 The quantile-quantile plot of the arrival-time difference between peaks D1 & D2 and peaks D2 & D3 in the (a, b) AL-FS mode, and (c, d) AL-DS mode, respectively.

Table 4.1 (a) The results of D’Agostino’s K^2 normality test on arrival time difference during fouling; (b) The P-value of hypothesis test of arrival-time difference at the beginning and end of fouling.

(a)

Membrane orientation	Arrival time difference between	P-value
AL-FS mode	Peak D1 & Peak A	0.149
	Peak D2 & Peak A	0.410
	Peak D3 & Peak A	0.356
AL-DS mode	Peak D2 & Peak D1	0.002*
	Peak D3 & Peak D1	0.210

* α value chosen in D’Agostino’s K^2 test is 0.05 in this study. The dataset with P-value smaller than α was marked by * indicating it is successful to reject the null hypothesis that samples are normal distributed.

(b)

Membrane orientation	Arrival time difference between	P-value
AL-FS mode	Peak D1 & Peak A	0.1109
	Peak D2 & Peak A	0.0063**
	Peak D3 & Peak A	0.0052**
AL-DS mode	Peak D2 & Peak D1	0.1114

**The result is significant at a confidence level of 0.99. The P-value is the probability that, when the null hypothesis is being rejected, should be equal or less than the chosen level of significance. In this study, given 0.01 as the significance level, only when the P-value was less than 0.01 can significant growth of cake layer be identified.

4.3.4 Short-Time-Fourier-Transform (STFT)

Fig. 4.10 2-D frequency components in the time-domain using the STFT technique in (a) AL-FS mode, and (b) AL-DS mode; fouling at (i) 0 min, (ii) 30 min, and (iii) 120 min. Initial flux ~15 LMH.

The STFT technique was applied to present the UTDR data in both the time- and frequency-domain, as shown in Fig. 4.10. The membrane at different stages of fouling were represented

by nattier blue and aqua green to yellow, respectively. For the clean membrane, it was observed that the peak frequency was around 5 – 10 MHz, which was in accordance with the specified peak frequency of 5 MHz transducer. In the AL-FS mode, the peak frequency was found to be 5.37 MHz, and its magnitude increased from 0.11 to 0.24 and 0.43 after 30 min and 120 min of fouling, respectively. In the AL-DS mode, the most noticeable change was at frequency of 7.32 MHz, which the magnitude was increased from 0.15 to 0.21 and 0.36 after 30 min and 120 min of fouling, respectively. The increase in magnitude in the frequency-domain indicated more energy was reflected from the fouled membrane due to higher acoustic impedance caused by silica particles (Sanderson et al. 2005a; Wang et al. 2018); thus the prominent peak that occurred near 4.8 μ s was due to external fouling by silica particle deposition.

One advantage of the STFT technique is the ability to extract information on the frequency components at each arrival-time, thus making it possible to present the data in both the time- and frequency-domain (Sanderson et al. 2005a). Peak A, which represented the interface at the draw solution/support-layer and draw solution/active-layer in the AL-FS mode and AL-DS mode, respectively, was free from the influence of peaks overlapping. In this regard, the frequency components of peak A were decomposed; the components near the peak frequency are shown in Fig. 4.11. As shown in Fig. 4.11, the frequencies of peak A with the highest amplitude were quite similar, 7.3 MHz and 7.8 MHz, in the AL-FS mode and AL-DS mode, respectively. When there was no fouling, the frequency components followed very similar distribution pattern for both membrane orientations, but lower amplitudes were observed in the AL-FS mode. This was attributed to less energy reflected from the uneven support-layer surface. In contrast, the active-layer surface was flatter, thus higher energy was reflected in the AL-DS mode. When the membrane was fouled, it was observed that there was no variation in the distribution pattern over time in the AL-FS mode, which suggested the acoustic properties of the media between the interfaces of the draw solution/support-layer and active-layer/feed solution remained unchanged over time. On the other hand, the high frequency components decreased sharply in the AL-DS mode, i.e., >30% loss of amplitude was observed for components with frequencies higher than 7.3 MHz and only 10% of the original amplitude was retained at frequency of 11.7 MHz after 120 min of fouling. The results showed that the frequency decomposition provided better sensitivity in the interpretation of internal fouling phenomenon than the time-domain analysis. Instead of considering the blocked-support-layer as a homogeneous media, it was found to be an anisotropic media made up of the membrane matrix, water and silica particles that demonstrated different degrees of transmission, reflection

and attenuation of the ultrasound waveform over time. Among the several possible sources of signal attenuation, grain-scattering, energy scattered by small, fixed, rigid spheres distributed in the non-homogeneous media, accounted for the signal loss(Ensminger et al. 2011). The attenuated waveform and attenuation coefficient were highly dependent on the frequency and grain size. The wavelength of the signal had frequencies ranging from 5.8 to 11.7 MHz in water was far larger than the diameter of the silica particles (i.e., ~7 nm). The fact that the ratio of the wavelength to average particle diameter was greater than 1 led to the occurrence of Rayleigh scattering. Under these conditions, the theory derived by Rayleigh shows the ratio of scattered intensity, P_s , to the intensity, I_o , of the incident phase wave is (Ensminger and Bond 2011):

$$\frac{P_s}{I_o} = \frac{\pi^2 T^2}{r^2 \lambda^4} \left(1 + \frac{3}{2} \mu\right)^2 \quad (4.5)$$

Where: P_s is the scattered intensity ($\text{W} \cdot \text{m}^{-2}$); r is the travel distance (m); I_o is the intensity of incident wave ($\text{W} \cdot \text{m}^{-2}$); T is the volume of sphere (m^3); λ is the wavelength (μm), μ is the cosine of the angle between scattering direction and reverse direction of incident wave (-). Eq. (5) indicates that Rayleigh scattering increases with a decrease in wavelength or increase in frequency. In the field of non-destructive membrane morphology characterisation, the study from Ramaswamy et al. showed that the amplitude reduction of high-frequency components was significantly related to the severity of scattering for both poly(vinylidene fluoride) (PVDF) and mixed cellulose ester (MCE) membranes (Ramaswamy et al. 2004). In summary, the sensitivity of the ultrasound signal was enhanced through discrete STFT; in addition, the decomposition of the non-overlapped signal nearest to the transducer was able to enhance interpreting the relationship between the internal pore-blocking phenomenon and the ultrasound signals.

Fig. 4.11 The profile of amplitudes of frequency components of peak A, which represented (a) interface of draw solution/support-layer in AL-FS mode, and (b) interface of draw solution/active-layer in AL-DS mode. The initial flux ~ 15 LMH.

4.3.5 Mass balance validation

An independent measurement based on the mass-balance method was conducted to verify the results obtained from the UTDR and UFDR measurements in both the AL-FS mode and AL-DS mode.

In the AL-FS mode, the thickness of the cake layer (i.e., external fouling) formed on the active-layer surface can be calculated via the mass-balance equation:

$$l_f = \frac{\sum_{t'=0}^{t'} C_{silica} \cdot J_w(t') \cdot \Delta t'}{(1 - \varepsilon_f) \cdot \rho_{silica}} \quad (4.6)$$

Where: $J_w(t')$ is the water flux at t' , C_{silica} is the concentration of silica measured via inductively coupled plasma (ICP), and ε_f is the porosity of the silica fouling layer, which was taken as 0.36 (Park et al. 2013). Meanwhile, the thickness of the cake layer can be obtained from the arrival-time shift of peak D3 based on differential signal in the time. Note that the thickness parameter was not used to characterize the external fouling in AL-DS mode. The theoretical detection limit for the cake-layer thickness was 3 μm , assuming that the sound velocity in the fouling layer was 1500 m/s and the sampling interval was 4 ns. As shown in Fig. 4.12, at an initial flux ~ 10 LMH and ~ 15 LMH, the results determined from UTDR were in excellent agreement with the data obtained from the mass-balance measurement. Discrepancies were observed toward the later stage of the fouling process when a correction factor was necessary: (i) the compaction of the fouling layer caused by destabilization of the colloidal silica as the mass fraction of particles near the membrane surface was increased that resulted in a lower ε_f (Sim et al. 2012); thus, a smaller thickness was expected by the mass-balance method; (ii) an increase in the sound velocity in the dense silica layer, i.e., >1500 m/s; thus, a larger thickness was expected by the UTDR method.

Fig. 4.12 Thickness of cake-layer on the membrane surface in the AL-FS mode at an initial flux (a) ~ 10 LMH and ~ 15 LMH obtained from the mass-balance and UTDR methods.

The total reflected power (TRP) was determined by integrating the amplitude of the reflected ultrasonic waves over the range of the frequencies selected; 10 frequencies surrounding the peak frequency were used in this study (Mi et al. 2008). In the mass-balance method, the cake layer (M_{cake}) was removed from the fouled membrane coupons and collected at different

intervals of 30, 60, 90 and 120 mins by rinsing with MQ water. The silica concentration in the washed solution was analysed by ICP-OES. The total mass of the deposits (M_{total}) was obtained from the mass-balance based on the permeate collected. The mass of the deposits inside the pores, M_{pore} , i.e., internal fouling, was estimated from ($M_{\text{total}} - M_{\text{cake}}$). The result is shown in Fig. 4.13, Fig. 4.14 and Fig. 4.15. To characterize the effect of fouling on the overall membrane and internal section of the membrane, the whole range of arrival-time points (corresponding to $\text{TRP}_{\text{all peaks}}$) and for peak A (corresponding to $\text{TRP}_{\text{peak A}}$) was selected for this integration calculation, respectively. In both the AL-FS (Fig. 4.13) and AL-DS mode (Fig. 4.14 and Fig. 4.15), the normalized $\text{TRP}_{\text{all peaks}}$ increased over time as fouling progressed, which was due to the particle accumulation on the external top surface of the membrane (i.e., external fouling). However, in the AL-FS mode, the normalized $\text{TRP}_{\text{peak A}}$ remained nearly unchanged, which corroborated with the constant acoustic properties of the interface of draw solution/support-layer. This provided another indication of the absence of pore-blocking, i.e., internal fouling. On the other hand, in the AL-DS mode, as shown in Fig. 4.14 and Fig. 4.15, the normalized $\text{TRP}_{\text{peak A}}$ decreased as the mass of the deposits inside the pores of support-layer increased. The negative relationship was due to the scattering effect when a sound wave propagated through the silica colloids that were accumulated in the pores of the support-layer (Ensminger and Bond 2011). The TRP analysis provided a clear and direct indication of the degree of external and internal fouling. Nevertheless, the use of a single transducer in this study did not allow simultaneous quantitative characterization of internal and external fouling in the AL-DS mode, i.e. only $\text{TRP}_{\text{peak A}}$ was correlated with the mass deposited in the pores of the support-layer, but the correlation between UTDR and UFDR with the external mass deposited was not established, due to significant attenuation of the sound wave as it passed through the blocked pore. To improve the analysis, a second transducer could be placed above the membrane, similar to the configuration used in RO applications, for detection of the external fouling on the top surface of the membrane.

Fig. 4.13 Normalized total reflected power (TRP) vs. total mass of silica deposited in the AL-FS mode at an initial flux ~ 10 LMH (a) and ~ 15 LMH (b).

Fig. 4.14 (a) Normalized TRP_{all peaks} vs. total mass of silica deposited; and (b) The correlation between normalized TRP_{peak A} and mass of silica inside of support-layer; the small figure inside shows the external and internal fouling measured by mass-balance method in AL-DS mode at initial flux ~ 10 LMH. Error bars were obtained from 3 replicate measurements.

Fig. 4.15 (a) Normalized TRP_{all peaks} vs. total mass of silica deposited; and (b) correlation between the normalized TRP_{peak A} and mass of silica inside the support-layer; the small insert shows the external and internal fouling measured by the mass-balance method in the AL-DS mode at an initial flux ~ 15 LMH. Error bars were obtained from 3 replicate measurements.

4.4 Conclusions

In this study the UTDR technique was applied to simultaneously characterise internal and external fouling during FO. This study discussed and addressed the limitations and challenges in applying UTDR to FO process relative to pressure-driven membrane processes such as RO. Compared to the previous studies, the novelty of this study is placing transducer on the bottom of membrane to allow ultrasonic sound propagate inside of membrane substrate for the purpose of simultaneous detection of internal and external fouling. Moreover, application of UTDR is not transferable directly from hydraulic-pressure driven process into osmotic pressure driven process. The characteristic of forward osmosis as well as forward osmosis membrane raise extra challenges in signal testing and signal analysis. The following conclusions can be drawn from this study:

(1). Qualitative analysis indicated that changes in the amplitude and arrival-time shifts of the UTDR signal were a more sensitive indicator of FO fouling than water flux decline. The change of peaks provides a direct and visualisable tool for early membrane fouling detection before water flux is essentially impacted;

(2). Quantitative analysis assessed the applicability, reliability, and detection limit for using the shifts in the arrival-time of peaks observed in the time-domain for determining the cake-layer thickness;

(3). The cake-layer thickness obtained via UTDR measurement was in good agreement with the thickness determined via mass-balance method for the AL-FS mode;

(4). The decomposition of non-overlapping peaks via STFT analysis revealed a significant decrease in the amplitudes of the high-frequency components due to a grain-scattering effect in the AL-DS mode, which increased as fouling progressed. In contrast, the frequency distribution remained unchanged in the AL-FS mode;

(5). The TRP calculations through all arrival-time points and key peaks in the frequency-domain were well-correlated with the overall fouling and internal fouling, respectively.

The information extracted from the UTDR signal in real-time provides a promising tool for real-time non-destructive early membrane fouling detection. With the development of sensors, such signal can be either used standalone or integrated with other signals to develop more automatic efficient membrane-cleaning protocols.

