Investigating microfiltration membrane fouling via network modeling and optical coherence tomography

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**INVESTIGATING MICROFILTRATION MEMBRANE
FOULING VIA NETWORK MODELING AND OPTICAL
COHERENCE TOMOGRAPHY**

**HAN QI
INTERDISCIPLINARY GRADUATE SCHOOL
NANYANG ENVIRONMENT & WATER RESEARCH
INSTITUTE
2019**

**INVESTIGATING MICROFILTRATION MEMBRANE
FOULING VIA NETWORK MODELING AND OPTICAL
COHERENCE TOMOGRAPHY**

HAN QI

**Interdisciplinary Graduate School
Nanyang Environment & Water Research Institute**

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

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

02/08/2019
Date

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare 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 prejudice.

02/08/2019

Date

Assoc. Prof. Chew Jia Wei

Authorship Attribution Statement

This thesis contains material from four papers published in the following peer-reviewed journal(s) in which I am listed as the first author.

Chapter 3 is published as Han Q., Li W., Trinh T. A., Liu X., Chew J. W. (2017). A network-based approach to interpreting pore blockage and cake filtration during membrane fouling. *Journal of Membrane Science*, 528, 112-125.

The contributions of the co-authors are as follows:

- Prof. Chew provided the initial project direction and finalized the manuscript.
- I did the experiment part and prepared the initial draft.
- Dr. Li proposed the initial idea, analysis the data and revised the manuscript.
- Thien An helped to improve the interpretation of the modeling.
- Dr. Liu lent me the membrane cell, trained me to conduct filtration experiments and taught me to characterize membrane fouling by Optical Coherence Tomography.

Chapter 4 is submitted as Han Q., Trinh T. A., Tanis M. B., Li W., Chew J. W. Assessing internal fouling during microfiltration using optical coherence tomography and evapoporometry. *Journal of Membrane Science*, 595 (2020) 117588.

The contributions of the co-authors are as follows:

- Prof. Chew provided the initial project direction.
- I performed the experiment part, analyzed experimental data and drafted the manuscript.
- Melike Begum trained me to use the Evaporimetry (EP) instrument and helped to conduct several sets of EP tests.
- Thien An helped to develop the fitting method of three-mechanism model and gave some suggestions about responses to the reviewers' comments.
- Dr. Li developed the OCT analysis code and authorized the application of the code in the current study.
- Prof. Chew finalized the manuscript.

Chapter 5 is published as Han Q., Li W., Trinh T. A., Fane A. G., Chew, J. W. (2018). Effect of the surface charge of monodisperse particulate foulants on cake formation. *Journal of Membrane Science*, 548, 108-116.

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- Prof. Chew provided the initial project direction.
- I performed the experiment part, analyzed experimental data and drafted the manuscript.
- Dr. Li developed the analysis method for OCT images and gave valuable suggestions about data analysis.
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- Prof. Chew and Prof. Fane helped to revise the manuscript.

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- Prof. Chew provided the initial project direction.
- I performed the experiment part, analyzed experimental data and drafted the manuscript.
- Thien An helped to revise the manuscript and improve the logic of the manuscript.
- Prof. Chew finalized the manuscript.

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ABSTRACT

The inevitable membrane fouling during membrane filtration processes hinder the further application of membrane technology. Developing techniques for effectively mitigating membrane fouling relies on an in-depth understanding of the fouling mechanisms. This study proposes a two-dimensional network-based approach where the membrane was discretized and the fate of each particle was monitored individually, to explore the underlying external fouling mechanisms during dead-end microfiltration using polycarbonate track-etched membrane with cylindrical uniform pores. Three fouling parameters, namely the probabilistic factor for deposition in the non-porous area (β), the initial cake resistance (R_{c0}), and the specific cake resistance with respect to cake thickness (R_c'), can be obtained to characterize the fouling behavior by best-fitting the experimental flux-decline data to the network model. In parallel to theoretical study, advanced membrane fouling characterization technology, namely three-dimensional optical coherence tomography (OCT) scanning also applied to investigate fouling mechanisms. Online non-invasive OCT technique was applied to characterize the BSA protein fouling development on three different kinds of membranes with similar vendor-given pore size and porosity and a layer-based OCT image analysis method was established. The results showed that OCT is able to successfully reveal the external and internal fouling, however the implementation of quantitative comparison of protein internal fouling among the membranes was impossible from OCT results. The coupling of the network model and OCT characterization was employed to investigate the effect of the surface charged of monodisperse particulate foulants on cake formation and the fouling cake evolution of bidisperse suspensions in dead-end microfiltration. The results showed for the negatively charged polycarbonate track-etched membrane, negatively charged latex tended to deposit on the pore and form cluster due to repulsive particle-membrane electrostatic interactions. The bidisperse feeds with low mass ration of large particles tended to form homogeneous cake but the presence of a higher concentration of large particles lead to heterogeneous cakes; the presence of a lower concentration of large particles enhanced clustering while a higher concentration reduced that.

Keywords: Microfiltration (MF), Membrane fouling, Network Modelling, Optical Coherence Tomography (OCT), Cake formation

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2. **Han Q.**, Trinh T. A., Tanis M.B., Li W., Chew J. W. “Assessing internal fouling during microfiltration using optical coherence tomography and evapoporometry. ”*Journal of Membrane Science*, 595 (2020) 117588.
3. **Han Q.**, Trinh T. A., and Chew J. W. “Cake formation of bidisperse suspensions in dead-end microfiltration.” *Journal of membrane science* 577 (2019), 31-40.
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Chapter 1 Introduction

1.1 Background

Water pollution is among the most critical challenges of modern society. The development of efficient and sustainable techniques for tapping unconventional sources of water is therefore of great importance. In recent decades, membrane-based technologies have become a rising star in the areas of water purification and sustainable energy regeneration [1, 2]. However, the inevitable membrane fouling is one of the major impediments for the widespread application of membrane systems [3]. Flux decline and transmembrane pressure increased could be caused by membrane fouling and thus increasing the operating and maintaining cost. For practical application, mitigating membrane fouling in an efficient way is urgently required which entails the information that accurately describe the variation of membrane, namely the mechanisms accounting for the evolution in fouling behaviour during a membrane filtration process and the impact of parameters that control fouling (e.g., flux and pressure, crossflow rate).

Conventional methods for investigating membrane fouling are to measure the tendency of permeate flux while maintaining the pressure at a constant value [4, 5] or to measure the variation of transmembrane pressure (TMP) under a constant flux mode [6]. The severity of fouling is then illustrated by a flux-decline or TMP-increment curve. It is a relatively convenient and simple way to test the changes of permeate flux or TMP increment for analysing membrane fouling. However, the information achieved in these ways for interpreting fouling behaviour are limited. Several coupled effects (e.g., concentration polarization (CP)), which could influence the fouling process significantly, may lead to misunderstanding of the data. In spite of experimental studies, mathematical models are established and play an essential role in interpreting various fouling mechanisms and extracting the intrinsic physics. To date, many fouling models have been proposed and applied to the studies on membrane fouling [3, 7, 8]. Iritani reviewed pore blocking models in membrane filtration work under constant pressure and constant flux operating modes and concluded that the pore blocking filtration laws are useful in the evaluation of the reduced pore size, maximum filtration volume and fouling potential [3]. Teychene et al. developed a membrane fouling model by modifying the resistance in series model which was able to account for the synergistic

effect of kaolin clay and organic matters during ultrafiltration [7]. Bacchin et al. proposed a theoretical model described the deposition of colloidal particles on membrane surface accounting for surface interaction by using Eulerian approach, which predicted a higher flux than other models in the range of colloidal sizes of 0.1 to 10 μm and was presumably able to solve the “colloidal flux anomaly” [8]. As reviewed by Li, although these models were described in different mathematical expressions, e.g. the classical blocking models proposed by Hermia et al [9], the resistance-in-series model [10], the combined fouling model developed by Ho et al [11], etc. most of them mainly tackle with the same three critical issues: i) the description of the clean membrane property; ii) determination of the fouling rate during membrane filtration; iii) evaluation of the fouled membrane during filtration process [12]. Sahimi et al. have reviewed a variety of models and concluded that there were two basic approaches to model the fouling phenomena, namely continuum and statistical approaches [13]. Continuum fouling models assumed the spatial domains (e.g. the membrane and the fluid channel), the velocity and concentration fields could be described by smooth functions and the dynamical processes during membrane filtration are described by the phenomenological relations [14, 15]. For discrete fouling model, the spatial domain was represented as a collection of unit cells and the species conservation law was adapted to the individual unit cells. Griffiths et al. proposed a combined network model and found this model enables post-experiment analysis to identify the dominant fouling modality at each stage and provide insight into selecting appropriate operating regimes [16]. Li et al. developed a network model to theoretically study the effect of membrane morphology on the interactions between the oil droplets and the porous membrane structures [17]. They found the topological structure of the network could have a significant impact on the trans-droplet pressure, which was markedly less than transmembrane pressure when the porous structure is highly connected. Compared with the continuum models, the discrete fouling model was able to account for the local fouling behavior at a scale defined by a unit cell, which offers a tool for the experimental observation from advanced characterization techniques for membrane fouling.

In parallel with the modeling efforts, a variety of characterization techniques have been applied to study the membrane filtration process which were reviewed by many previous studies [18-20]. Much information could be obtained by autopsies of used membranes, such as scanning electron microscopy (SEM), atomic force

microscopy (AFM), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), and contact angle measurements [19]. However, observation in-situ conditions in real time can provide significant insight of the fouling process which is not accessible by other means. Recently, many non-invasive in-situ advance visualization techniques, such as ultrasonic time domain reflectometry (UTDR) [21, 22], electrical impedance spectroscopy (EIS) [23-25], direct observation through the membrane (DOTM) [26], confocal laser scanning microscopy (CLSM) [27-29] and optical coherence tomography (OCT) [30] are getting more and more attentions. Whereas DOTM, CLSM and OCT are optical techniques that provide visual images, UTDR and EIS are based respectively on ultrasound wave and alternating current. While DOTM provides two-dimensional images, CLSM and OCT provide three-dimensional ones. Compared with CLSM, OCT is able to scan the sample at a relatively higher rate and furthermore achieves a higher microscale resolution [31]. Valuable insights have been obtained regarding the cake layer formation process. Tanudjaja et al. [32] used DOTM to reveal the differences in cake thickness, mobility and resistance between particulate and oil emulsion foulants. Gao et al. [33] employed low coherence interference OCT to monitor the velocity field and the depth growth of the cake. The growth of a biofilm in a membrane cell, evolution of cake formation and effect of spacer orientation on fouling morphology has also been unveiled via OCT [31, 34, 35]. A recent study used OCT for understanding internal cake fouling and developed a new model to account for this fouling mechanism [36].

Recently, more and more studies tried to couple the fouling models and advanced characterization techniques which could help to obtain a deeper understanding of the fouling mechanism in a theoretical and experimental way [37-39]. Sun et al. characterized protein fouling in-line and analysed the fouling behavior quantitatively by applying a combined fouling model which account pore blocking, cake formation and pore constriction [37]. They found the data obtained from the model was in good agreement with the experimental data and the theoretical analysis implied the cake formation was the main fouling mechanism. Bacchin et al. examined the effect of colloidal surface interaction on membrane filtration process theoretically and experimentally and concluded both the two approaches represent the significant contribution of surface interaction to the filtration process [38]. Later, Bacchin and his co-workers continue to study the effect of connectivity and tortuosity of the channels on clogging of latex particle during microfiltration by combining numerical approaches

and direct observation with video microscopy [39]. They found the increase in tortuosity in the micro-separator leads to a higher chances of clogging but the numerical simulations of filtration failed to describe the kinetics of particle deposit behaviors accurately which is probably due to lack of accuracy to depict particle-particle interactions. Despite these past efforts on membrane fouling models and characterization of cake formation, the coupling between modelling and characterization approaches at a pore scale, which is crucial to reach a full understanding of fouling mechanism during membrane filtration, has not been undertaken yet. This study was aimed at bridging this gap.

1.2 Objectives and Scope

The main objectives of this study are to develop a novel network model to describe the fouling behaviour during membrane filtration at multiple scales and incorporate the network modeling with advanced fouling characterization, namely optical coherence tomography (OCT), to explore the underlying fouling mechanisms. Specifically, the proposed studies include:

- Develop a systematic approach to constructing a network that is able to approximate symmetric membrane with uniform straight-through cylindrical pores while accounting for the topological aspects via probabilistic descriptions.
 - Establish a series of criteria for determining the fouling behavior of individual particles in terms of the network.
 - Explore the way of incorporating the network model with regression analysis for obtaining the fouling parameters via nonlinear curve fitting.
- Improve the method of characterizing membrane fouling via OCT for resolving more details about the fouling process in a more precise way.
 - Establish a layer-based OCT image data analysis method which is able to quantify the extend of membrane fouling by evaluating the fraction of fouling voxels versus time at varied depths.
 - Obtain topological information of the deposits by analyzing the patterns of the fouled voxels.
 - Explore the dynamic behavior of the foulants by analyzing the changes in the fraction of fouling voxels per unit time.

- Explore the way to couple the network model and OCT characterization technique to obtain a mechanistic understanding of the fouling mechanism.
- Apply the developed network model and characterization methods to study membrane fouling processes involving foulants having complicated physicochemical properties, such as proteins and functional particles.