CHAPTER 5. Dynamic colloidal particle deposition in forward osmosis (FO) in active layer facing draw solution (AL-DS) mode: Quantitative interpretation by combination of optimization techniques and back-propagation neural networks (BPNNs)

5.1 Introduction

Water supply is facing increasing pressures with the intensification of global water scarcity due to exponential population growth and severer water quality standards (Hightower 2008). Membrane technologies are playing critical role in addressing the water challenges in recent years. Forward osmosis (FO) is classified as a type of membrane process which draws pure water from low concentration side (i.e., feed solution) to high concentration side (i.e., draw solution) through chemical potential gradient across a semi-permeable membrane. FO is a non-pressure driven process and the net driving force is based on the osmotic pressure difference between the two solutions, hence it is free from the constraint of hydraulic pressure unlike the pressure driven membrane processes. Due to the advantages of FO process, numerous lab-scale research work have been explored in water reclamation (Lundin et al. 2010), desalination (McGinnis et al. 2007; Yangali et al. 2011; Ling et al. 2011), osmotic membrane reactor (Lay et al. 2012; Cornelissen et al. 2011), sludge dewatering (Cornelissen et al. 2008; Tung et al. 2015), pharmaceutical applications (Santus et al. 1995; Nayak et al. 2010) and many more. However, the wide industrial application of FO technology is still limited for several reasons. Apart from the necessity of a high performance FO membrane with low internal concentration polarization (ICP) and back solute diffusion (BSD), a good draw solution with ease and low energy of regeneration, the unavoidable problem of membrane fouling that lowers the process efficiency is also a major concern. Some studies showed that when in active layer facing feed solution (AL-FS) mode, the cake layer formed on the surface of FO membrane is less compact and has higher reversibility than on the surface of RO membrane due to the absence of hydraulic pressure (Tang et al. 2010; She et al. 2016), in which the cake layer can be easily removed by crossflow tangential force (Yangali et al. 2011; Ling et al. 2011). On the other hand, when in active layer facing draw solution (AL-DS) mode, despite higher initial flux due to lower ICP effect, membrane fouling is more persistent as the porous support is vulnerable to both pore-plugging and external cake layer formation (Tang et al. 2010; Wang et al. 2010; Parida et al. 2013). In addition, pore-plugging phenomenon cannot be easily mitigated through increasing the crossflow rate, thus the accumulation of solutes in the pore accelerates the

destabilization of colloidal particles and further exacerbates fouling in return (Tang et al. 2010; She et al. 2016; She et al. 2012). In general, the deposition of undesirable substances on or/and inside of FO membrane can cause an increase in resistance, enhanced external and internal CP, enhanced or reduced BSD. The inter-relationships between membrane fouling and these phenomena as well as parameters such as membrane orientation, foulant concentration, feed and draw concentrations (Xie et al. 2014), membrane properties (i.e., hydrophilicity and surface charge), structural parameter of support layer (Manickam et al. 2015), hydro-dynamic conditions (Shakaib et al. 2009; Kim et al. 2012; She et al. 2013) are complicated. Usually experimental based studies were conducted to elucidate membrane fouling in FO.

The quantitative modeling of fouling process in FO is still a challenging problem, especially fouling that occurs in AL-DS mode. The main obstacle is the unavailability of local microscopic status near support layer, which plays critical role in pore-plugging. For example, Tang et al. investigated the coupled effects of ICP enhanced by pore-blocking and resistance by applying a series of draw solutions but did not address the foulants deposition process (Tang et al. 2010). In modeling approach, the classical coagulation theory condenses the interaction between foulants and solid surface through a particle deposition parameter K_p (-), which describes the probability of successful particle attachment when it was brought towards the membrane via flux. Thus, the rate of particle deposition can be described by $dm_f/dt = K_p \cdot (J_{w\text{ real}} - J_{\text{limiting}}) \cdot C_{\text{foul}}$

where m_f is the mass of particle deposited inside and on the surface of membrane ($kg \cdot m^{-2} \cdot s^{-1}$), J_w is water flux ($m^3 \cdot m^{-2} \cdot s^{-1}$), J_{limiting} is the water flux which is sustainable for long-term ($m^3 \cdot m^{-2} \cdot s^{-1}$), C_{foulants} is foulants concentration ($kg \cdot m^{-3}$).

Based on a given value of K_p , it is possible to model the rate of particle deposition and thus the corresponding changes in membrane performance through empirical or semi-empirical models. However, K_p is also a variable depends on the non-linear relationship between water chemistry and hydrodynamic conditions (Chong et al. 2008; Liu et al. 2018; Park et al. 2013). In this regard, available simplified models either proposed a constant K_p or focused on conditions in which particle deposition kinetics can be built on knowledge-based mechanics. For example, Park et al assumed a constant K_p in the first-order kinetic equation applied to model colloidal particles deposition in AL-FS mode (Park et al. 2013). Despite excellent agreement between simulation and experimental data in previous studies, the hydrodynamic conditions and local concentrations of NF/RO and FO in AL-FS mode are far less complicated than in the FO

support layer in AL-DS mode, in which they are highly uncertain due to pore constriction (i.e., changing pore geometries), particle-fouled membrane interaction, pore-blocking enhanced ICP and BSD, and cake layer enhanced ECP effects. As such, it is difficult to simulate particle deposition in AL-DS mode simply based on phenomenological or empirical models with experimentally measurable parameters.

Supervised learning, such as artificial neural networks, is an emerging technology to be applied in the membrane field. The advantage of these learning algorithms over the traditional knowledge-based model is their capacity in handling non-linear multivariate problem when the internal coupling mechanisms are not fully understood. Through training sets of data with several experimentally accessible parameters, such as run time, flow rate, pressure, temperature, concentrations, pH and turbidity, supervised learning has been proven as a potential tool in predicting water flux decline in lab-scale study (Teodosiu et al. 2000), total hydraulic resistance (Dornier et al. 1995), chemical oxygen demand (Giwa et al. 2016) and feed pressure (Cabrera et al. 2017) in membrane processes including MF, UF and NF/RO. With respect to optimizing network structure, Chen and Kim compared the prediction performance of the back-propagation neural network (BPNN) and radial basis function neural networks (RBFN) in the predictability of water flux challenged by colloidal suspension. Cheng proposed an overlapped type neural network to construct layers through considering the data distribution of flux decline. Sahoo et al integrated genetic algorithm with neural networks for providing optimized parameters of network before any data was input and trained inside of system. The success achieved in lab scale investigation thus triggered attempts of integrating learning algorithm to full-scale membrane system (Shetty et al. 2003; Veerapaneni et al. 2010; Peleato et al. 2017). In a recent study, artificial networks were developed to quantify membrane fouling in a three-stage RO system and to select the main predictive bulk water quality parameters through training of six-year process database (Roehl et al. 2018). Nevertheless, majority of current works focus on utilizing water characteristics to predict water flux and permeate quality. The complementary characteristics of mathematical model and neural networks give us an alternative tool to understand the process involving the parameters which are influenced by multiple changing variables. To the best of our knowledge, this is the first time that neural network approach is applied to study particle deposition process in forward osmosis in AL-DS mode.

In this study, a mathematical model was developed to obtain particle deposition factor, K_p , as function of time through an optimization technique. Then, the obtained data were fed to an optimized back-propagation neural networks, and the results are then analyzed based on the bulk characteristics selection, number of neurons in layers and predictability performance on training and test dataset. The contributions of real-time parameters including water flux, solute flux, draw concentration on particle deposition factor were analyzed through gradient-based indices.

5.2 Model development

5.2.1 Water flux and solute flux in virgin FO membrane in AL-DS mode

Fig. 5.1 Water flux and solute flux in FO process in AL-DS mode.

As illustrated in Fig. 5.1, four layers are adopted in virgin FO membrane system including active layer, porous support with internal concentration polarization (ICP) layer, diluted external concentration polarization (DECP) layer on draw side and concentrative external concentration polarization (CECP) layer on feed side. The concentration profile in each layer can be solved by integrating mass balance differential equation with different sets of boundary conditions:

$$J_s = -D \frac{dc}{dx} - J_w \cdot C \quad (5.1)$$

2219 where: J_s is the reverse solute diffusion flux (mol/(m²·s)); D is the diffusivity of solute (m²/s),
 2220 C is the solute concentration (mol/L). Positive direction is defined as the solute flux direction
 2221 ($x=0$ at high concentration boundary). In virgin FO membrane system, the pure water flux is:

$$2222 \quad J_w = \frac{(C_a - C_i) \beta R_g T}{\mu R_m} \quad (5.2)$$

2223 where: β is the van't Hoff coefficient (e.g. $\beta=2$ for sodium chloride); R_g is the universal gas
 2224 constant (8.314 L·kPa·K⁻¹·mol⁻¹); and T is the absolute temperature (K); μ is the viscosity of
 2225 solvent (Pa·s).

2226 The unknown parameters C_a and C_i are obtained through integrating equation (1) on each side
 2227 of active layer:

$$Ln \frac{J_w \cdot C_i - J_s}{J_w \cdot C_f - J_s} = J_w \left(\frac{S}{D_u} + \frac{1}{K_{exf}} \right) \quad (5.3a)$$

$$Ln \frac{J_w \cdot C_d - J_s}{J_w \cdot C_a - J_s} = J_w \left(\frac{1}{K_{exd}} \right) \quad (5.3b)$$

2228 Thus, the overall representation of water flux equation in AL-DS mode is:

$$J_w \quad (5.4)$$

$$= \frac{\{[C_d + \left(\frac{J_s}{J_w}\right)] \exp\left(-\frac{J_w}{K_{exd}}\right) - [C_f + \left(\frac{J_s}{J_w}\right)] \exp\left[\frac{J_w}{(K_m)} + \frac{J_w}{K_{exf}}\right]\} \beta R_g T}{\mu \cdot R_m}$$

2229 where: S and D_u are the structural parameter and solute diffusivity inside support layer,
 2230 respectively. Most studies adopted the definition of S and D_u as:

$$S_m = \frac{\lambda_m \cdot \tau_m}{\varepsilon_m} \quad (5.5)$$

$$D_m = \frac{D \cdot \varepsilon_m}{\tau_m} \quad (5.6)$$

2231 where: λ_m , ε , τ correspond to thickness (m), porosity (-) and tortuosity (-), respectively, of
 2232 porous support. K_{exd} (m/s) and K_{exf} (m/s) are mass transfer coefficient in the vicinity of active
 2233 layer and support layer, respectively.

2234 The transport in active layer was governed by solution-diffusion; while the convective-
 2235 diffusion described the transports in porous support, blocked support layer, cake layer, and
 2236 boundary layers on both draw and feed sides. The controlled-volume approach was applied to
 2237 simulate particle deposition in the vicinity of porous support (Park et al. 2013). A probabilistic
 2238 factor called ‘particle deposition factor’, K_p , was lumped to describe the possibility of particle

deposition at various feed conditions investigated in this study. As a continuum model, the resistance-in-series model was applied to represent the average properties of membrane, in which the water and solute transport in each layer can be quantified with relative simplicity. The assumptions made in the model included:

(1) In solution-diffusion model, the solution concentrations on each side of active-layer are assumed to be in equilibrium with the adjacent active-layer surface (Wijmans et al. 1995);

(2) The active-layer's water permeability, i.e., A value, hence R_m , as well as solute permeability, i.e., B value, are assumed to be constant;

(3) The pores in the porous support-layer are assumed to have uniform cylindrical geometry, each pore has a surface area of A_p (m^2), and total surface area of n pores is nA_p (m^2);

(4) The partition of deposited colloidal particles inside pores and on external surface of porous support-layer depends on the ratio of pore surface area/porous support-layer surface area, (nA_p/A_m), or equivalent to surface porosity of porous support-layer, ε_s (-);

(5) The deposited colloidal particles build up layer-by-layer inside pores and on external surface of porous support-layer. The hydraulic resistances induced by pore blocking and cake layer formation are simulated simultaneously until all the pores are completely filled;

(6) The deposited mass compared to incoming mass are relatively insignificant such that the concentration of particles, C_{foul} , remains unchanged from inlet to outlet of flow channel.

5.2.2 Fouling model development

5.2.2.1 Correlating deposition kinetics with pore geometry

For FO in AL-DS mode, two different fouling mechanisms are possible: pore-blocking of the porous support and cake layer formation on the external surface of the porous support. Prior to deciphering the results induced by colloidal deposition, it is necessary to set the particle deposition kinetics. In this study, since the diameter of model foulants silica colloids (around 7 nm) are much less than the pore size of support layer (20-50 nm) it is reasonable to assume the all particles shares the same probability of deposition in a certain time point when water characteristics and hydrodynamic condition are relatively unchanged. Instead of anatomizing the sophisticated physicochemical interactions including van der Waals force, Lewis acid-base interaction, electrostatic double layer interactions and fluid dynamics between individual

particles, it is more practical to consider the overall particle deposition based on a controlled volume method (Park et al. 2013) .

$$M_d = K_p \cdot C_{foul} \cdot \int_0^t (J_w(\xi) - J_{limiting}) d\xi \quad (5.7)$$

Where: K_p is used for the potential of particle deposition under controlled hydrodynamic and feed chemical conditions, and it is also the factor extracted from regression analysis. The fluctuation of bulk foulants concentration during fouling process aren't taken into consideration in this model. Fortunately, the concentration fluctuation during fouling process are quite subtle based on our previous experiments, otherwise this assumption should be relaxed by incorporating foulant concentration profile. Euler method was adopted to calculate mass of particle deposition in quite small test intervals for approximation:

$$M_d = K_p \cdot C_{foul} \cdot \frac{T}{n} \sum_{i=0}^n (J_w(t_{n-1})) \quad (5.8)$$

Where: T is the whole test period (s), n is the sampling number in a specific test period, $\frac{T}{n}$ gives the sampling interval (s), $J_w(t_{n-1})$ is used to indicate $J_w(t_{n-1})_{real\ time} - J_w_{limiting}$

Theoretically, shortening sampling interval are able to increase the accuracy of model. However, in this case the calculation load is increased in regression test exponentially, and numerical stability are also compromised a lot. The trade-off should be made between modeling precision and experimental limitation restricted by measurement conditions. 5 mins are adopted as a suitable interval for obtaining stable water flux and solute flux values accessible in experimental conditions based on pre-experiments.

Fig. 5.2 the schematic graph of pore structure (a) and mass transfer (b) in asymmetrical membrane during fouling period.

Structural parameter S are widely adopted as a yardstick to characterize support layer, which incorporates impact of both porosity of support layer and tortuosity of pores (Kim et al. 2017). The effective pore length L_p was adopted to characterize the length of individual cylindrical pores, which refers to the average length of effective route for solute transport in the porous support. The L_p is related to tortuosity τ_m , and thickness of porous support, λ_m :

$$L_p = \tau_m \cdot \lambda_m \quad (5.9)$$

As mentioned before, porosity and structural parameter S are experimental accessible, which make it possible to factor L_p out. In order to characterize the degree to which pores are blocked, effective pore length being blocked was quantified as L_f . Corresponding to L_f , length of pores that maintain properties of clean membrane is presented by L_{uf} . In this scenario, another layer of resistance was introduced into original resistance-in-series model: resistance introduced by blocked-pore, thus the support layer is divided into two parts: the blocked layer with decreasing porosity, increasing porosity, increasing thickness and increasing resistance; the unblocked layer that retains all properties of clean membrane but constantly reduced thickness, ideally.

$$L_p = L_f + L_{uf} \quad (5.10)$$

where L_p (m) is the effective pore length that accounts for the tortuosity factor, for clean membrane, $L_p = \tau_m \cdot \lambda_m$; L_f (m) and L_{uf} (m) represent the fraction of pore length that is fouled and un-fouled, respectively. Correspondingly, λ_f (m) and λ_{uf} (m) represent the thickness of porous-support layer that is fouled and un-fouled, respectively. For simplicity, it is assumed that the pore length is proportional to the thickness:

$$\frac{L_p}{\lambda_m} = \frac{L_f}{\lambda_f} = \frac{L_{uf}}{\lambda_{uf}} = \tau_m \quad (5.11)$$

Eq (1) is used to account for the total mass of deposited colloidal particles, M_d . Euler method is adopted to approximate M_d in small time intervals. The partition of deposited colloidal particles into the pore, M_{dp} ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), and on external surface of porous support-layer, M_{dc} ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), depends on the surface porosity of porous support-layer, ε_s :

$$M_d = M_{dp} + M_{dc} = M_d \varepsilon_s + M_d (1 - \varepsilon_s) \quad (5.12)$$

The relationship between fouled fraction of pore length and mass of deposited colloidal particles inside pores is expressed as:

$$L_f \rho_p (1 - \varepsilon_p) n A_p = M_d \varepsilon_s A_m \quad \text{or} \quad L_f = \frac{M_d}{\rho_p (1 - \varepsilon_p)} \quad (5.13)$$

where ε_p (-) is the porosity of deposited colloidal particles inside pore; ρ_p (kg/m³) is the density of colloidal particle; n (-) is number of pores; and A_p and A_m (m²) are surface area of pore and membrane, respectively. There are two main adverse effects caused by increasing L_f , namely the enhanced ICP effect and additional hydraulic resistance.