1.3 Thesis Outline

This thesis includes seven chapters, which are highlighted as follows:

Chapter 1: Introduction - Background information and objectives of this study are provided.

Chapter 2: Literature Review – This chapter is divided into three parts. The first part is the review of the membrane fouling models. It starts with the introduction of the previous classical fouling models followed by the new developed discrete fouling model. The second part of the literature study contains various advanced characterization techniques applying in monitoring fouling behaviours. The third part is the summary of literature review.

Chapter 3: A Network-Based Approach to Interpreting Pore Blockage and Cake Filtration During Membrane Fouling – this chapter proposed a new network fouling model, the details of the construction of network model and the correlation of the simulation results with experimental results.

Chapter 4: Assessing fouling evolution during protein microfiltration – the layer-based 3D OCT image analysis method was developed and applied in monitoring both external and internal fouling development during BSA filtration. Two other off-line characterization techniques, namely Evaporimetry and Atomic Force Measurement are also employed to get further understanding of fouling mechanism.

Chapter 5: Effect of the surface charge of monodispersed particulate foulants on cake formation – the combination of the network model and OCT characterization were employed to attain a mechanistic understanding of the counter-intuitive filtration performance of the three monodispersed particulate foulants with different surface charges.

Chapter 6: Cake formation of bidisperse suspensions in dead-end microfiltration – the network modeling was modified to account for the bidisperse suspension and the

fouling parameters were obtained by best-fitting of the experimental flux decline data with the network modeling, thus attaining the theoretical understanding of cake evolution of the bidisperse particles. OCT characterization also was applied in this study to provide experimental evidence which may support the theoretical findings from the network model fouling parameters or provide a new perspective to understanding the bidisperse particles fouling behaviors.

Chapter 7: Conclusion and future work – The important findings of this study and recommendations area summarized in this chapter.

Chapter 2 Literature Review

Microfiltration is a process that applying in the separation of particles with size of approximately $0.1 - 10 \mu\text{m}$ from fluid by a membrane or other filter medium. This size range involves a wide variety of natural and industrial particles, including biological cells, clays, paint pigments and polymer latexes [40-42]. Compared with ultrafiltration and reverse osmosis, the particles separated by microfiltration are larger. The transmembrane pressure drop that drives the microfiltration process is relatively small and the osmotic pressure for microfiltration is negligible. There are two traditional approaches to carry out microfiltration processes: dead-end and crossflow (Fig.2-1). In dead-end filtration, the pressure-driven feed stream is perpendicular to the membrane (Fig. 2-1a) while it is tangential to the surface of the membrane in crossflow filtration (Fig. 2-2b).

Figure 2-1 Membrane operation in (a) Dead-end mode and (b) Crossflow mode.

In this thesis, all the studies were carried out in dead-end filtration mode during microfiltration. This chapter reviewed the fouling models and fouling characterization methods developed in recent decades and summarized the advantages and limitations of models and fouling characterization techniques that have been reviewed.

2.1 Membrane Fouling Models

Membrane fouling, which is the accumulation of foulants on the membrane surface or within the membrane pores during membrane filtration, could be generally classified into four categories, namely organic fouling, inorganic fouling (scaling), colloidal fouling and biofouling [43]. In order to optimize membrane filtration

performance and prolong membrane lifespan, the understanding membrane fouling process is of great importance. During last three decades, a lot of research work focused on membrane modelling which is used to understand the fouling process and predict the process tendency. The following are the conventional used models:

2.1.1 Resistance-in-series model

Resistance-in-series model is one of the simplest and most widely used models to describe and explain the membrane fouling phenomena [44]

$$J = TMP / (\eta \times R_t) \quad (2-1)$$

$$R_t = R_m + R_c + R_f \quad (2-2)$$

where J is permeation flux, TMP means transmembrane pressure, η is dynamic viscosity of the permeate, R_t represents total resistance, R_m equals intrinsic membrane resistance, R_c equals (reversible) cake resistance and R_f equals (irreversible) fouling resistance. The reversible fouling is caused by the cake layer deposited on the membrane surface while the irreversible fouling is produced by adsorption of dissolved matter (pore constriction) and/or pore blockage within the membrane (pore plugging). It is obviously to notice that, in this model, flux is proportional to transmembrane pressure and inversely proportional to the product of feed water dynamic viscosity and total resistance. The total resistance is composed of discrete different resistances.

In this model, through a series of pure-water filtration, pollutant-water filtration and pure-water filtration after cleaning, different resistances could be measured. However, the model assumption, which completely decouples all resistances, is not always applicable. In order to apply this model in a more proper way, many studies have been done to identify components of resistance. In Choo's research, a gel layer resistance and a concentration polarization resistance were identified as the reversible fouling component [45]. However, differentiating different resistant components based on arbitrary physical tests is questionable. To solve the problem, many researchers prefer to use a combined resistance value, R_f , to present all resistances offered except that of the clean membrane [46].

2.1.2 Pore blocking model

Blocking filtration laws were first proposed by Hermans [14] and later developed by Gonsalves [47]. This model always used to describe the membrane

fouling by colloidal particles. The blocking filtration model includes four mechanisms which are shown in Fig. 2-1: 1) complete pore blocking which is also called pore sealing; 2) standard pore blocking which is also called pore closure; 3) intermediate pore blocking and 4) cake filtration. For pore sealing mechanism, there is an assumption that particles reach the membrane and block pores without superimposing over other particles. For pore closure, particles are assumed to deposit in the membrane pores and the decrease of pore volume is proportional to the volume of deposited particles. For intermediate blocking, it is supposed that some particles deposit onto other particles while the rest particles deposit on membrane pores. Referring to the cake filtration mechanism, it is assumed that the particles do not block the pores either because the membrane is dense or the pores were already covered by other particles. The characteristic form of the blocking law at constant pressure mode is [9]:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad (2-1)$$

Where t is the filtration time, V represents the filtration volume and k is regarded as resistance coefficient, n is a dimensionless filtration constant that characterizes the mode of the fouling model involved. Table 2-1 showed the results of the resistance coefficient k as a function of the initial flowrate (Q_0 or u_0), and the parameters α , γ , s , σ , A , R_0 , m , C and L are cake specific resistance, filtrate density, mass fraction of solids in slurry, blocked area per unit filtrate volume, filter membrane surface area, filter resistance, mass ratio of wet to dry cake, volume of solid particles retained per unit filtrate volume and membrane thickness, respectively.

Table 2-1 Summary of blocking laws for constant pressure filtration mode [9].

Law	k	n
Cake filtration	$K_c = \frac{\alpha\gamma s}{AR_0Q_0(1-ms)}$	0
Intermediate	$K_i = \frac{\sigma}{A_0}$	1
Standard law	$K_s' = \frac{2C}{LA_0}Q_0^{1/2}$	$\frac{3}{2}$
Complete blocking	$K_b = u_0\sigma$	2

Membrane filtration process generally is operated in two modes: constant pressure mode and constant flux mode. For constant pressure filtration, normally a rapid flux decline could be observed at the start of filtration, then a more gradual decrease would happen until a steady state or a pseudo-steady state flux is reached. All the four mechanisms stated above imply a tendency of flux decline based on the ratio of the particle diameter to the pore size [48]. In colloid filtration or protein filtration, pore closure and cake filtration models are supposed to be the most suitable models to predicting initial flux decline [49].

Figure 2-2 Schematic illustration of mechanisms of four blocking filtration laws [3].

In particle application of membrane filtration system, the operation is often carried out at constant flux mode. For constant flux filtration process, membrane fouling often causes the increase of transmembrane pressure. As reviewed by Iritani et al. [3], the characteristic form of blocking law at constant flux mode could be deduced based on similar analysis used in the derivation of constant pressure blocking filtration equations and can be represented as:

$$\frac{dp}{dV} = k'p^{n'} \quad (2-2)$$

Where n' is the blocking index that characterizes the mode of the fouling model involved, k' is the resistance coefficient and p is the pressure drop during constant flux operation. The calculation of k' and the exponent n' in Eq.2-2 are the same for different modes of fouling model with the one for constant pressure mode (Table 2-1). In generally membrane filtration process, all the four mechanisms are supposed to prevail in sequence. However, it should be noticed the back-transport of particles from membrane surface to the bulk of feed water is not considered in the blocking models, which narrows their applications.

2.1.3 Combined fouling models

The fouling behaviors cannot be described by a single classical filtration model when filtrating complex feeds, especially when filtration operated for an extended period of time [50, 51]. Ho and Zydney proposed a combined fouling model which could account for pore blockage and cake filtration in one mathematical equation [52]. Like pore blockage model, it also assumes that the membrane surface is covered by foulant particles gradually (Eq. 2-3). The different thing is that in Ho's assumption, the cake layer formed on the blocked area is permeable and the cake resistance is a function of filtration time t and the time t_p at which that particular region is first covered by foulant particle. The total flow rate (Q) is supposed to be the sum of the flowrate (Q_u) within the unblocked area (A_u) and the flow (Q_b) within the blocked area (A_b):

$$Q = Q_u + Q_b \quad (2-3)$$

$$Q_u = \frac{\Delta p}{\mu R_m} A_u \quad (2-4)$$

$$Q_b = \int_{A_b} \frac{\Delta p}{\mu(R_m + R_{p0} + R_p)} dA \quad (2-5)$$

Where Δp is the transmembrane pressures, μ is the viscosity of the fluid, R_m represents the membrane resistance, R_{p0} and R_p are the initial resistance caused by the interaction between membrane and foulant particle and cake resistance, respectively. According to the pore blockage model, the flux decline during filtration is due to the blockage of membrane pore. The fouling rate is related to the variation rate of the unblocked membrane area:

$$\frac{dA_u}{dt} = -\alpha Q_u C_b \quad (2-6)$$

α is the pore blockage parameter representing the membrane area blocked per unit mass of foulant, C_b is the bulk foulant concentration. From the cake filtration model mention in previous section, the flux decline during filtration is because of the growth of the cake layer. Therefore, the fouling rate is related to the variation rate of the mass of deposited foulant per unit membrane area (m_p):

$$\frac{dm_p}{dt} = J C_b \quad (2-7)$$

The mathematical expression for the total flowrate could be obtained by combining Eqs. (2-3) to (2-7):

$$\frac{Q}{Q_0} = \exp\left(-\alpha \frac{\Delta p}{\mu R_m} C_b t\right) + \int_0^t \frac{\alpha \Delta p C_b}{\mu(R_m + R_{p0} + R_p)} \exp\left(-\alpha \frac{\Delta p}{\mu R_m} C_b t_p\right) dt_p \quad (2-8)$$

Lately, Duclos-Orsello *et al.* proposed a three-mechanism model [53] that combines complete pore blockage, pore constriction and cake filtration fouling modes. This model assumes that pore constriction occurs until the pore entrance is blocked by foulant, after which a cake forms on the membranes. Despite having different focuses on membrane fouling, these fouling models are based on the assumption that not only the spatial domains (e.g., the membrane and the fluid channel) but also the velocity and concentration fields can be described by smooth functions; the dynamical processes are described by the phenomenological relations [14, 52], while ignoring the topological aspects of membrane fouling, such as the connectivity of the porous structure and the distribution of the deposits, owing to mathematical complexities.

2.1.4 Back transport models

The blocking model is not applicable for membrane filtration process which has shear force such as crossflow filtration and stirred dead-end filtration. In these cases, the fouling layer will contribute to a great resistance to filtration and the permeate flux will decline quickly and then reach a steady or quasi-steady state. The back transport models which describe the steady state of the permeate flow, includes three mechanisms, namely Brownian diffusion, shear-induced diffusion and inertial lift [54].

Brownian diffusion is a model that describe the transportation particle towards the membrane at steady state was balanced by Brownian diffusion and convection away from the membrane, as described by a mass-transfer coefficient [55]. The mathematical expression for laminar flow using Brownian diffusion approach is:

$$\langle J \rangle = 0.81(\gamma_0 D_B^2 L)^{1/3} \ln(\phi_w / \phi_b) \quad (2-8)$$

$$D_B = kT / (6\pi\mu_0 a) \quad (2-9)$$

Where $\langle J \rangle$ is the length-averaged permeate flux, γ_0 is the shear rate at the surface of the membrane resulting from the bulk laminar flow, D_B is the Brownian diffusivity, and ϕ_w and ϕ_b are the volume fractions of the rejected species in the bulk suspension and at the edge of the fouling layer respectively, k is the Boltzmann constant, T is the absolute temperature and a is the particle radius and μ_0 is the fluid viscosity [56]. However, models based on Brownian diffusion, as promoted by concentration polarization, are

known to substantially under predict the flux obtained during colloid filtration, which was called “flux paradox” [57].