5.2.2.2 Enhanced internal concentration polarization (ICP)

Regarding characterization of solute diffusion inside of cake layer, the parameter called cake layer structural parameter S_c was developed in recent studies for AL-FS mode. This term holds quite straightforward physical meaning. Since the porous cake layer hinders both convection and diffusion process the pores of porous cake layer could be treated as having much longer effective length than thickness of cake layer λ_c by multiplying a coefficient τ_c which presents the tortuosity of complicated pore-geometry of cake layer. Meanwhile, the porosity of cake layer ε_c is incorporated into S_c calculation as:

$$S_c = \frac{\lambda_c \cdot \tau_c}{\varepsilon_c} \quad (5.14)$$

where λ_c (m), ε_c (-), and τ_c (-) correspond to thickness, porosity and tortuosity of cake layer, respectively. Thus, the mass transfer in cake layer, K_c (m·s⁻¹), is:

$$K_c = \frac{D_c}{S_c} = \frac{D \cdot \frac{\varepsilon_c}{\tau_c}}{\frac{\lambda_c \cdot \tau_c}{\varepsilon_c}} = \frac{D}{\lambda_c \cdot s'} \quad (5.15)$$

Where: $s' = (\frac{\tau_p}{\varepsilon_p})^2$, the parameter was factored out to characterize the structural traits of cake.

The porosity of cake layer is modelled as a transition process until the unit thickness reaches a minimum porosity, which will be illustrated in section 5.2.2.3.

Hydraulic tortuosity was proposed by Carman et al. who discovered there was unneglectable discrepancy between the water flow in tortuous media and the one in straight path (Carman 1938). However, the proper characterization of tortuosity never reached consensus. Apart from numbers of different denotations, such as quantities as τ , τ^2 and τ^3 applied in (Carman 1938)

(Clennell 1997) , the elongation of stream path also results in changes on other transport phenomenon thus leading to multiple definition of several types of experimentally measurable tortuosity (Lorenz 1961; Johnson et al. 1982). With the assistance of computational and simulation tools, many semi-empirical relationship between porosity and tortuosity were developed for porous media such as the media composed of freely deposited system, various arrangement of cylinders, fixed beds of parallel epipedal particles and suspension of glass sphere (Weissberg 1963; Comiti et al. 1989; Ho et al. 1981). With respect to study focusing on random deposition of sphere-shaped colloidal particles, the one is developed from Lattice gas automata method, which is firstly introduced by Koponen. et al using porosity as the only controlling parameter (Koponen et al. 1996). The flow solutions in model were solved by Lattice Boltzmann model (LBM), the model proved to be useful in microscopic simulation of flow in porous media for wide range of flow regimes, with result in great agreement with equation:

$$\tau = 1 - p \ln(\varepsilon) \quad (5.16)$$

for freely deposited media with porosity less than 0.8 (where p is dimensionless coefficient obtained through fitting as 0.77) (Matyka et al. 2008). In the case of colloidal particle deposition, the porosity as 0.36 was accepted as a reasonable approximation (Park et al. 2013), which falls into the region where the relationship was applicable. However, it must be said that there is no universal relationship between porosity and tortuosity, what is applied here is a relatively optimal choice which is developed under similar colloidal deposition condition (Batys et al. 2014). In future, incorporating the dependence of tortuosity on fouling growth is expected to relax this assumption.

Considering pore-blocking effects in AL-DS mode, the characteristics of pore should be incorporated. In lieu of incorporating porosity of cake layer alone, the porosity of support layer must be taken into consideration since the volume occupied by membrane matrix should be ruled out in calculating effective route for solute transport. In this scenario, the whole porosity of blocked pore is quantified as $\varepsilon_f(-)$:

$$\varepsilon_f = \varepsilon_m \cdot \varepsilon_p \quad (5.17)$$

The calculation of structural parameter still requires the vertical thickness of blocked pore λ_f as well as tortuosity of blocked pore τ_f .

As mentioned before, all the pores in this model are assumed as the tube-like pores with averaging tortuosity τ_m . Like the λ_m which is proportional to the whole L_p , the vertical thickness of blocked pore is proportional to length of pores being blocked:

$$\tau_m = \frac{L_f}{\lambda_p} = \frac{L_p}{\lambda_m} \quad (5.18)$$

Considering the tortuosity of stochastic particle deposition is much larger than that of membrane pores, τ_f can be replaced by tortuosity of cake layer τ_p . Thus, the overall mass transfer parameter in blocked pore is calculated through:

$$S_f = \frac{\lambda_f \cdot \tau_f}{\varepsilon_f} = \frac{\frac{L_f}{\tau_m} \cdot \tau_f}{\varepsilon_m \cdot \varepsilon_p} = \frac{\frac{L_f}{\tau_m} \cdot \tau_p}{\varepsilon_m \cdot \varepsilon_p} \quad (5.19)$$

Considering the tortuosity of stochastic particle deposition is much larger than that of membrane pores, the tortuosity of fouled fraction, τ_f , can be replaced by tortuosity of deposited colloidal particles inside pore, τ_p . Then the mass transfer of the fouled fraction, K_f ($\text{m} \cdot \text{s}^{-1}$), is:

$$K_f = \frac{D_f}{S_f} = \frac{\frac{D \cdot \varepsilon_m \cdot \varepsilon_p}{\tau_p}}{\frac{\frac{L_f}{\tau_m} \cdot \tau_p}{\varepsilon_m \cdot \varepsilon_p}} = \frac{D \cdot \tau_m \cdot \varepsilon_m^2}{L_f \cdot \left(\frac{\tau_p}{\varepsilon_p}\right)^2} = \frac{D \cdot \tau_m \cdot \varepsilon_m^2}{L_f \cdot S''} = \frac{D \cdot \tau_m \cdot \varepsilon_m^2}{L_f S'_{fully-developed}} \quad (5.20)$$

where $S'' = \left(\frac{\tau_p}{\varepsilon_p}\right)^2$ is factored out to characterize the structural traits of deposited foulants in pore. Note that based on random particle deposition mechanism, both deposited foulants in pore and fully-developed cake layer formation on external surface have similar characteristics:

$$\tau_{c \text{ fully-developed}} = \tau_p \quad (5.21)$$

$$\varepsilon_{c \text{ fully-developed}} = \varepsilon_p \quad (5.22)$$

$$S'_{fully-developed} = S'' \quad (5.23)$$

(refer to Section 5.2.2.3 for description of fully-developed cake layer). With the development of pore blocking process, L_f keeps increasing until it is equal to L_p , which means all pores are fully blocked. Further particle deposition is captured as blocks to form cake layer on external surface of porous support-layer only. Equation 5.20 was transformed as:

$$K_f = \frac{D \cdot \rho_p \cdot (1 - \varepsilon_p) \cdot \tau_m \varepsilon_m^2}{M_d \cdot S'_{fully-developed}} \quad (5.24)$$

According to (5.24), K_f is influenced by multiple parameters include mass of particle deposition, tortuosity and porosity of foulant inside pore, solute diffusivity, tortuosity and porosity of porous support-layer, density of foulant.

The mass transfer in un-fouled fraction, K_{uf} ($\text{m} \cdot \text{s}^{-1}$), in which it maintains the tortuosity and porosity of virgin membrane, is

$$K_{uf} = \frac{D_{uf}}{S_{uf}} = \frac{D_{uf} \frac{\varepsilon_{uf}}{\tau_{uf}}}{\lambda_{uf} \frac{\varepsilon_{uf}}{\tau_{uf}}} = \frac{D_{uf} \frac{\varepsilon_m}{\tau_m}}{\frac{(L_p - L_f) \cdot \tau_m}{\tau_m} \frac{\varepsilon_m}{\varepsilon_m}} = \frac{D \varepsilon_m^2}{(L_p - L_f) \tau_m} \quad (5.25)$$

5.2.2.3 Fouling-enhanced hydraulic resistance

The FO membrane resistance, R_m (m^{-1}), is mainly contributed by the dense active-layer while the porous support-layer has comparatively negligible resistance; thus it is assumed R_m remains unchanged during fouling. Additional hydraulic resistances that reduce the flux are caused by cake layer formation, R_c (m^{-1}), and pore blocking, R_f (m^{-1}), as such the total hydraulic resistance, R_T (m^{-1}):

$$R_T = R_m + R_c + R_f \quad (5.26)$$

where R_c can be estimated via the Kozeny-Carmen equation:

$$R_c = \left[\frac{180(1-\varepsilon_c)}{\rho_p d_p^2 \varepsilon_c^3} \right] M_{dc} = \left[\frac{180(1-\varepsilon_c)^2}{d_p^2 \varepsilon_c^3} \right] \lambda_c \quad (5.27)$$

while R_f is contributed by the colloidal particles deposited in the individual pore, R_p (m^{-1}), which can be calculated using resistance-in-parallel model:

$$R_p = \left[\frac{180(1-\varepsilon_p)}{\rho_p d_p^2 \varepsilon_p^3} \right] \frac{M_{dp} A_m}{n A_p} = \left[\frac{180(1-\varepsilon_p)}{\rho_p d_p^2 \varepsilon_p^3} \right] M_d = \left[\frac{180(1-\varepsilon_p)^2}{d_p^2 \varepsilon_p^3} \right] L_f \quad (5.28)$$

$$\frac{1}{R_f} n A_p = \sum \frac{1}{R_p} A_p \quad (5.29)$$

$$R_f = R_p = \left[\frac{180(1-\varepsilon_p)^2}{d_p^2 \varepsilon_p^3} \right] L_f \quad (5.30)$$

In order to simulate external cake layer compaction, the changes in porosity are simulated by adopting the method introduced in a recent study (Su et al. 2019). In this method as illustrated in Fig. 5.3, the cake layer thickness is divided into two portions: fully-developed portion and

developing portion; where fully-developed portion has porosity of 0.36, while the porosity of developing portion above the fully-developed portion has porosity >0.36 . The transition from concentrated particles layer or fluid-cake layer to cake layer formation, the changes in porosity are calculated through the following steps:

(1) A threshold cake layer thickness h_{min} is defined, which is $0.5 \mu m$ in this study;

(2) At $T = t$, the mass of particles deposited on the membrane is classified into two groups: (a) the fully-developed cake layer with porosity as $\epsilon_{c \text{ fully-developed}}$, which is 0.36 in this study; (b) the fluid-cake interface layer above the fully-developed cake layer with porosity $\epsilon_{c \text{ transitional}}$. For single layer, the fully-developed cake layer is connected with fluid-cake interface layer through same cell height h_{min} , as such:

$$\frac{m_{\text{fully-developed cake layer}}}{m_{\text{fluid-cake interface layer}}} = \frac{1 - \epsilon_{c \text{ transitional}}}{1 - \epsilon_{c \text{ fully-developed}}} \quad (5.31)$$

(3) At $T = t + \Delta t$, the mass of newly deposited particles is first placed into fluid-cake interface layer until the porosity of this layer reaches $\epsilon_{c \text{ fully-developed}}$. Then, the rest of mass is placed to form new cell with height h_{min} and porosity $\epsilon_{c \text{ transitional}}$;

(4) Repeat (2) and (3) until T is 10 h, the fouling period applied in this study.

Fig. 5.3 Simulation of growth of cake layer on external surface of porous support-layer of FO membrane in AL-DS mode (adopted from (Su et al. 2019)).

5.2.3 Back-propagation neural networks (BPNN)

Neural networks can be constructed in multiple ways, forward propagation and back-propagation neural networks (BPNN) was widely used due to its well-defined and explicit equations for weights correction (Cheng et al. 2008). The detailed and deep discussion of

BPNN can be found elsewhere (Monica et al. 1998), here basics of neural networks with one hidden layer was outlined. The process of obtaining weights matrix in each layer consist of two processes: forward propagation and back propagation. In this study, the maximum iteration number was set as 100 and epochs size, the number of data trained in one iteration, was set as 432. The number of cross validation data and that of test data were 168 and 120, respectively. The effects of number of neurons in hidden layer and selection of input dimension on prediction performance are studied.

The criteria used to evaluate prediction results including final value of cost function, Pearson's coefficient and R^2 , which are widely used in previous studies (Zhu et al. 2019; Roehl et al. 2018; Cabrera et al. 2017), in which Pearson's coefficient (P) was defined as:

$$P = \frac{\sum_{i=1}^m ((h_{\theta}(\vec{x}^{(i)}) - \overline{h_{\theta}(\vec{x})}) \cdot (y^{(i)} - \overline{y}))}{\sqrt{\sum_{i=1}^m (h_{\theta}(\vec{x}^{(i)}) - \overline{h_{\theta}(\vec{x})})^2} \sqrt{\sum_{i=1}^m (y^{(i)} - \overline{y})^2}} \quad (5.32)$$

Where m is the total number of samples. $\widehat{h_{\theta}}$ and $\widehat{y^{(i)}}$ are predicted value and actual value obtained through optimization, respectively. Among these three indexes, the accuracy of prediction was increased by larger Pearson coefficient, larger R^2 and lower final value of cost function in test dataset.

5.2.4 Numerical roadmap

5.2.4.1 Obtaining particle deposition factor

The methodology consists of three main procedure: (1) obtaining particle deposition factor K_p as function of time through development of mathematic model and optimization techniques; (2) training K_p and corresponding bulk characteristics, either water characteristics or hydrodynamic conditions, in BPNN and obtaining the weights matrix for the algorithm; (3) evaluating the performance of algorithm through test set.