Zydney and Colton [58] proposed a possible solution to solve the flux paradox problem by replacing the Brownian diffusivity by the shear-induced hydrodynamic diffusivity (D_s):

$$D_s = 0.03\gamma_0 a^2 \quad (2-10)$$

Another approach to solve the flux paradox problem is the inertial lift mechanism [55, 56] which assumed the back-transport of the particles away from the membrane was accelerated by a lateral migration of particle due to inertial lift. The permeate flux at a steady state predicted by inertial lift for laminar flow is:

$$J = 0.036\rho_0 a^3 \gamma_0^2 / \mu_0 \quad (2-11)$$

From the Eqs. (2-8) to (2-11), it is clear that the back-transport mechanisms are strongly depended on the particle size and shear rate while they are less relied on the concentration of particles in the bulk solution. Fig. 2-3 showed the variation of dominant mechanisms with the increase of particle size. Generally, Brownian diffusion is most important for particles with size less than 0.5 μm and low shear rates, whereas inertial lift is dominant mechanism for large particles and high shear rates. For particles with intermediate range of $0.5 \mu\text{m} < 2a < 20 \mu\text{m}$ and intermediate shear rate, shear-induced diffusion is the dominant mechanism. The back transport models provide a better understanding of the role of hydrodynamics in membrane fouling [59], however, some factors including the dissolved and colloidal species are not considered in these models.

Figure 2-3 Comparison of the predicted steady-state permeate flux versus particle size for Brownian diffusion, shear-induced diffusion and inertial lift back-transport mechanisms with thin cake layers providing the controlling resistance. The suspending fluid is water at 20°C and the nominal shear rate is $\gamma_0=5,000 \text{ s}^{-1}$ [54].

2.1.5 Discrete fouling models

Taking advantage of the advancement in computational techniques, discrete models are getting more attention in the field of membrane process simulation. Instead of using the continuous treatment, a discrete model represents the spatial domain as a collection of unit cells and thereby adapts the species conservation law to the individual unit cells. When well organized to form a topology, the collection of unit cells is referred to as a network in a general sense. A network-based method was proposed by Li [12] to investigate the effects of membrane asymmetry on membrane fouling; this method was also extended to account for the concentration polarization within the supporting structure of a forward osmosis (FO) membrane [60].

A recently published study by Griffiths *et al.* [61] employed a similar network model to theoretically interpret the flux-decline behavior during membrane fouling. Fig. 2-4 illustrated the network approximated the membrane which composes of a two-dimensional $m \times n$ array of uniform pores. The discrete network model can describe the inherent inter-relation among various mechanism during membrane filtration. Specifically, this model captures pore constriction by the entry of particles into the pores and attached onto the pore walls which allows a finite number of particles before the pore becomes completely blocked. After that, the particles will continue deposited on the membrane surface, formed a cake layer and further contribute to membrane fouling. From this model, each of the three fouling mechanisms (i.e. standard blocking, complete blocking and cake filtration possesses a characteristic signature graph where the permeate flux was plotted as a function of volumetric throughput, which enables post-experiment analysis to differentiate the dominant fouling modality at each stage and provide new insight on the microscopic blocking mechanisms. However, this discrete network model only simulated the membrane with straight-through pores with is unable to account for the inter-pore flow within the membrane.

Recently, Li. et al. proposed another network model to study the effect of membrane morphology on the rejection of oil droplets [17]. As shown in Fig. 2-5, the

membrane was discretized into a set of cubic unit cells whose coordinate directions were employed to derive a bond-node structure. This model is able to approximate membranes with different porous structures, the pressure redistribution and flows within the pore structure. However, this network modelling as well as the previous one developed by Griffiths et al. [61] only presented theoretical simulation results by applying their models. Experiments shall also be implemented to provide supporting information for the model predictions in the future.

Figure 2-4 Schematic diagram of a portion of the membrane set-up considered. The membrane comprises a total of $m \times n$ pores [61].

Figure 2-5 Schematic of constructing a network for approximating the membrane with a porous structure. The spatial domain is discretized into a system of cubic unit cells, whose coordinate directions are exploited to generate a bond-node structure with geometrical characteristics at a micron scale [17].

A key advantage of network models highlighted by these studies is the ability to account for the local fouling behavior at a scale defined by a unit cell, which offers a tool for correlating the experimental observations from advanced characterization techniques for membrane fouling, such as the characterization methods based on direct observation through the membrane (DOTM) [26] and optical coherence tomography (OCT) [33]. In addition, the network-based approach provides a highly flexible framework whereby different mechanisms can be readily combined to simulate fouling processes with various operating conditions. Especially, it is more amenable for a network model to accommodate random processes by establishing a series of probabilistic criteria [12]. This advantage is of critical value for simulating membrane fouling as the local fouling behavior is stochastic in nature. However, to construct a complex network and describe of fouling behaviours for individual foulant requires high computational capability, which indicated a trade-off should be made to balance the numerical efficiency and accuracy in terms of simulation, prediction or post-experimental analysis. Table 2-2 summarize the advantages and drawbacks of the membrane fouling models applied for understanding fouling mechanisms.

Table 2-2 Models applicable in studies of membrane fouling

Membrane fouling models	Advantages	Limitations	Reference
Resistance-in-series model	Simplest and most widely used to explain fouling phenomena	Differentiating different resistant components is challenged. Unable to reveal details about the membrane fouling	[44-46]
Pore blocking models	Prevail generally filtration processes; provide most classical categorization of fouling mechanisms	unable to explain fouling behaviors when filtering complex feeds by applying one single blocking model; not applicable in filtration with	[3, 9, 14, 47-49]

		significant back transport effects	
Combined fouling models	Applicable to prevail sequential variation of dominant fouling mechanisms vs time during filtration	Unable to account for the topological aspects of the membrane and pore connectivity within the membrane	[11, 53, 62]
Back transport models	Provide better understanding of the role of hydrodynamics in membrane fouling	Factors including the dissolved matters and colloidal species are not taken account	[54-59]
Discrete fouling models	Account for the local fouling behavior at a scale defined by a unit cell; flexible to adjust to simulate different membranes and different feed solutions; able to couple with advanced in-situ fouling characterization techniques	Require high computational capacity; Relatively low numerical efficiency	[12, 16, 17, 60]

2.2 Characterization methods of membrane fouling

Visualization of membrane fouling is crucial for developing effective fouling control strategies. During last several decades, many techniques have been applied to characterize the deposition of particles and drops and formation of cake and gel layers on membrane surfaces. A general overview of techniques for visualizing particulate fouling of membranes is given by several recent papers [63-65]. In this chapter, the related techniques were classified into two broad categories: invasive and non-invasive.

2.2.1 Invasive techniques

Invasive fouling characterization techniques can provide substantial information about the state of membrane fouling and could potentially provide guidance to optimal fouling control strategies [66]. These methods involve removing the membrane from modules and sometimes cutting it into pieces before sampling and testing [67]. In general, both virgin and fouled membrane specimens are explored in the same characterization to enable comparisons with the baseline (i.e. clean membrane). Scanning electron microscopy (SEM), atomic force microscopy (AFM), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), Evaporimetry (EP), etc. More than one invasive techniques are usually simultaneously employed to visualize membrane fouling.

SEM is a widely used imaging technique to visualize foulants on the membrane surface. Hwang et al. applied SEM to visualize membrane surface morphology for different kinds of membranes [68]. Lammien et al. employed SEM in their study to characterize the changes of the cake morphology related to different fouling cleaning processes [69]. Hong et al. applied field emission SEM to observe oil film deposited on the membrane surface and found that oil coverage increased with an increase in the applied pressure [70]. The formation and condensation of oil droplets on the membrane surface were captured by SEM at 1600x magnification by Mah et al. [71]; from the patterns of fouling by palm oil (Fig. 2-6(a)), oleic acid (Fig. 2-6(b)) and their mixture (Fig. 2-6(c)) on the PVDF 30 kDa membrane surface, Mah et al. identified internal fouling and cake formation as dominant fouling mechanisms. Larger oil droplets, as pointed out by the arrows in Fig. 2-6(a), were formed as a result of droplet collision, condensed on the membrane surface and tended to form a cake layer. Fig.2-6(b) shows

many smaller oleic acid droplets; compared to the palm oil, smaller droplets of oleic oil caused severe flux decline in the early stage of filtration due to internal fouling. Fig. 2-6(c) shows an SEM image of membrane surface fouled by the mixture of palm oil and oleic acid. Both large and small droplets were observed to condense on the membrane leading to severe fouling. In the highlighted box in Fig. 2-6(c), the smaller oleic acid droplets are seen adsorbed by palm oil molecule to form bigger droplets enhancing formation of the cake layer.

Figure 2-6 SEM images of PVDF 30 kDa membrane fouled by (a) 0.1 g/L palm oil, (b) 0.1 g/L oleic acid and (c) 0.1 g/L palm oil + 0.1 g/L oleic acid [71].

Energy dispersive X-ray spectroscopy (EDS) which always couples with SEM, is an element analysis technique. Coupling EDS and SEM can not only identify the foulants on the membrane surface but also differentiate the species [72]. Annop et al. detected inorganic elements such as Mg, Al and Fe on the surface of fouled PVDF membranes after filtration of mill effluent [73]. Although SEM imaging can achieve nano-meter resolution, the complicated and invasive preparation procedure inhibits its wider application in characterizing fouling layers on membranes. Particularly, the high vacuum circumstance during SEM observation would cause the turnups of fouling layer due to dehydration [74] thus affecting the SEM results.

Atomic force microscopy (AFM) is a high-resolution type of scanning probe microscopy with spatial resolution on atomic scale which was also widely used in membrane surface characterization. It could be used to estimate of the pore size, pore density, pore size distribution of the membrane structure and the surface roughness of membranes [75]. Bowen et al. employed AFM to study the deposition of BSA onto the surface of two polymeric membranes of similar molecular weight cut-off but different

surface roughness and surface chemistry [76]. The AFM results showed that: i) the low protein-binding hydrophilic membrane benefit the protein filtration over a hydrophobic one; ii) the surface roughness of the membrane play an important role in flux decline. No special specimen preparation was required to conduct AFM measurement compared with SEM which means the measurements can be carried out in atmosphere or in liquid environment. However, the AFM tips, which were brought to the surface periodically, may result in artefacts in the measurement results. Moreover, the scanning depth in AFM measurement is limited by the size of probe tips.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) has been broadly used to analyze the chemical composition of the foulants/coated materials on a membrane. It can quantify the composition of foulants on membrane surface as well as the changes in functional groups of the membrane using ATR-FTIR spectrum of an unfouled membrane as a baseline [77]. Hu et al. have applied this technique to confirm the presence of organic foulants the membrane surface by detecting the peaks typical for hydrocarbons [78]. Compared with EDS, ATR-FTIR measurements are more convenient. It is carried out without complicates sample preparation or high vacuum. However, the major disadvantage of ATR-FTIR is that the objective must contact the sample which may probably damage the sample surface [79]. Furthermore, it is unable to obtain visual image of fouling on the membrane.

Evaporimetry (EP), which first developed by Krantz et al, is an indirect technique used to measure the pore size distribution (PSD) of porous materials by applying the Kelvin equation to derive pore diameter from the vapor pressure of a wetting liquid at the pore opening[80]. Since larger pores have greater vapor pressure, the volatile wetting liquid will evaporate first from the largest pores, then from smaller and smaller pores. Akhondi et al. [81, 82] employed EP to characterize the pore-size distribution of clean and fouled PVDF hollow fiber membranes and found left-shifted pore-size distribution in fouled membrane implying the pore constriction due to membrane pore constriction, which provide insights into the extents of internal fouling. However, EP is not suitable for characterizing membranes with low porosity and its accuracy will decrease with the increase of pore size and limiting for the one with pore size larger than 150 nm. Although EP is a quite straightforward method for characterizing the pore size distribution for symmetric membranes, the analysis method

needs to make corrections before characterizing asymmetric membranes. It is also unable to provide visual image of the foulants on the membrane.

2.2.2 Non-invasive techniques

Despite the invasive techniques performed on fouled membranes can provide detailed information on the chemical makeup and structure of fouling layers, the techniques are *ex situ*, invasive and often expensive. Over the last several decades, many non-invasive techniques have been employed to visualize membrane fouling processes. The following sections describe several such methods: optical microscopy (OM), Confocal laser scanning microscopy (CLSM), nuclear magnetic resonance (NMR) chemical shift selective (CHESS) micro-imaging, direct observation through the membrane (DOTM), optical coherence tomography (OCT), electrical impedance spectroscopy (EIS) and ultrasonic time-domain reflectometry (UTDR).

2.2.2.1 Optical microscopy

OM can be used for *in situ*, non-invasive monitoring of membrane surfaces. Generally, the microscope is combined with a camera to enable real-time recording. Due to fast scanning, OM can record evolution of fouling at the membrane surface. For example, Lee et al. employed OM to observe the gel layer formed on the surface of an UF membrane [83] when they studied oil emulsion separation by membrane technology. A drawback of the optical imaging is its relatively low resolution that is fundamentally limited by the wavelength of visible light. Therefore, this technique can be used to visualize fouling on the micrometer scale but the observation of foulants with smaller sizes such as polysaccharides and proteins is usually not possible. The maximal feed pressure that one can apply is limited since the observation is made through a glass window. Moreover, membrane modules should be optically transparent when wet to allow the light to go through and reach the membrane surface.