The modeling procedure for obtaining K_p was presented in Fig.5.4. The parameters used in modeling are listed in Tab.5.1, and flow chart was presented in Fig.5.5. All equations involved were derived and explained in previous sections. As shown in Fig.5.4, the procurement of K_p

was accomplished by non-linear multivariate regression by minimizing the square error cost function between experimental flux value and modeling flux value. This target function was defined as $J_{(Kp)}$ was defined as:

$$J_{(Kp)} = \frac{1}{N} \sum_{t=0}^T \left[\left(\frac{J_{w(t)exp} - J_{w(t)model}}{\overline{J_{w(t)}}} \right)^2 + \left(\frac{J_{s(t)exp} - J_{s(t)model}}{\overline{J_{s(t)}}} \right)^2 \right] \quad (5.33)$$

Where: N is the number of sampling points being optimized. In modeling, the number of points in every interval with pre-determined length, here 30 mins, is used as N. $J_{w(i)experimental}$ is the experimental value ($m^3/(m^2 \cdot s)$), $J_{w(i) modeling}$ is the modeling value predicted by algorithm ($m^3/(m^2 \cdot s)$), $\overline{J_{w(t)}}$ are average of experimental and modeling value of water flux and solute diffusion flux at time point t, respectively.

Since ICP-compensation effect should be considered in every sampling point, $J_{w(i) modeling}$ was resolved from following equations by using iterations:

$$J_{w(t)model} = \frac{\left\{ \left[C_d + \left(\frac{B \cdot \mu \cdot R_m}{\beta R_g T} \right) \right] \exp \left(-\frac{J_{w(t)}}{K_{exd}} \right) - \left[C_{f(t)} + \left(\frac{B \cdot \mu \cdot R_m}{\beta R_g T} \right) \right] \exp \left[J_{w(t)} \left(\frac{1}{K_{f(t)}} + \frac{1}{K_{uf(t)}} + \frac{1}{K_{c(t)}} \right) + \frac{J_{w(t)}}{K_{exf}} \right] \right\} \beta R_g T}{\mu \cdot (R_m + R_{f(t)} + R_{c(t)})} \quad (5.34a)$$

$$J_{s(t)model} = \left\{ \left[C_d + \left(\frac{B \cdot \mu \cdot R_m}{\beta R_g T} \right) \right] \exp \left(-\frac{J_{w(t)}}{K_{exd}} \right) - \left[C_{f(t)} + \left(\frac{B \cdot \mu \cdot R_m}{\beta R_g T} \right) \right] \exp \left[J_{w(t)} \left(\frac{1}{K_{f(t)}} + \frac{1}{K_{uf(t)}} + \frac{1}{K_{c(t)}} \right) + \frac{J_{w(t)}}{K_{exf}} \right] \right\} B \quad (5.34b)$$

The modeling algorithm was programmed in *Visual Basic of Application (VBA)* environment, and iterative process as well as regression analysis are accomplished by *Microsoft. Solver* with evolutionary method.

Table 5.1 Modelling parameters

Parameter	Value	Reference
Cell length, H (m)	0.085	This study
Width, W (m)	0.039	This study
Height, H (m)	0.03	This study
Crossflow rate, Q (LPM)	1	This study
Bulk Diffusivity, D ($m^2 \cdot s^{-1}$)	1.61×10^{-9}	(Park et al. 2013)
Density of Silica, ρ ($kg \cdot m^{-3}$)	2600	Manufacturer
Particle size, d_p (nm)	7	Manufacturer's technical literature

Porosity of support layer, ε (-)	0.6	This study
Porosity of silica deposition in fully developed portion ε_p (-)	0.36	(Park et al. 2013)
Membrane thickness, λ_m (μm)	50	This study
Silica concentration, C_{foul} ($\text{mg} \cdot \text{L}^{-1}$)	2000	This study
Tortuosity of silica particle deposition, τ_p (-)	$1-0.77\ln(\varepsilon_p)$	(Matyka, Khalili, and Koza 2008)
Feed concentration (M)	0.05	This study
Draw concentration (M)	1~4	This study
Dynamic viscosity of solutions, μ ($\text{Pa} \cdot \text{s}$)	0.0010978	(Park et al. 2013)

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Fig. 5.4 Flow chart of obtaining K_p through optimization technique

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2498 5.2.4.2 Training BPNN with data set

Fig. 5.5 The application of BPNN in this study

As illustrated in Fig.5.5., this study consists of mainly three important parts: (i) Obtain particle deposition factor through model derivation and optimization (as mentioned above); (ii) Correlate measurable parameters to particle deposition factor through training neural networks, (iii) Based on weights matrix of neural networks with the best performance, interpret contribution of parameters on deposition factor in different fouling stage. In the section of training neural networks, the data set are shown in Fig 5.5, each column stands for a set of data containing the information characterizing the conditions of a corresponding K_p . In this study, the fouling period was monitored in whole 10 hrs and two draw concentrations are tested with triplicate in each condition. Thus, totally 720 sets of data can be extracted, of which 70% and 30% of data was used as training set and test set, respectively. The training set are data used to training the BPNN, and test set were used to evaluate the performance of BPNN trained. The three criteria were used to evaluate the performance of BPNN on three datasets, respectively. It is noteworthy that focusing on training set may results in overfitting problem, which cause high variance on test set. The main objective of this study is to investigate the possibility of correlating particle deposition factor with numerous experimentally accessible parameters for better monitoring fouling growth in FO process on AL-DS mode thus test set are used as an independent validation of prediction accuracy. In the process of training model, the hyperparameters including learning rate, number of hidden layers and number of nodes in each hidden layer are carefully tuned with trial and error method. The training of neural networks

and calculation of gradient-based interpretable indices are accomplished by code developed mainly using *TensorFlow* open-source platform based on *Python*.

5.3 Experimental procedures

5.3.1 Materials and apparatus

The FO membrane used in this study was a commercial asymmetric cellulose triacetate membrane (HTI-CTA) from Hydration Technology Innovations, Albany, OR. A woven fabric polyester mesh was embedded below CTA active layer for providing mechanical strength and decreasing overall membrane thickness (Cath et al. 2006). According to previous study (Tang et al. 2010), the overall thickness of HTI-CTA membrane was $\sim 50 \mu\text{m}$; the pore size near support layer/water interface was 30-80nm based on FESEM image, shown in Fig 5.6(a). Compared to a conventional thin film composite (TFC) RO membrane, HTI-CTA FO membrane was much thinner, which resulted in lower ICP effect and higher flux (Tang et al. 2010). Hence, the HTI-CTA FO membrane has been used extensively in the research work on ODMs like FO and PRO (William et al. 2010; Zou et al. 2013; McCutcheon et al. 2005; McCutcheon et al. 2006). Proper characterization membrane parameter is of significance to ensure numerical stability in modeling process. The membrane properties which is experimentally accessible include 6 parameters: intrinsic membrane resistance (R_m), solute permeate coefficient (B), structural parameter (S), support layer porosity (ϵ), membrane thickness (λ_m) and percentage of open area on support skin (x). R_m , B and S value are simultaneously determined through the optimization method (Tiraferri et al. 2013). ϵ was adopted as 0.6, which is measured by water loss of wet membrane in dehydration process. λ_m was obtained by averaging the multiple values measured in different points on HTI-CTA membranes through digital calibrator. Compared to thickness of support layer (in micrometer magnitude), that of active layer was much thinner hence it's negligible in the study. λ_m is determined as $\sim 50 \mu\text{m}$, which is quite close to previous calibration and microscopic observation (Wang et al. 2010). Since there is thin skin layer on support layer surface for mitigation of ICP, some of particles was retained on the surface while some enter pores. The partition of particle mass was approximated by percentage of open area on support skin, which is measured by calculating the percentage of pixels on SEM images by selecting proper RGB value presenting pores. The details are shown in Appendix B.1. The partition of mass deposition inside and on

support skin is assumed to be equivalent to the percentage of pores on the membrane surface. As presented in Fig.5.6 (b), the pores are colored with the percentage of 15.87%.

Fig. 5.6 The SEM image of skin on support layer: (a) original FESEM images; (b) the FESEM image in which the pore areas are colored with read for calculation of percentage of pore-area on the surface.

In this study, a spacer was placed on draw side to fix external mass transfer coefficient to 5.17×10^{-5} m/s under crossflow rate as 1LPM, and empty channel was applied in feed side for preventing interruption on cake layer formation and thus resulting in mass transfer coefficient as 2.73×10^{-5} m/s. The specification of pacer can be found in details in (She et al. 2013). The model salt in feed and draw are both sodium chloride with ACS grade, and all solution are prepared using ultrapure water processed by Mill-Q system (Millipore integral 10 water purification system). Sodium chloride was chosen as model draw solution due to high solubility in water, high osmotic pressure, ease of measuring the concentration, nearly constant diffusivity over the range of concentration employed and no significant deviation from the Van't Hoff equation. The initial feed concentration was fixed at 50mM, while four stepping draw concentrations ranging from 1M to 4M were employed in critical flux determination. The concentration values above critical flux was selected for fouling experiment. The model colloidal foulants used in this study is LUDOX[®] SM-30 colloidal silica, which is monodispersed and with specific surface area as 320-440 (m²/g) and diameter as 7 nm based

on the information provided by manufacturer. The concentration of silica colloidal was fixed at 2g/L in all experiments.

The crossflow FO apparatus was presented in Chapter 3. To maintain constant weight/mass, DI water was added through a digital pump. The water flux J_w during period of T :

$$J_{w(T)} = \frac{(W_{DI(t_0)} - W_{DI(t_1)})}{\rho_w A_m T} \quad (5.35)$$

Where: $W_{DI(t_0)}$, $W_{DI(t_1)}$ represent the weight of DI water at the beginning of observation ($t=t_0$) and at the end of observation ($t=t_1$), T equals to $t_1 - t_0$ (s), ρ_w is the density of pure water ($\rho_w=1000\text{kg/m}^3$) and A_m is the effective membrane area (m^2).

The change in concentration of feed solution as a function of time was used to calculate the solute back diffusion flux:

$$J_{s(T)} = \frac{(C_{f(t_1)} - C_{f(t_0)})V}{A_m T} \quad (5.36)$$

Where: $C_{f(t_0)}$, $C_{f(t_1)}$ represent the concentration of feed side at the beginning of observation ($t=t_0$) and at the end of observation ($t=t_1$), V is the volume of feed solution (m^3), which was maintained at constant level.

5.3.2 Fouling experiments

Feed solution contained 2000 mg/L colloidal silica and 50 mM NaCl was used in all fouling experiments. The membrane orientation used in this study is all AL-DS mode. First, draw solution concentration-stepping (equivalent to flux-stepping in pressure-driven membrane processes) experiments from 1 to 4 M were performed to identify the critical concentration (equivalent to critical flux in pressure-driven membrane processes) of FO process under which negligible fouling was observed. Each step lasted 2 hours. It was identified that the critical concentration of draw solution in this study was between 2 M and 3 M. Thus, subsequent long-term fouling experiments of 10 hours were conducted at draw solution concentrations of 3 M and 4 M, which were above the critical concentration. Triplicate fouling experiments at each condition were performed.

5.4 Results and discussion

5.4.1 water flux profile

Fig. 5.7 Comparison of experimental flux data and the results obtained through the model. Modelling results and experimental data were obtained through averaging triplicates: (a) Baseline, (b) Fouling with 2000mg/L silica colloids. R^2 is 0.99, 1.00 for draw solution of 3 M and 4 M NaCl, respectively. Membrane orientation: AL-DS mode. Error bar in fouling experiments represents standard deviation of triplicates (blue: draw concentration is 3 M NaCl, red: draw concentration is 4 M NaCl)

Fig. 5.8 Particle deposition factor extracted from optimization process under different fouling stage (blue triangle: draw concentration is 3 M NaCl, red dot: draw concentration is 4 M NaCl). The particle deposition factor is obtained from flux/solute flux data every 30mins.

In osmotically-driven membrane process, monitoring flux baseline provides a benchmark for judging if fouling process starts. The information is of significance in understanding the degree to which membrane is fouled and subsequent replacement plan in industrial system. Unlike pressurized membrane process such as RO, in which water flux stays relatively unchanged in foulants-free condition, in FO process flux declines when solute molecules diffuse or (and) feed/draw solutions are not immediately replenished. In this experiment, experimental condition is simulated as: replenishing feed solution to monitor back solute diffusion; keeping draw concentration constant through dosing higher concentration NaCl. As shown in Fig. 5.7, experimental data are in good agreement with modelling results. Experimentally and numerically, enhancement of draw concentration from 3M to 4M has nearly non-observable effect on percentage of flux decline in foulants-free condition. Enhancement of BSD on higher draw solution condition increases the bulk feed concentration, which was then further magnified through concentration polarization in return. As result, flux profile under two conditions nearly in parallel, in which nearly 5% flux decline was observed after 200 mins.

As shown in Fig.5.7 at the end of 10hrs fouling process the flux retained in 3M and 4M draw concentration conditions are 16.6 ± 0.6 LMH and 14.6 ± 0.2 LMH, respectively. Curve fitting process in 3M, 4M conditions achieves R^2 above 0.95, which indicates the excellent simulation

of experimental flux decline. The results are comparable to the values achieved by a similar study modeling colloidal deposition on AL-FS mode (0.905 and 0.980 in two colloidal concentration, respectively) (Park et al. 2013). This study and (Park et al. 2013) adopted empirical equation and Carman-Kozeny equation to simulate fouling-enhanced concentration polarization and fouling-enhanced resistance respectively. With respect to the similar sustainable flux at the end of fouling in two operating conditions, it is in agreement with previous studies which proposed interaction energy between new foulants and deposited foulants plays a dominative role in determining sustainable flux (Bacchin et al. 2006; Hughes et al. 2006).

The particle deposition factor, K_p , as a function of time extracted from modeling is shown in Fig. 5.8. It is noted that K_p varies as fouling progresses and displays a parabolic profile, in which it increases at early stage and decreases at late stage of fouling. In addition, the magnitude of enhancement at early stage of fouling appears to be more drastic for 4 M NaCl draw solution. The reasons and interpretation are discussed based on several indices in BPNN as presented in Section 5.4.3.

Fig. 5.9. Profile of (a) mass transfer of fouled fraction of blocked pore, K_f , (b) mass transfer of cake layer, K_c , (c) ratio of overall mass transfer to initial mass transfer;

(d) hydraulic resistance of blocked pore, R_f , (e) hydraulic resistance of cake layer, R_c , (f) ratio of total resistance to initial resistance as a function of time obtained through modeling. Error bar represents standard deviation of triplicates (blue triangle: draw concentration is 3 M NaCl, red dot: draw concentration is 4 M NaCl).

The R_f , R_c , K_f , K_c are obtained through modeling as a function of fouling time and presented in Fig. 5.9 (data are processed through algorithmic function for better illustration). As shown, higher draw solution concentration, i.e., 4 M NaCl, accelerates overall mass transfer decline (Fig. 5.9(c)) and total resistance enhancement (Fig. 5.9(f)). In details, the impact of fouling on overall mass transfer is more significant, in which ~70% and ~85% decline is observed at 3 M and 4 M NaCl draw solution, respectively; while only ~35% to ~40% increase in total resistance is observed at 3 M and 4 M NaCl draw solution, respectively. Thus, the enhanced internal concentration polarization is greater than hydraulic resistance as a result of FO fouling in AL-DS mode. In addition, it is found that resistance and internal concentration polarization due to cake layer, i.e., R_c and K_c , respectively, are greater than due to pore blocking, i.e., R_f and K_f , respectively. Previous work (She et al. 2016) assumed the overall contribution of pore blocking and cake layer formation on flux decline but did not identify individual contribution as these parameters during fouling could not be measured experimentally. Nonetheless, take note that current simulation only considers fouling without membrane cleaning in one cycle of operation, i.e., 10 h. Typically, the cake layer can be easily removed via physical cleaning, i.e., reversible fouling, while the blocked pore is typically irreversible fouling, thus the long-term impact of pore blocking and cake layer formation may change in multiple cycles of operation that include membrane fouling and cleaning.

5.4.2 Analysis of BPNN

As the important part of neural networks optimization, three important hyper-parameters are optimized through trial and error method: learning rate, number of nodes in each layer and number of layers. The optimization process of tuning learning rate and number of nodes in NN based on Pearson coefficient and R^2 are presented in Fig.5.9, in which two numbers are both in the range between 0 and 1. The higher of Pearson's coefficient and R^2 , the better performance of NN in test data set. It is noted that the test set is the data set which is not used to train NN thus is normally used as a reliable check to avoid over-fitting problem. As shown in Fig. 5.10,

the performance of NN is positively related to number of nodes in hidden layers in each level of learning rate. With increasing number of nodes and complexity of NN, it's capable of capturing more non-linear relationship which is overlooked by simpler model. The highest R^2 and Pearson's coefficient obtained from the models trained in this study reaches over 95.2% and 97.5% respectively. Even in the NN with the simplest structure (50 nodes in both first and second hidden layer), the R^2 and Pearson's coefficient are able to reach 76.1% and 87.5% respectively. The result shows the great capability of NN in predicting particle deposition factor with changing experimental variables. The great agreement between test data set and predictions proves the accuracy of prediction ability of NN on small dataset with low dimensionality (Zhu et al. 2019; Ahmad et al. 2017). Moreover, the model is also sensitive to learning rate. When learning rate is low, i.e. 0.0002 and 0.005, increasing number of nodes in hidden layer results in significantly increase of prediction accuracy. By contrast, when learning rate is high as 0.005 and 0.01, the influence of number of nodes in prediction accuracy is quite fluctuating, which is attributed to the local minimum problem caused by large learning step. Besides of number of nodes and learning rate, another important parameter is number of layers. Increasing number of layers has potential to increase prediction accuracy by addressing more non-linear characteristics between output and features, while calculation time is also increased. Trial-and-error test of sets of parameter combination was presented in Tab 5.2. As shown by results, increasing number of nodes does not leads to much higher accuracy when structure of neural networks is too simple: increasing nodes from 100 to 500 in NN with only one hidden layer increase R^2 from 0.736 to only 0.776. By contrast, increasing 100 nodes to 500 nodes in NN with 2 hidden layers increase R^2 from 0.787 to 0.907 in test set. This is explained by simple structure fails to capture non-linear relationship between variables. Moreover, adding number of layers is not always helpful in prediction accuracy enhancement: adding one more hidden layer to NN with 2 hidden layers and 500 nodes in each layer reduces both R^2 and Pearson's coefficient in training set and test set. Finally, the positive correlation between R^2 in training set and test set indicates the mitigation of over-fitting problem, i.e. the NN with structure that makes it perform well in training set also results in high prediction accuracy in the test set.

Table 5.2 The influence of number of hidden layers on performance of neural networks in training set and test set

Number of hidden layers	Number of nodes in each layer	R^2 (training set)	R^2 (test set)	Pearson's coefficient (training set)	Pearson's coefficient (test set)
1	50	0.741	0.701	0.864	0.846
1	100	0.755	0.736	0.870	0.859
1	500	0.731	0.776	0.870	0.897
2	50	0.831	0.728	0.912	0.855
2	100	0.846	0.787	0.921	0.890
2	500	0.952	0.907	0.976	0.955
3	50	0.900	0.800	0.947	0.901
3	100	0.956	0.872	0.979	0.937
3	500	0.923	0.840	0.970	0.936

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Fig. 5.10. The Pearson's coefficient and R^2 of predictions on test set based on different learning rate and number of nodes NN with 2 hidden layers (H1, H2 indicate hidden layer 1 and hidden layer 2, respectively.)

The neural networks with the hyper-parameters which gives the best performance in training set are used to validate its applicability in test set. The profile of cost function, the prediction accuracy in training set/ test set are shown in Fig.5.11 (a), (b). As shown in (a), the learning rate as 0.0005 results in overall monotonic reduction of cost function as number of epochs grows in training set. The final result of cost function (RMSE) as 0.0035 suggests the effectiveness and stability of Adam optimizer, the one used in this study, in optimizing neural networks. The R^2 and Pearson's coefficient in test set are 0.938 and 0.970, respectively, which indicates the prediction accuracy of optimized neural networks in independent test set. The high prediction accuracy of neural networks is resulted from its ability to capture non-linear relationship between output and features. Moreover, when sample size is small, neural networks are expected to have improved prediction accuracy on dataset with low dimensionality(Zhu et al. 2019; Ahmad et al. 2017), which is in agreement with the real case of our study. In order to further analyse the sources of deviation in particle deposition factors under different experimental conditions, the deviation between result from curving fitting and result from neural networks are calculated through subtracting the former by the latter and

presented in Fig. 5.12. As shown in result, corresponding to low particle deposition factors under 3mol/L as draw solution, the deviation between results from curving fitting and neural networks is also small, with mean and standard deviation as -0.008 and 0.040, respectively. Increasing draw conc. into 4mol/L not only increases a portion of deposition factor above 0.6, the upper bound for the counterpart under 3mol/L at draw solution, but also enlarges the deviation, which is indicated by mean difference as -0.01 and standard deviation as 0.071. The higher deviation on data under higher draw solution conditions can be attributed to two factors: (a) In optimization process, although real-time experimentally measurable parameters, such as water flux, solute flux, feed concentration are measured every 5 mins, particle deposition data are obtained through curve fitting these parameters in a pre-defined period as 30 mins (30 mins are determined through pre-experiments: data stability is compromised during shorter period due to high measurement errors relative to small changes in flux and concentration; data sensitivity is reduced during longer period due to severe changes on physiochemical properties of both membrane, particle and feed components). In this regard, particle deposition factor in every consecutive period with length as 30 mins are assumed to be same in optimization, while they can be different when they are predicted by neural networks, which makes prediction based on data obtained every 5 mins. This inherent difference results in non-avoidable deviation as result. (b) At high draw solution concentration, the higher water flux, server back solution diffusion is expected to change particle-particle interaction and particle-membrane interaction more severely through accelerating colloidal destabilization, enhancing surface roughness of membrane et al. Besides of main driving force and shear stress, these factors are proved to contribute to revolution of particle deposition factor in previous studies(Henry et al. 2012; Hoek et al. 2003).

Fig. 5.11 (a) the profile of cost in 2000 epochs, in each epoch the mini batch consisting of 100 data randomly selected from training set. (b) The results of data in training set and test set (blue square: particle deposition factor obtained from curve fitting experimental data, red triangle: particle deposition factor obtained from neural networks; the data from curve fitting are placed in ascending order for better illustration)

Fig. 5.12 Deviation of particle deposition factor between data from curving fitting and predicted data from neural networks with optimized structure (number of hidden layers: 2; number of nodes in each layer: 700, learning rate:0.0005).

5.4.3 Interpretation of weights matrix of BPNN

BPNN is proven to be effective in predicting multivariate data with non-linear characteristics, but in most cases they are treated as a ‘black box’ where the interpretability of weights matrix is vague (Maier et al. 2000). In engineering study, understanding the way inputs relate to the output is of great significance in shedding light on experimentally inaccessible process and providing suggestion to operating conditions. Sometimes the interpretability of model is as important as the prediction accuracy of model. Driven by this incentive, interpretability of neural networks is drawing increasing attention, thus several traditional and innovative indices are raised in recent papers (Gevrey et al. 2003; Shrikumar et al. 2017; Lundberg et al. 2017; Zhu et al. 2019). In this study, the gradient-based indices ‘*Partial Derivatives*’ (*PaD*) is selected to generalize change of driving forces of particle deposition in fouling process. In order to determine the negative/positive impact of various input parameters as fouling grows, ‘*PaD*’ method is applied to calculate the partial derivative of output prediction corresponding to various input parameters. The average of ‘*PaD*’ with respect to each parameter in early fouling stage (0 – 5 h), late fouling stage (5 – 10 h) and overall fouling time (0 – 10 h) are shown in Fig. 14. and separate data are presented in Fig. 15. Mapping partial derivative corresponding to input parameters enable direct access to the influence of input on output (Gevrey et al. 2003). If the partial derivative corresponds to an input parameter is positive, the output is expected to increase as this parameter increases, and vice versa. In this regard, the

change of sign of contribution of a factor in time domain is attributed to switching from positive (negative) role to negative (positive) role.

The '*fouling time*' parameter is identified as positive contributor to particle deposition at early fouling stage and strongly negative contributor at late fouling stage. Despite difference of definition, i.e., Chong et al. incorporated the critical flux concept (Chong et al. 2008) while Tang et al. (Liu et al. 2018) incorporated membrane-particle interaction energy barrier, the particle deposition factor was obtained as a fixed value and it was assumed that initial flux provided greatest driving force at early stage of fouling. Despite excellent prediction accuracy in pressure-driven process like NF/RO, dilute foulant assumption was adopted in these models, in which particle-particle interaction was either neglected or assumed to be much less than particle-membrane interaction (Liu et al. 2018). On the other hand, increasing number of works revealed the important transition from particle-membrane interaction to particle-particle interaction due to factors include colloidal destabilization in concentration polarization layer (Bacchin et al. 2002) and altered surface roughness (Hoek et al. 2003). The contribution of '*fouling time*' parameter is in agreement with the two-stage theory of particle deposition: (i) In early stage, the energy barrier between newly deposited particle and membrane is gradually decreased due to increasing coverage of deposited particles on membrane surface, which is reflected as increasing particle deposition factor; (ii) In late stage, when the membrane surface is fully covered by colloidal particles, the convective driving force dominates again and results in the decreasing particle deposition factor profile. The average contribution of '*feed concentration*' is slightly negative as -0.29 in early stage and changes to positive as 0.99 in late stage of fouling. The increasing positive contribution of feed concentration in late stage is ascribed to increasing internal concentration polarization in cake layer, in which high solute concentration is expected to promote colloidal destabilization in cake layer (Boo et al. 2012). On the other hand, the contribution of '*draw concentration*' is strongly positive as 0.87 in early stage but diminishes to 0.02 in late stage of fouling. It is not surprising that positive contribution from draw concentration since higher draw concentration is always expected to promote higher initial flux (i.e., higher driving force) and solute flux. In late stage of fouling, when J_w approaches $J_{w\text{ limiting}}$, the role of draw solution becomes less critical.

In summary, the above three parameters are identified to play changeable roles on particle deposition in different stages of fouling due to complicated interactions between hydrodynamic

conditions and feed/draw concentrations. This non-constant property is observed to be magnified under high draw concentration and long fouling time. In early stage of fouling, particle deposition is promoted by high draw concentration and transition from particle-membrane interaction to particle-particle interaction. During this period, reducing convective drag force and impeding early coverage of particle on membrane are important for fouling control. In late stage of fouling, especially after membrane is covered by foulants, the role of feed concentration is important as high ionic strength promotes colloidal destabilization. During this period, altering the feed concentration is expected to be effective in fouling mitigation.

Fig. 5.13 Average 'PaD' on (a) early fouling stage; (b) late fouling late; (c) overall fouling process.

Fig. 5.14 The individual ‘*PaD*’ with respect to each real-time parameter in overall 10-hrs fouling period.

5.5 Concluisions

Interpreting colloidal fouling in forward osmosis (FO) process in active-layer facing draw solution (AL-DS) mode is challenging due to continuously changing real-time parameters associated with transport mechanisms and process parameters as well as lack of availability of local conditions in the porous support-layer. In this study, artificial back-propagation neural networks (BPNN) is optimized and applied to train real-time particle deposition factors, K_p , which are extracted from an optimization process on a mathematical model. The K_p extracted from optimization process is not a constant, which increases at early stage and decreases at later stage of fouling. Correlating K_p with real-time experimental parameters through trained BPNN achieves high prediction accuracy with R^2 and Pearson’s coefficient as 0.938 and 0.970, respectively. Using the gradient-based indices is able to identify the positive/negative contributions of real-time parameters on particle deposition at different fouling stages: early stage includes fouling time and draw concentration, while later stage includes feed concentration. The result is in agreement with ‘two-stage’ fouling theory, which is characterized by transition from particle-membrane to particle-particle interactions. This study provides a new perspective to bridge traditional fouling model with machine learning techniques for interpreting particle deposition mechanism in FO process influenced by various inter-related parameters.

Compared to previous studies which rarely focus on flux performance prediction, this study further explores the contributions from multiple factors in changing micro-conditions in the process of membrane fouling, which provides more interpretable analysis rather than treating

2863 whole process as a black box. Admittedly, the training set is relatively small due to limitation
2864 in lab scale. However, with assistance of large amount of historical data in industrial scale, it's
2865 believed that this model is of great potential in contributing to early-stage fouling identification
2866 and development of auto-responsive cleaning strategies in future.

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CHAPTER 6. Modelling of microscopic particle trajectories on pore-blocking in forward osmosis (FO) process

6.1 Introduction

Membrane fouling is one of the main obstacles in forward osmosis (FO) process, which resulted in performance loss. More importantly, unlike the hydraulic-pressure driven membrane processes, membrane fouling in FO process is influenced by the membrane orientations. In the active-layer facing the feed-solution (AL-FS) mode, only external fouling occurs on the dense active layer of FO membrane, which results in the additional hydraulic resistance and cake layer-enhanced concentration polarisation effect. In contrast, the fouling of FO membrane is more complicated in the active-layer facing the draw-solution (AL-DS) mode as both external cake-layer and internal pore-blocking can occur simultaneously. Therefore, interpreting pore-blocking phenomenon is of importance to understand fouling mechanism in FO process.

In general, particle attachment in membrane process is complex that involves the interplay of particle properties, membrane properties, hydrodynamic conditions and feed components. For example, the reversed solute diffusion can impact on the feed bulk concentration and concentration polarisation in FO process (Park et al. 2013; She et al. 2016). For colloidal fouling in RO process, the enhancement of ionic strength near the membrane surface was found to destabilize silica colloidal particles (Sim et al. 2014), which can be explained by the DLVO theory (Magan et al. 2006; Hoek et al. 2003). The size of particles influenced the interaction energy in particle-particle and particle-membrane system (Foley et al. 1995; Henry and et al. 2012). In addition, the roughness of RO membrane surface as demonstrated by AFM analysis was found to impact the particle attachment (Hoek et al. 2003).