2.2.2.2 Confocal laser scanning microscopy (CLSM)

Compared to the conventional OM, confocal laser scanning microscopy (CLSM) can provide a better resolution with enhanced contrast. High-resolution CLSM images at different depths (“optical sections”) are amenable to 3D reconstruction [65]. This advantage avoids the physical slicing used in invasive techniques to obtain the sectional information. CLSM images provide information on the membrane structure, foulant

deposition on the membrane surface or inside membrane pores as well as differentiation of various components of the foulants. The most powerful feature of CLSM is fluorescence imaging, which can reduce the background signal and achieve higher resolution in comparison with that of a conventional fluorescence microscopy. Ferrando et al. investigate the proteins microfiltration by applying CLSM and observed the foulants deposit on the membrane surface or into the membrane pores [84]. Hassan et al. used CLSM to visualize the cake formation by a model bidisperse suspension containing two fluorescence latex particles with different sizes [29]. However, in applications where foulants do have possess an inherent fluorescence, conducting CLSM characterization required the foulants to be dyed with a fluorescent dye. The procedure requires caution to avoid influencing other properties of foulant that affect its interaction with a membrane. Due to the small penetration depth, CLSM applications to membrane fouling characterization have been restricted to MF membranes. Besides, the CLSM image quality is still not comparable to scanning electron microscopy (SEM) and often limited by the signal-to-noise ration.

2.2.2.3 NMR Chemical Shift Selective Micro-imaging (CHESS)

NMR imaging has been extensively employed for non-invasive study of flow fields including flows in membrane modules [85-87]. Examples include visualization of shell-side nutrient supply in bioreactors [88], flow distribution in tubular and hollow-fiber membrane modules [89, 90], and monitoring membrane fouling during crossflow filtration [91]. For example, Yao et al. employed NMR to characterize flow profiles during hollow fiber membrane filtration of oil-water emulsions [92] by mapped flow distribution and measuring flow rates of both feed and permeate under different operating conditions. Using chemical shift imaging methods, the formation of fouling layer was visualized directly and non-invasively.

Pope et al. quantified concentration polarization in tests with 5% v/v oil emulsion doped with CuSO_4 using chemical shift selective micro-imaging method, wherein specific species were mapped by selective excitation [93]. 2D oil-selective images were acquired every 10 min to follow the development of the oil layer on the membrane surface. 2D cross sectional images showed that the thickness of the oil concentration polarization layer was not uniform during the filtration process. The oil polarization layer was responsible for a major part of the overall resistance to permeate

flow. When studying the fluidity of the concentration polarization layer using chemical shift selective NMR flow imaging, Yao et al. [94] measured the net axial flow rate of $< 7.5 \mu\text{m/s}$ under the conditions tested (TMP of 70 kPa and Reynolds number in the 100 to 1000 range). NMR-CHESS microimaging is able to image opaque samples along any selected plane across the sample, quantitative imaging as well as spatial and chemical differentiation in dynamic systems. However, the cost for this technique is high and the size of the image domain is limited. The imaging process also takes relatively long time to operate.

2.2.2.4 Direct Observation through the Membrane (DOTM)

Direct observation through the membrane (DOTM) is one of significant applications of optical microscope. It was firstly reported in 1993 [95] and further developed by Li et al. in 1998 to observe the deposition of latex particles at the membrane surface and estimate the critical flux [96]. This technique has been a valuable tool in visualization of membrane fouling process. In a typical DOTM system (Fig. 2-7), it includes an optical microscope with both transmitted and reflected light source options and a crossflow membrane module made of transparent materials as well as a glass window on the permeate side. In the measurement, the microscope objective fitted with a video camera was positioned at the permeate side of membrane. The light from the microscope transmitted through the membrane. Images were recorded by the video camera, which was focused through the membrane and onto the feed side. The key point of this technique is to use a special membrane, which should be transparent during the filtration to allow the light to go through.

Figure 2-7 Schematic illustration of the DOTM setup [97].

Recently, Wang et al. applied DOTM to investigate the effect of granular activated carbon (GAC) on critical flux in the microfiltration of micro size latex particles [98] and they found the presence of fluidized GAC increased critical flux by an order-of-magnitude to that in the absence of GAC (Fig. 2-8). In spite of critical flux study by using DOTM, this technology is also widely used in the observation of the behavior of oil-water emulsions at different kinds of membranes [97] [99, 100]. Although DOTM is able to provide some interesting in-situ online information about fouling behavior, this technique is based on the use of optical microscope; therefore the resolution of the imaging technique is relatively low which limits DOTM application to visualizing the foulants with smaller size ($< 1 \mu\text{m}$). The required optical transparency of the membranes used in DOTM tests is another significant constraint.

Figure 2-8 DOTM images of polystyrene particles deposited on the membrane surfaces: (a) in the presence of fluidized GAC particles, and (b) in the absence of GAC particles [98].

2.2.2.5 Optical Coherence Tomography (OCT)

Optical coherence tomography (OCT) is a non-invasive imaging technique, which was developed for and first used in medical applications [101-103]. The application domain expanded to include imaging biofilms [104-106] and visualizing other objects and processes including membranes and membrane separations [107-109]. OCT can produce 2D and 3D images of the internal microstructure at a relatively fast rate [110] and visualize velocity profiles of the foulants by analyzing the OCT Doppler images. The basic principles of OCT have been described in detail by Schmitt et al. and by Fercher et al. [111, 112]. There are two scan procedures in OCT based on low time-coherence interferometry in the time domain: the OCT depth-scan and the lateral scan.

The depth-scan is performed by shifting the reference mirror. The lateral scan is performed by moving the sample or by scanning the probe beam across the sample. In addition to visualization of sample structures, OCT can obtain velocity profiles based on the Doppler effects. Gao et al. successfully used Doppler OCT to visualize flow patterns inside the unit cell of a spacer in a membrane filtration module [107], to visualize cake layer, and quantify its growth on membrane surfaces [108]. Inspired by the successful application of OCT in membrane filtration, they explored the feasibility of applying OCT techniques to visualize and quantify the growth of cake layer during membrane filtration [108].

Recently, Trinh and his coworkers employed 3D OCT characterization to analyze membrane fouling during microfiltration of oil-water emulsions [113, 114]. Analysis of the variation in OCT intensity at various distances with respect to feed-membrane interface revealed external and internal fouling by oil. The evolution of membrane fouling was quantified in terms of the fraction of “fouling” voxels as a function of time at varied depths. Figure 2-9 shows the temporal sequence of OCT 2D cross-sectional images: the upper dark regions correspond to the feed liquid phase, whereas the bright regions resulted from the changes in the refractive index because of the discontinuity of the media when the incident light penetrated liquid-polymer boundaries. Beneath the feed-membrane interface, another horizontal bright region is apparent, which corresponds to the porous stainless-steel plate supporting the membrane. Bright spots correspond to the deposition of the foulants starting ~ 10 min into filtration. A clear increase in the fraction of fouling voxels observed for the layers both above and below the feed-membrane interface (Fig. 2-10) shows that OCT can detect both external and internal fouling in real time. However, the relatively low resolution of OCT, the requirement of having a transparent observation window, the need for specialized equipment (membrane module) and complexity of data analysis limit broader application of this technology.