Based on these experimental findings, simulation and modelling tools are utilized by to explore the fouling mechanism, but previous work are limited to pore-blocking process in the hydraulic-pressure driven membrane processes, such as nanofiltration, microfiltration and reverse osmosis. The models with particle transport have been widely applied to simulate particle behaviour in a microscopic perspective (Henry et al. 2012). Frey et al. investigated the effect of hydrodynamic conditions on particle trajectories, in which the probability of particle

capture at the model filter surface were related to parameters such as pore size, particle radius and number of previous deposited particles (Frey et al. 2000). Gassara et al. further included the effect of ratio of particle size to pore size on percentage capture in microfiltration process, where the single trajectories of particle were visualized through the coupling forces of fluid, membrane and other particles. Moreover, the reduced permeability caused by particle deposition was calculated through the percentage of volume of deposited particles on pre-defined unit mesh (Gassara et al. 2008). In addition, a recent study by Agbangla et al. investigated the collective effects from hydrodynamic and colloidal interaction on the formation of pore-blocking, which was visualized in 3D meshes. Through the DLVO repulsive forces and particle interaction, five types of pore-blocking mechanisms were resulted from simulation which included monolayer deposition, no deposition, arch and dense deposit and bloc of non-adhered particles (Agbangla et al. 2014). In current study, the simulation approach based on integration of Langevin Equation on trajectory of single particle was applied to simulate particle deposition at the entrance of pore on support layer of FO membrane.

In this study, the effects of particle size of silica colloids on fouling in forward osmosis (FO) process were investigated via experimental, real-time detection technique as well as simulation and modelling approach. Firstly, different concentrations of particles in various sizes were studied in mono-dispersed system. In the experimental section, two types of particles were used to simulate the effect of pore-blocking and external fouling in AL-DS mode. Then, UTDR was applied to characterize internal and external fouling caused by silica colloidal particles with different particle size. Finally, dynamic modelling based on N-particles trajectories was applied to simulate pore-blocking percentage under different hydrodynamic conditions and feed components, which aimed to provide theoretical interpretation of internal fouling in FO process in AL-DS mode.

6.2 Model development

6.2.1 Computational domain

Fig. 6.1 The schematic view of 2D simulation domain in this study

The simulation conducted in this study was based on the computational domain shown in Fig 6.1. The thickness of computation domain is set to be 2 times of particle radius, which was also applied in previous study (Agbangla et al. 2014). All scales of particles and computational scale was set in nano-meter scale with boundary condition. All the particles were simulated and injected from random x position on the top of computational domain with certain frequency based on the flow rate and concentration of particles in feed solution. Based on the calculation consumption and modelling purpose, there were some adjustments and approximation applied as below.

As for the boundary condition L_y , since there was no crossflow applied in the experiments, a very high external concentration polarisation factor was resulted. Based on the flux data with pre-determined A value, B value, structural parameter S and external diluted concentration polarisation factor, the mass transfer coefficient was $\sim 5.16 \times 10^{-7}$ m/s. The boundary layer thickness was $\sim 1.1 \times 10^{-4}$ m which is calculated by mass transfer coefficient and diffusivity of silica colloid. The diffusivity of spherical silica colloid through liquid is calculated as 5.68×10^{-11} m²/s through Einstein equation (Henry et al. 2012). It is seen that the boundary thickness was significantly larger than the effective range of van der Waals and electrostatic double-layer

forces, as shown in Section 6.4.3.1. In this regard, since our focus is the situation near membrane surface, the thickness of boundary layer was set as 1000 nm. For dilute solution, based on the v/v as $7.7 \times 10^{-4} \text{ m}^3/\text{m}^3$, the interaction between particles was not considered outside of computational domain. The length of pore, which was $\sim 120 \mu\text{m}$ (i.e., based on SEM images), was larger than the effective range of short-range forces; thus the pore length was simulated as 100 nm since particle-particle interaction was negligible as distance was lower than 40 nm, as shown in Section 6.4.3.1. Since TFC FO membrane has very porous support-layer structure, the pore-blocking process was simulated to be fully governed by the particle-particle and particle-membrane interactions as well as hydrodynamic conditions, i.e., the pore was considered as completely filled when the force balance of single particle rejected its deposition into pores. The porosity of blocked-pore was simulated by random placement of N stationary particles inside of pores, and N was based on pore size R_p in simulation. Using silica particle with 7 nm diameter as example, the number of particles deposited in blocked-pore with certain porosity are calculated as:

Table 6.1 (a) The size information of silica particles used in this study; (b) The number of particles deposited in blocked-pore with different porosity

(a)

Particle size (m)	7×10^{-9}
Volume of particle (m^3)	1.79×10^{-25}

(b)

Porosity of blocked-pore (-)	Pore size (m)		
	20×10^{-9}	50×10^{-9}	200×10^{-9}
	Pore volume (m^3)		
	1.4×10^{-23}	3.5×10^{-23}	1.4×10^{-22}
1 (i.e., unblocked-pore)	0	0	0
0.5	39	98	392
0.1	55	137	548

Boundary L_x was adjusted based on the simulation of porosity of support-layer, in which pore was assumed to be straight cylindrical pore, and in current computational domain, the length

of L_x was inversely proportional to the porosity of support-layer when pore size was fixed as a constant. For example, when a support-layer with porosity of 0.8 and pore with diameter of 100 nm, then L_x was set as 125 nm. Moreover, with the change of L_x , the number of particles injected into the computational domain was also adjusted.

The first step was to estimate the pore size as well as porosity of support-layer, then the width of computational domain, L_x , was calculated. Since the computational domain was set, based on different water fluxes, the number of injected particles at time step Δt can be calculated. For example, at flux of 13 LMH, support-layer with pore diameter of 200 nm and porosity of 10%:

Table 6.2 Parameters used in simulation

Volume of particle (m^3)	1.79×10^{-25}
Water flux ($\text{m}^3/(\text{m}^2 \cdot \text{s})$)	3.61×10^{-6}
Computational width (m)	2000×10^{-9}
Computational surface area (m^2)	14×10^{-15}
Flow rate of water permeating through computational surface area (m^3/s)	50.54×10^{-22}
v/v of silica colloids at 2000 mg/L concentration (m^3/m^3)	7.7×10^{-4}
Number of silica colloids ($\text{particles}/\text{m}^3$)	4.31×10^{21}
Flow rate of silica colloids permeating through computational surface ($\text{particles}/\text{s}$)	22
Time step (s)	1×10^{-1}
Frequency of silica colloids injected into simulation per time step ($\text{particles}/\text{Time step}$)	2.2

The force components on single particle i are calculated as follows:

Fig. 6.2 The force components of from other particle and membrane on particle i

2983

2984 As shown in Fig. 6.2:

2985 $\tan \theta = \frac{y_j - y_i}{x_j - x_i}$ (6.1)

2986 The forces component from particle j on particle i along x axis:

2987 $F_{j_i x} = -F_{p-p} \cdot \cos \theta$ (6.2a)

2988 The forces components from particle j and membrane m on particle j along y axis:

2989 $F_{j_i x} = -F_{p-m} - F_{p-p} \cdot \sin \theta$ (6.2b)

2990 The particle attachment on surface covered by mono-layer particles are achieved by energy
2991 barrier approach (Henry et al. 2012), in which deposition occurs only when the kinetic energy
2992 of particle overcomes the energy barrier calculated through DLVO curve, otherwise the particle
2993 bounced back to the bulk:

2994 If: $\frac{1}{2} m_p V_p^2 > E_{barrier}$ *deposition* (6.3a)

2995 If: $\frac{1}{2} m_p V_p^2 < E_{barrier}$ *rebound* (6.3b)

2996 All the particles are treated with infinite small volumes, which enables overlap of particles in
2997 mono-layer formed on the surface.

2998

2999 **6.2.2 Particle trajectories**

3000 The particle trajectories are simulated by numerically integrating the Langevin Equation (Kim
3001 and Zydney 2005):

3002 $m_{pi} \frac{\partial \vec{u}_{pi}}{\partial t} = \vec{F}_c + \vec{F}_{VDW} + \vec{F}_{DL} + \vec{F}_B$ (6.4)

3003 Where $\vec{u}_{pi}$ stand for the velocity vector for single particle; $\vec{F}_c$, $\vec{F}_{VDW}$, $\vec{F}_{DL}$, $\vec{F}_B$ stand for the
3004 force vector representing convective drag force, sum of van der Waals forces of particle-
3005 particle and particle-membrane, sum of electrostatic forces of particle-particle and particle-
3006 membrane, random Brownian forces, respectively.

3007

The van der Waals forces of particle-particle and particle-membrane, i.e., between a particle with diameter d_1 and a membrane surface plane, between two particles with diameter d_1 and d_2 , are estimated (Hamaker 1937):

$$F_{p-p} = \frac{A}{12d_1} \left[\frac{y(2x+y+1)}{(x^2+xy+x)^2} + \frac{y(2x+y+1)}{(x^2+xy+x+y)^2} - \frac{y(2x+y+1)}{(x^2+xy+x)(x^2+xy+x+y)} \right] \quad (6.5a)$$

$$F_{p-m} = \frac{A}{12d_1} \left[\frac{1}{(x^2+1)^2} + \frac{2}{x+1} + \frac{1}{x^2} - \frac{2}{x} \right] \quad (6.5b)$$

Where: $x = \frac{d}{d_1}$, $y = \frac{d_2}{d_1}$, A is Hamaker's constant, d stands for the shortest distance between two spherical particles along the centre-centre direction.

For electrostatic interaction, the interaction energy is calculated by integrating differential electrostatic energy $e_{DL}(h)$ with respect to the area, dA , which is the differential projected area of small particles on membrane or large particle, as shown in Fig. 6.3. In cylindrical coordinates:

$$E_{DL} = \iint_{particle} e_{DL}(h) dA \quad (6.6)$$

$$E_{DL(h) p-m} = \int_0^{2\pi} \int_0^{d_1} \frac{\epsilon\epsilon_0\kappa}{2} [(\psi_m^2 + \psi_p^2)(1 - \coth \kappa h) + \frac{2\psi_m\psi_p}{\sinh \kappa h}] r dr d\theta \quad (6.7a)$$

$$E_{DL(h) p-p} = \int_0^{2\pi} \int_0^{d_1} \frac{\epsilon\epsilon_0\kappa}{2} [(2\psi_p^2)(1 - \coth \kappa h) + \frac{2\psi_p^2}{\sinh \kappa h}] r dr d\theta \quad (6.7b)$$

Where: ϵ_0 is the dielectric permittivity of vacuum, ϵ is the dielectric constant of the solvent, κ is the inverse Debye screening length, and ψ_p and ψ_m are the surface potentials of the sphere and the membrane, respectively. For particle-membrane, $h = d + d_1 - \sqrt{d_1^2 - r^2}$; for particle-particle, $h = d + d_1 + d_2 - \sqrt{d_1^2 - r^2} - \sqrt{d_2^2 - r^2}$

Fig. 6.3 The schematic illustration of p-m and p-p system in electrostatic energy calculation

Similar to calculation of Van-Der-Waals force, differentiation of interaction energy expression with respect to d gives the expression of electrostatic force:

$$F_{DL(h) p-m} = \int_0^{2\pi} \int_0^{d1} \frac{\epsilon\epsilon_0\kappa}{2} \left[\frac{(\psi_m^2 + \psi_p^2)\kappa}{(\sinh \kappa h)^2} + \frac{2\psi_m\psi_p\kappa}{\sinh \kappa h \cdot \tanh \kappa h} \right] r dr d\theta \quad (6.8a)$$

$$F_{DL(h) p-p} = \int_0^{2\pi} \int_0^{d1} \frac{\epsilon\epsilon_0\kappa}{2} \left[\frac{(2\psi_p^2)\kappa}{(\sinh \kappa h)^2} + \frac{2\psi_p^2\kappa}{\sinh \kappa h \cdot \tanh \kappa h} \right] r dr d\theta \quad (6.8b)$$

Where h maintains the same definition as it is in equation (6.8).

In order to further consider the effect of back solute diffusion on ionic strength, which promotes colloidal destabilization, ϵ , κ , ψ_p and ψ_m are further connected with local ionic strength.

Dielectric constant for sodium chloride solution ϵ is correlated with solution concentration c (Gavish et al. 2016):

$$\epsilon(c) = \epsilon_w - \beta L \left(\frac{3\alpha}{\beta} c \right) \quad (6.9)$$

$$L(v) = \coth v - \frac{1}{v}$$

Where: $\beta = \epsilon_w - \epsilon_{ms}$, ϵ_w , ϵ_{ms} stand for dielectric constant for pure water and limiting dielectric constant of the highly concentrated electrolyte solution, respectively; c is the concentration of electrolyte.

For monovalent ions, inverse Debye screening length κ are correlated to solution concentration c (Dukhin et al. 2017):

$$\kappa(c) = \frac{\sqrt{2c}}{0.304} \quad (6.10)$$

The random Brownian forces are simulated through Gaussian white noise process (Kim et al. 2005; Li et al. 1992):

$$\vec{F}_B = \gamma_1 \sqrt{\frac{12\pi\mu k_B T}{\Delta t}} \hat{i} + \gamma_2 \sqrt{\frac{12\pi\mu k_B T}{\Delta t}} \hat{j} \quad (6.11)$$

Where: k_B is the Boltzmann constant, μ is the solvent viscosity, T is the absolute temperature, and Δt is the magnitude of the time step, γ_1 and γ_2 are independent random numbers obtained from Gaussian distribution with zero mean and unit variance.

The convective drag force acting on every single particle was expressed by Stokes force expression (Gassara et al. 2008):

$$\vec{F}_c = 6\pi\eta r(u_p - u_f) \quad (6.12)$$

Where η presents fluid viscosity (Pa·s), r presents particle radius (m), u_p, u_f present velocity of particle and fluid, respectively.

6.3 Experimental methods

6.3.1 Materials and experimental setup

The FO membrane coupons used in this study was cut from the commercial thin film composite (TFC) FO spiral wound module (FO0404, Toray Chemical Korea Inc). The TFC FO membrane consisted of a polyamide dense selective-layer on a polysulfone porous support-layer with an embedded woven mesh to enhance the mechanical strength. The overall thickness of FO membrane was ~ 100 - $120 \mu\text{m}$ without observable spatial difference. The TFC FO membrane's resistance, salt permeability (i.e., B value), and structural parameter (S value) were measured using the RO-FO protocol as $7.15 \pm 0.04 \times 10^{12} \text{ l/m}$, $2.14 \pm 0.14 \times 10^{-7} \text{ m/s}$ and $780 \pm 111 \mu\text{m}$, respectively. Mono-dispersed and bi-dispersed systems of silica colloids with diameters of 7 and 300 nm were used in this study; the test solutions were prepared from stock solution (Sigma Aldrich, LUDOX[®] SM-30, specific surface area of 320-440 m^2/g , diameter = 7 nm) and by dissolving silica microspheres (ITS science& medical) in deionized water, respectively. The test solutions were sonicated to disperse the particles. No adjustment was made to the testing solutions at $\sim \text{pH } 6$.

The FO setup and UTDR setup was as described in Chapter 3 and Chapter 4, respectively.

6.3.2 Fouling experiment

In the FO fouling experiments, the draw side was operated in crossflow mode at 250 mL/min, while the feed side was operated in dead-end mode. The test conditions are summarized in Table 6.3. The purpose of experiments are as follow:

- (i) In AL-FS mode, M1, M2, M3, M4 are to investigate the effects of particle size and initial flux on particle deposition, and the data are used for real-time UTDR characterization;
- (ii) In AL-DS mode, M5, M6, M9, M12 are to investigate the effects of particle size and initial flux on particle deposition;
- (iii) In AL-DS mode, M7, M8, M9 are to investigate the effects of particle (300 nm) concentration on pore-blocking process; M10, M11, M12 are to investigate the effects of particle (7 nm) concentration on pore-blocking process.

Table 6.3 Experimental conditions

No.	Membrane orientation	Draw solution conc. (M)	Conc. of 300 nm silica colloids (mg/L)	Conc. of 7 nm silica colloids (mg/L)	Initial flux (LMH)
M1	AL-FS mode	1	2000	0	~13
M2		2	2000	0	~20
M3		1	0	2000	~13
M4		2	0	2000	~20
M5	AL-DS mode	0.5	0	2000	~13
M6		0.5	2000	0	~13
M7		1	500	0	~20
M8		1	1000	0	~20
M9		1	2000	0	~20
M10		1	0	500	~20
M11		1	0	1000	~20
M12		1	0	2000	~20

6.4 Results and discussion

6.4.1 Experimental results

6.4.1.1. Effect of draw concentration on pore-blocking

Fig. 6.4 Water flux profile under different initial flux and particle size conditions, concentration of silica colloids is fixed at 2000 mg/L on AL-DS mode (The number refers to experimental conditions listed in Tab 6.3).

The water flux profile under low and high initial flux on AL-DS mode are presented in Fig. 6.4. As shown, the normalized flux decline for smaller particles with diameter of 7 nm was greater than larger particles with diameter of 300 nm. In addition, the impact of initial flux on fouling of smaller particles was more significant, while only marginal difference was observed for bigger particles.

6.4.1.2 Effect of total particle concentration (mono-dispersed system)

Fig. 6.5 Water flux profile under different particle concentration in AL-DS mode.

The draw concentration is fixed as 1mol/L. (The number refers to experimental conditions listed in Tab 6.3)

As shown in Fig.6.5, in mono-dispersed system, the effect of concentration of particle on flux decline was noted only when silica colloids with diameter of 7 nm was used as foulant, i.e., lowering the concentration from 100% to 50% of 2000 mg/L reduced the fouling rate. However, only marginal reduction in fouling rate was observed with further reduction of particle concentration to 25% of 2000 mg/L. In contrast, no significant difference in the flux decline profiles when different concentrations of feed solution containing 300 nm silica colloids was used. The result is attributed to difference of fouling type caused by colloidal particles with

different size compared to pore size. The rapid flux decline was resulted from strong internal concentration polarization in fouling experiment challenged by 7nm colloidal particles, while particle with 300nm diameter only caused surface fouling.

6.4.2 UTDR Characterization of membrane fouling in TFC membrane

The application of UTDR and UFDR on fouling detection on CTA membrane is already made and analysed in details in Chapter 4. Due to the difference of membrane structures and mechanism of fouling deposition, the UTDR real-time characterization was also made on fouling deposition on TFC membrane used in this study. The purpose of this section is to provide a comparison of signals obtained from TFC membrane and CTA membrane as responses to fouling in same initial flux condition. The experimental conditions include both AL-FS mode and AL-DS mode with feed solution mono-dispersed with silica colloids with different particle size.

As shown in Fig. 6.6, the UTDR signal reflected from membrane surface after 0 min, 30mins, 60mins, 90 mins and 120 mins of fouling on AL-FS mode are presented: (a) presents the signal from membrane fouled by 7nm 2000ppm silica colloids; (b) presents the signal from membrane fouled by 300nm 2000ppm silica colloids. As the results show, the peaks near 4.7 μ s was detected, which presents the groups generated by placement of membrane. As fouling proceeds, nearly no observable signal changes are detected with respect to both amplitude and arrival time. The result is quite different from the results obtained from CTA membrane under same initial flux in Chapter 4. The result indicates that under AL-FS mode, UTDR is unable to detect cake layer build-up regardless of size of silica particle. This different can be attributed to difference of structures of support layer between CTA membrane and TFC membrane. As shown in Chapter 4, the structure of support layer of CTA membrane is more asymmetrical than the structure of support layer of TFC membrane. The high porous structure with pores towards different directions is expected to cause strong signal attenuation, which results in much less energy was transmitted into active layer.

Fig. 6.6 The UTDR signal of TFC membrane fouled by 2000ppm silica colloids after 0 min, 30mins, 60 mins, 90 mins and 120 min on AL-FS mode. Other experimental conditions: particle size 7nm (a), 300nm (b), crossflow rate on draw size: 250mL/min; feed solution: DI water; draw solution: 2mol/L; initial flux: ~20LMH.

The result under same initial flux on AL-DS mode are presented in Fig. 6.7. As same as the experimental condition applied on AL-FS mode, (a) presents the signal from membrane fouled by 7nm 2000ppm silica colloid and (b) presents the signal from membrane fouled by 300nm 2000ppm silica colloids, respectively. As shown as (b) below, the UTDR signal reflected from

membrane fouled by silica colloids with different size exhibit significant difference. When 300nm silica particle was applied, nearly no change on signal was detected, which is quite similar to the signal profile on AL-FS mode. By contrast, as shown by (a), when fouling is initiated by silica particles with size as 7nm, sensitive change was detected after 30mins of fouling with respect to both arrival time and amplitude. For better illustration, the signals on 0 mins, 30 mins, 60 mins, 90 mins, 120 mins in (a) are shifted parallelly and presented as small graph in (a). As shown by (a), the UTDR signal is observed to shift towards left with increasing period of fouling. Moreover, a small peak was raised at the end of signal. Based on the previous experimental on AL-FS mode, it's concluded that UTDR is unable to penetrate TFC support layer due to complex porous structure. Meanwhile, the change of peak occurred at the first peak, which indicates interface of draw/membrane bottom. All these are combined to prove that the change of signal on AL-FS mode fouled by 7nm silica particle is the result of severe pore-clogging. By contrast, the nearly no response on membrane fouled by 300nm silica particle on AL-DS mode is result of external fouling. Even though membrane was operated on AL-DS mode, the fact that particle size is larger than pore size on support layer makes the fouling is only a surface phenomenon. To further characterize TFC membrane fouled by small particles, the time domain signal is further transformed into time-frequency domain through Short-Time Fourier Transform (STFT). All peaks are included in calculation of total reflected power to characterize overall fouling status, which is shown in Fig.6.8. As the result shows, growth of fouling increases overall total reflected power, which is similar to the result obtained in fouled CTA membrane from Chapter 4. However, it's noteworthy that enhancement of total reflected power from fouled TFC membrane almost happens at the first 30 mins of fouling. After that, the total reflected power is kept at the relatively stable status even though fouling still exists at later stage. This result can be explained by highly porous structure of TFC membrane substrate, which causes internal fouling quite quickly at first 30mins due to high initial flux. After that, strong internal concentration polarization and repulsive effect from deposited particles slow down the internal fouling process. The growth of TRP trend also suggest the internal fouling is severe at membrane with highly porous substrate on AL-DS mode.

Fig. 6.7 The UTDR signal of TFC membrane fouled by 2000ppm silica colloids after 0 min, 30mins, 60 mins, 90 mins and 120 min on AL-DS mode. Other experimental conditions: particle size 7nm (a), 300nm (b), crossflow rate on draw size: 250mL/min; feed solution: DI water; draw solution: 1mol/L; initial flux: ~20LMH.

Fig. 6.8 The normalized total reflected power of TFC membrane fouled by 2000ppm silica colloids after 0 min, 30mins, 60 mins, 90 mins and 120 min on AL-DS mode. Other experimental conditions: particle size 7nm; crossflow rate on draw size: 250mL/min; feed solution: DI water; draw solution: 1mol/L; initial flux: ~20LMH. The result is average of duplicates.

6.4.3 Modelling on pore-blocking process

6.4.3.1 Interaction energy in particle-particle (p-p) system and particle-membrane (p-m) system

The interaction energies of particle-particle and particle-membrane systems under different background NaCl concentrations are presented in Fig. 6.9 and Fig. 6.10. A positive interaction energy value indicates the amount of energy required to decrease the distance between particle-particle and particle-membrane, which is contributed by the electrostatic double layer force. A negative interaction energy value indicates the attraction between particle-particle or particle-membrane as they approach, which is contributed van der Waals force. The sum of both refers to the energy barrier that particle-particle or particle-membrane need to overcome before attachment can occur.

3215 The interaction energy is significantly influenced by particle size; at 0.001 M NaCl, the energy
 3216 barrier required to overcome by particle with 300 nm is nearly 80 times more than particle with
 3217 7nm. Moreover, increasing the concentration of NaCl, the electrostatic repulsive interaction
 3218 energy is suppressed, i.e., when the background NaCl is increased from 0.001 to 0.01 M, the
 3219 distance which makes electrostatic interaction energy becomes zero decreases from 20 nm to
 3220 7.5 nm due to reduction in Debye-Huckel length (Henry et al. 2012).

3221

3222

Fig. 6.9 DLVO reaction energy between two sphere silica colloidal particles in different background NaCl concentration, which is presented in KT (K is Boltzmann constant $1.38 \times 10^{-23} \text{J} \cdot \text{K}^{-1}$, T is temperature K). Red dash line: electrostatic double layer interaction energy; Green dash line: Van Der Waals interaction energy; Blue solid line: Total interaction energy.

Fig. 6.10 DLVO reaction energy between a sphere silica colloidal particle and membrane surface in different background NaCl concentration, which is presented in KT (K is Boltzmann constant $1.38 \times 10^{-23} \text{J} \cdot \text{K}^{-1}$, T is temperature K). Red dash line: electrostatic double layer interaction energy; Green dash line: Van Der Waals interaction energy; Blue solid line: Total interaction energy

6.4.3.2 Effect of initial flux

In order to investigate the effect of initial flux on distribution of particles inside pore, on external surface of porous support-layer and in suspension, different initial fluxes are tested in AL-DS mode: 13 LMH and 20 LMH. The initial flux impacts on simulation in two perspectives: (a) injection frequency of particles need to be adjusted since more particles are brought by water flux in certain time step; (b) the initial convective drag force on single particle should be increased. The simulation period for both are 1200 time steps, which correspond to 120 particles and 204 particles under 13 LMH and 20 LMH, respectively. The simulation parameters are shown below:

Table 6.4 The parameters for simulation of effect of initial flux

Simulation periods (s)	30
------------------------	----

Simulation pore length (nm)	120
Pore radius (nm)	200
Porosity of membrane (-)	0.66
Background NaCl concentration (M)	0.001
Total time steps (-)	1200
Total number of particles (-)	120 under 13 LMH
	204 under 20 LMH

As shown in Fig 6.11. increasing the initial flux results in increasing number of particles into computational domain after 10 s and 30 s, respectively. It is no surprise that nearly all particles are deposited inside pore at early stage of fouling for both initial flux conditions. The number and distribution of particles in suspension, on external surface of porous support-layer and inside pore are summarized in Fig. 6.9 (a) and (b), respectively; and the changes in porosity of porous support-layer is summarized in Fig. 6.11(c). The porosity decreases sharply at higher initial flux of 20 LMH, in which ~90% of injected particles are deposited inside pore at early stage of fouling that leads to severe internal concentration polarization. As fouling progresses, for example from 1st 10 s to the 2nd 10 s, the percentage of newly injected particles that deposited inside pore are decreased from ~90% to ~65%. Meanwhile the percentage of newly injected particles that deposited inside pore is just slightly decreased from 0.875 ± 0.000 to 0.872 ± 0.036 under 13LMH. Moreover, at the 3rd 10s, the percentage of newly injected particles that deposited inside pore is 0.663 ± 0.018 and 0.668 ± 0.04 under 13LMH and 20LMH, respectively. The result suggests that the more old particle deposited inside of pore the less new particle will be deposited inside of pore. It also explained why increasing initial flux results in much significant water flux on AL-DS mode on early stage and become stable at later stage: at beginning, increasing water flux impacts on not only increasing dragging force but also more particles towards membrane. Moreover, in membrane with large pore size and highly porous structure nearly all particles deposit on pores, which is shown in simulation as around 90%, and the resultant internal concentration decrease water flux rapidly as result (not shown in current simulation). With increasing number of particles in pores, not only does convective dragging force decreases but also strong repulsive force from deposited particles decrease the ratio of particles in pore to newly injected particles.

(a) Initial flux as 13 LMH

(b) Initial flux as 20LMH

Fig. 6.11 The simulation results of particles behavior under two initial flux conditions (The framework of graph shows the simulation domain with unit as nm in both x and y axis).

Fig. 6.12 (a) The number of particles in suspension, on external surface of porous support-layer, inside pore as a function of total particles: empty marker presents value at 13 LMH, filled marker present values at 20 LMH; (b) the percentage of particles in suspension, on external surface of porous support-layer, inside pore as a function of total particles;(c) The changes in porosity of porous supported-layer as a function of simulated time period.

6.4.3.3 Effect of silica concentration on pore-blocking: Early stage of fouling

Based on water flux profile, it is seen that on early stage increasing particle concentration is plays dominative role in water flux profile. Moreover, water flux is not only impacted by blocking status of pore but also water flux because of ICP-compensation effect: the water flux decline is mitigated by fouling due to mitigation of internal concentration polarization. More specifically, the blocking process is also governed by two factors: concentration of silica colloids and percentage of silica entering the pores. In order to study silica concentration on percentage of particles distributed in suspension, deposition and blocking, the simulation conducted fixing initial flux as 13LMH, pore size 200nm, porosity as 0.67. The back ground

NaCl concentration is set as 0.001M. The size of particle is 7nm. The different concentration of silica colloids is realized through injecting particles into computational domain with different frequency while keep all other parameters constant: 1 particle/ 40 time steps, 1 particles/ 20 time steps, 1 particles/ 10 time steps. Totally, 1200 time steps are tested in simulation.

The profiles of dynamic particle location are shown in Fig.6.13. and results of simulation is presented in Fig 6.14. As shown in Fig 6.13 (a), (b). when silica concentration is low, under such dilute condition nearly all particles injected into computational domain are deposited inside of pores, which cause severe internal concentration polarization. With increasing of particle concentration, it's seen that some particles are suspended back toward bulk after 20s as simulation period as shown in Fig.6.13 (c). Moreover, after 30s, increasing number of particles is either suspended or deposited on the surface sounding the pore. It suggests a transition that, even at simulation condition with large pore size and high porosity, percentage of particle blocking is decreased with increasing number of particles already deposited. It's noteworthy that constant water flux was applied in this simulation. By contrast, in reality water flux is negatively influenced by particle deposition, which decreases convective force dragging particles towards membrane. It is expected that the effect of repulsive forces from deposited particles on new particles will be increasing obvious as fouling proceeds. The summary of simulation is presented in Fig: (a) indicates the number of particles in suspension, deposited on membrane and blocked inside of pores in different simulation periods with different injection frequency; (b) Indicates the percentage of particles in different sinks during different simulation term. For example, 0.663 ± 0.018 'blocking' at 120 total particles indicates that 0.663 ± 0.018 percentage of particles depositing in pores out of 40 particles which injected from 20ns to 30ns interval. (c) indicates the porosity of blocked pores in simulation. As Fig 6.14(a) shows, the particle deposited inside of pores are nearly same to total particles in simulation when particles inside of pores and on surface are quite low. This period pore blocking process is governed by concentration of silica the ratio of particle blocking pores to total particle in simulation is close to 1, as shown In Fig. 6.11(b). Moreover, when injection rate is 1 particle/10 time steps, the percentage of particles in suspension increases from 0 to 0.125 from 1-10s to 20s-30s and percentage of particles deposited on membrane surface increases from 0.125 to 0.213 from 1-10s to 20s-30s. With increasing number of particles deposited near inside or pores and near region surrounding pores, the strong repulsive forces between deposited particles and new particles make the new particles bounced back to the bulk, which finally deposited on

membrane surface with a smaller number of deposited particles or suspended near membrane surface. This indicates the transition was made from ‘silica concentration dominative’ to ‘deposited particles dominative’ after early fouling stage. Finally, the simulated porosity of blocked pores is presented in Fig. 6.14(c), it’s seen that the porosity of pores is still very large even though nearly 100% of particles are deposited on pores, especially in simulation on membrane with high porosity and large pore size, as the membrane we used in this study. In this regard, the phenomenon that obvious effect was not observed when increasing silica concentration from low concentration should not attributed to pore blocking coefficient but insignificant porosity reduction of highly porous support layer since pore blocking coefficient is nearly close to 1 in early fouling stage. Moreover, with increasing number of deposited particles, the percentage of particles blocked in pores out of newly injected particles would be decreased due to increasing strong repulsive forces near membrane surface.

(a) injection rate: 1 particle/40 time steps

(b) injection rate: 1 particle/20 time steps

(c) injection rate: 1 particle/10 time steps

Fig. 6.13 The simulation results of particles behavior under three injection frequencies (The framework of graph shows the simulation domain with unit as nm in both x and y axis).

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Fig. 6.14 (a) The number of particles in suspension, deposition on membrane surface, blocked in pores as function of total particles in simulation: grey marker, empty marker, filled marker present injection frequency at 1 particle/40 time steps, 1 particle/20 time steps, 1 particle/10 time steps, respectively; (b) the percentage of particles in suspension, external fouling on membrane surface, inside of pores in newly injected particles as function of as function of total particles in simulation: grey marker, empty marker, filled marker present injection frequency at 1 particle/40 time steps, 1 particle/20 time steps, 1 particle/10 time steps, respectively; (c) The porosity of simulated pore as function of simulated periods under three injection frequencies.

6.4.3.4 Maintainable flux

Simulation was conducted in order to investigate the maintainable flux on later fouling stage, which was characterized as the flux in which no observable water flux was observed as fouling proceeds. In simulation, instead of initialized fouling with clean membrane, like what is done in studying fouling on early stage, certain number of particles are placed inside of simulated pores based on the calculation in section 6.2.1. The assumption was made that water profile is dominated by internal fouling though external fouling also has minor impact on water flux decline. Based on pore with length as 120nm, 100nm radius and cross-section with only 7nm thickness, the number of particles required to achieve certain porosity is as follows:

Table 6.5 The number of particles used in simulated blocked pore

Porosity (-)	Number of particles
0.95	39
0.9	78
0.8	157
0.7	235
0.5	292

The percentage of particles deposited inside of pore out of total newly injected particles is expressed as pore-blocking coefficient, which excludes the particles placed in pore in initialization. The pore-blocking coefficient at different flux and different blocking status was shown in surface graph shown in Fig 6.15. The maintainable flux is obtained at the water flux under which pore-blocking coefficient equals zero at certain blocking status. As the result

shows, decreasing porosity of blocked pore increased maintainable flux at all conditions due to strong repulsive effect. Only when particles with higher convective drag force can it overcome strong interaction between it and deposited particles. Moreover, this repulsive effect become less important with increasing of magnitude of blocking. At severely blocked pores, decreasing porosity from 0.8 to 0.5 only results in maintainable enhancement from 68LMH to 72LMH. By contrast, when porosity is around 0.9 and 0.95, even though water flux was fixed at around 13LMH, there is still 10% and 8% particles deposited inside of pores. This can be explained through distribution of particles inside of TFC membrane and corresponding setting we used in simulation. In simulation, the particles are uniformly distributed inside of pore rather than deposited layer by layer in pore, which is decided by real EDX images shown in Fig 6.16. As shown in EDX graphs of TFC membrane fouled by 2000ppm silica at 13LMH for 30mins and 2hrs, it is seen that particles are nearly uniformly distributed inside of pores. Since DLVO reactions are both short-range forces, with increasing degree of pore-blocking, more newly deposited particles move towards the bottom of membrane. In this regard, increasing distance between two deposited particles and new particles make the repulsive effect turn stable as fouling proceeds. Moreover, with reduction of water flux, the reduction of drag force also decrease the mass of particle deposited either inside of pore or on surface. This simulation enables us to study how blocking behaviors change while water flux was kept as constant, which is normally cannot realized through experiment.

Fig. 6.15 The relationship between pore-blocking coefficient and water flux/porosity of blocked pore in later stage of fouling through simulation

Fig. 6.16 EDX garphs of TFC membrane fouled by 2000ppm silica colloids under 13 LMH flux.

6.5 Conlusions

In this study, two types of silica colloids are used as model foulants in membrane fouling experiments on TFC membrane on AL-DS mode, which represent external fouling and internal fouling. The fouling experiemnts and real-time characerization are tried to test their influence on water flux and ultrasonic signal. Furthermore, in order to study pore blocking process on membrane fouled by 7nm silica partciles, a model with single particle transport was developed. The novelty of this study is to explain difference on fouling characterization and fouling behaviours caused by membrane structure and foulants properties. From aspect of real-time membrane fouling characterization, following the study in Chapter 4, it's revealed that signal damping issue should not be neglected for TFC membrane with such high porosity. Moreover, the study reveals the different fouling behaviors caused by colloidal foulants with different size. In more complicated scenario, the clogging process is simulated through particle trajectories in forward osmosis, which provides more theoretical background for studying inter-particles interaction and maintainable flux determination. There are several conclusionse extracted from this section:

(1). The membrane fouling induced by 7nm particles are greatly influenced by particle concentration and initial flux at early stage; by contrast, the fouling induced by 300nm particles are very insensitive to increasing particle concentration and initial flux;

(2). Through UDTR characterization, ultrasonic signal provides are very unique signal on pore-blocking process in TFC membrane on AL-DS mode. By contrast, surface fouling on either AL-DS mode or AL-FS mode cannot be measured by ultrasonic signal due to high signal attenuation over highly porous membrane matrix;

(3). Through model with silica colloidal transport, under current experimental condition, the pore-blocking coefficient is dominated by particle concentration at early fouling stage, in which nearly all particles transported from bulk ends up with blocking pore. Moreover, with increasing number of particles deposited inside of pores, the strong repulsive effect from deposited particles repels deposition of new particles;

(4). At late fouling stage, the maintainable flux can be obtained through simulating blocked pore with certain porosity. The result was obtained at condition in which nearly zero particles deposit in pore. The results show at late fouling stage, the status of blocked pore plays dominative role in determining the maximum flux in which no pore blocking occurs. This provides a new tool on studying influence of water flux and pore geometry on fouling behavior.

CHAPTER 7. Conclusions and Future Works

7.1 Overall Conclusions

Osmotically-driven membrane processes (ODPMs) in gaining increasing attention from both academic researches as well as industrial applications. This study focused on a main part in ODPMs: Forward osmosis. The main advantages of forward osmosis include low energy consumption, spontaneity as well as ease of being integrated with other membrane processes. However, the membrane fouling is still a big obstacle in promoting this process further. This thesis focuses on characterization and modelling of fouling in forward osmosis from different perspectives through utilizing silica colloids as model foulants.

Chapter 4. focuses on application of real time ultrasonic time domain reflectometry (UTDR) to characterize membrane fouling on AL-FS mode and AL-DS mode, respectively. By reversing the placement of transducer on bottom of membrane, the UTDR is able to characterize external fouling and internal fouling on CTA membrane with signal processing on both time domain and frequency domain which is accomplished by using short-time Fourier transform. Through time domain analysis and frequency domain analysis, the internal fouling are characterized by STFT and TRP of key peak, and external fouling on AL-FS mode are characterized by arrival time shift. Finally, overall fouling is characterized by TRP of all peaks after STFT transformation. To expand the application of UTDR from experimental conditions in **Chapter 4.** (CTA membrane and same particle size) to more cases, in **Chapter 6.** UTDR was tested in TFC membrane and silica particles with different size. Through STFT and TRP analysis, the pore-clogging process is identified when TFC membrane was challenged by small particles. Also, the result also suggests pore-clogging merely happens at first 30mins for TFC membrane due to highly porous substrate and strong ICP in later fouling stage. Based on strong internal fouling characterized by UTDR, attempt was made to develop particle trajectory model to identify how particle-particle interaction and particle-membrane interaction affect particle deposition in cylindrical pore environment, the parameter which is experimentally inaccessible. Although ideal particle deposition factor is assumed to be 100% in dead-end condition, the strong ICP and particle-particle repulsive effect makes a part of particles in suspension. With assumption of initial flux and initial particle clogging situation, the contribution from particle concentration and particle-particle repulsive effect on number of particles in pore, surface and suspension are identified in different fouling stages. In **Chapter 5,** the complexity of experiment condition is increased after incorporating crossflow rate, which results in extra part

of particles being removed by crossflow. Due to lack of studies providing good determinist model on this particle deposition factor, machine learning method and traditional mass transfer model are applied to fitting particle deposition factor with multiple experimentally accessible parameters. After tuning hyper-parameters and optimizing structure of neural networks, the relationship was established with relatively r square number. This method provides a promising tool to link this particle deposition factor with many testable parameters. In summary, **Chapter 4** validates the possibility of application of UTDR in forward osmosis characterization in dead-end cell and validated by mass balance calculation using 100% particle deposition factor. To extend the application of UTDR on crossflow condition, one key obstacle for mass balance validation is that particle deposition factor is no longer 100%. In **chapter 5**, the study was developed to bridge this unknown particle deposition factor with many experimentally testable parameters. Together with results obtained from **Chapter 4** and **Chapter 5**, this thesis provides the basis of testing and validating use of UTDR in more complex condition with cross flow in future studies.

7.2 Recommendations for future works

The potential future works for this study are listed:

(1). In characterization of membrane fouling in forward osmosis, ultrasonic techniques have quite different response to different types of foulants due to various acoustic properties as well as complex acoustic phenomenon which includes but not is limited to reflection, inflection, scattering, attenuation and phase transformation. Studying each foulant involves understanding acoustic properties of foulants as well as mechanism involved. In future works, besides of colloids, organic fouling and bio-film on forward osmosis process can be studied then providing a more comprehensive scope on real-time characterization on combined fouling brought by real wastewater.

(2). In modelling fields, based on the results of chapter 4 and chapter 5, the pore-clogging status predicted by UTDR can be further tested and validated in cross flow condition;

(3). The neural networks are quite efficient in capturing non-linear relationship between high-dimensional data. However, in membrane process, the limited number of data may compromise its effectiveness. In future, focus can be put on how can we use real-time data to make

3503 prediction in a real-time manner. In traditional models, some assumptions are subject to
3504 challenges in varying operating conditions;

3505 (4). In modelling pore blocking coefficient process, current model can be further developed
3506 after considering how clogged-pore impacts ICP, concentration distribution and water flux in
3507 return.

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Appendix A

A.1 Measured silica concentration during FO fouling process.

To validate the concentration stability of silica during FO fouling process, the feed solution was extracted every 10 mins before addition of dosing solution with same concentration of silica (i.e. 2000mg/L) and analysed through Inductively coupled plasma optical emission spectrometry (ICP-OES, optima 8000, Perkin Elmer, USA).

Before testing, the sample are prepared following steps below: Firstly, 5mL feed solution was extracted and diluted into 45mL using deionized water to make concentration of sample fall into testable range of ICP-OES (0.5ppm- 500ppm in this study); Secondly, the sample was ultrasonized and then passed through 0.45 μm filters before analysis. Finally, the solution was filled with 5mL 1% HNO_3 to make sure the samples are in acid condition. During testing, standard solutions are also diluted with 5mL 1% HNO_3 to reach 50mL for calibration. The samples are measured with duplicates and the average was presented below.

Fig A.1 silica concentration during FO fouling process

Appendix B

B.1 Estimation of percentage of pore area on support layer skin

In order to model external fouling and internal fouling simultaneously, the distribution of mass deposited on and inside of membrane should be determined. In this model, it is proposed that the distribution coefficient is equivalent to the percentage of area occupied by pores on effective membrane area. To estimate the value in a quantitative manner, SEM image was applied to get original picture in which pores are randomly distributed and presented by darker color, as shown in Fig B.1 (a). The different RGB values are tried to find the optimum value which covers the pores most properly. Fig B.1 (b), (c), (d) shows three presentative cases in which the selected value underestimate, properly estimate and overestimate pore areas, respectively. As shown in (b) a lot of pores are not accounted when RGB was selected as [28,28,28], while increasing this value into [44,44,44] results in overestimation of pore area in (d). Consequently, the most proper value was selected as [36,36,36], as shown in Fig. B.1 (c).

Fig. B.1 (a) the original SEM graph of support skin of clean CTA membrane; (b), (c), (d) the same SEM graph in which pixels with RGB value lower than a threshold value (24 for (b), 36 for (c), 40 for (d)) was colored by red.

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