Figure 2-9 Temporal sequence of the 2D cross-sectional images of the membrane and the foulants during the dead-end filtration ($0.45 \mu\text{m}$ PVDF membrane, $\text{TMP} = 40 \text{ kPa}$) of the feeds containing 5 ppm hexadecane oil droplets obtained using the OCT [113].

Figure 2-10 Evolution of fouling in terms of the fractions of the fouling voxels in the various layers (a) above the feed-membrane interface; (b) below the feed-membrane interface [113].

2.2.2.6 *Electrical impedance spectroscopy (EIS)*

Electrical impedance spectroscopy (EIS) has been widely used in probing biological membranes and interfaces [115]. The EIS system was modelled by the Maxwell-Wagner equation, which characterizes the capacitance and conductance of the components of the system as a function of the sinusoidal voltage wave. During the membrane filtration process, an alternating current is directly injected into the coat via electrical contacts on the edges of the membrane. The current in the membrane flows across the interfacial region and disperses into the bulk and permeate solutions. The spatial dispersions will change with the variation of the frequencies. This dispersion phenomenon can be characterized by the capacitance and conductance of various components in the filtration system. Once the membrane is fouled, the dispersion of current would change. Therefore, measuring the variation of the electrical impedance in membrane filtration process can be used to monitor fouling [116]. To date, many membrane fouling studies with RO, FO, and NF flat sheet membranes have been carried out [117-119] where EIS provided useful functional and structural characterization data on the fouling layer at a sub-micron level. The dielectric structural modeling of EIS measurements could detect and characterize five electrically distinct layers and a concentration/diffusion polarization element throughout the filtration experiment [120]. Recently, Bannwarth et al. reported a two-electrode technique, by which EIS method can be expanded to in situ monitor fouling on the hollow fiber membrane [121]. At the same time, quantitative description of the changes in electrical properties has been studied in RO membrane fouling process [122]. However, conductive materials and special membrane module required for the testing will still limit the application of EIS.

2.2.2.7 *Ultrasonic time-domain reflectometry (UTDR)*

Ultrasonic time-domain reflectometry (UTDR) was developed by Peterson et al. to measure membrane compaction during reverse osmosis [123]. UTDR uses sound waves to locate an interface (moving or stationary) and can provide information on the physical characteristics of the media through which the waves travel. A non-invasive real-time technique, UTDR has been extensively used to monitor membrane compaction as well as growth of membrane fouling layers during filtration [124-126]. Ultrasonic frequency spectra can be transformed into wavelets, which can provide information on the growth and change in density of the fouling layer [124, 127-130].

Silalahi et al. used UTDR to explain the effect of droplet size on membrane fouling during crossflow MF of oil emulsions [131]. When the droplet size was larger than the membrane pore size, the fouling was a two-step process where droplet attachment was followed by cake layer formation. Liu et al. applied UTDR to monitor membrane fouling in a hollow fiber module by filtering wastewater with three different oil concentrations [132] and proposed a new signal analysis protocol to analyze fouling and cleaning processes. Figure 2-11 shows that reflected ultrasonic energy decreases with time, which can be attributed to the attachment of oil droplets to the membrane surface. The variation in the reflected energy was in agreement with the flux decline trends pointing to the suitability of UTDR as a method for detecting membrane fouling [132]. UTDR can provide rich information on fouling layers and without constraints on the type and material of the filtration module. However, UTDR has a response time limitation. If the fouling layer is too thin, ultrasonic signals do not generate an echo at the feed/fouling layer interface. Further, although the low-frequency ultrasonic sensor gives well separated waves of large amplitude, the lateral resolution is poor. Moreover, since the penetration of the acoustic waves at low frequencies is much greater than that at high frequencies but the resolution is greater at high frequencies, a trade-off between the attenuation and the resolution of the acoustic waves is required.

Figure 2-11 Acoustic spectrum (a) and ultrasonic reflected energy (b) vs operating time during ultrafiltration for wastewater with oil concentration of 500 mg/L [132].

Characterization techniques for membrane fouling monitoring can provide valuable insights into the fouling mechanisms and inform fouling control strategies. Invasive techniques are destructive to the membrane and are usually conducted *ex situ*. However, compared to the common non-invasive techniques, they have their unique advantages, such as detailed information on the composition of foulants. Table 2-3 summarizes advantages and drawbacks of the techniques applied for characterizing membrane fouling.

Table 2-3 Invasive and non-invasive visualization techniques applicable in studies of membrane fouling.

Visualization techniques	Advantages	Disadvantages	Reference
Invasive			
SEM	high resolution; identification of foulant morphology	requires high vacuum; complex sample preparation	[70, 71, 133-138]
AFM	high-resolution 3D image; ability to qualified surface roughness; measurement could be done in air or in liquid	presence of artifacts; potential to damage the sample	[135, 137]
ATR-FTIR	Identification of chemical composition; easy sample preparation	Unable to provide visualized image	[77, 78, 135, 138]
EP	Quantitative measurement of pore size distribution for clean and fouled membrane	Unable to provide visualized image; correction needed for testing asymmetric membrane	[139, 140]
Non-invasive			
Optical microscopy	Fast imaging	Low resolution; requires transparency of the membrane and membrane module	[83]
CLSM	High resolution; three-dimensional images; differentiating different species; Assess morphology	Required addition of a fluorescer; small penetration depth	[27, 28, 84]
NMR	Quantitative; provides spatial and chemical information	Requires special membrane module; slow imaging process; small image size	[92-94]
DOTM	fast time scale; interaction study between membrane and oil droplets	Low resolution; requires special membrane and membrane module	[97, 99, 100, 141]
OCT	Real-time and cross-sectional imaging	Low depth resolution; requires special	[113, 114]

		membrane module design	
EIS	Quantitative; online monitoring; early and multilayer detection	Requires special membrane module design and conductive materials	[142, 143]
UTDR	Quantitative; real-time imaging	Slow response time; poor lateral resolution; unavailable for thin fouling layers	[131, 136]

2.2.3 Summary of Literature Review

Fig.2-12 represents the summary of the literature review in this chapter, the highlighted boxes in blue color are the dominant methods employed to investigate membrane fouling mechanism in the whole thesis. Microfiltration is an attractive membrane filtration process due to its relatively lower operating pressures and higher permeation fluxes. However, membrane fouling due to the accumulation of foulants on/within the membranes during filtration process leads to not only the reduction of productivity but also damage membrane functionality, which makes the process less efficient and increase operating cost. Developing effective techniques for mitigating membrane fouling relies on an in-depth understanding of the fouling mechanisms. Many previous studies have been investigated membrane fouling by applying fouling models and/or by characterize fouling behaviors with a variety of visualization techniques. However, the combination of modelling and real time in-situ characterization approaches at a pore scale, which is significant to obtain a deeper insight of understanding fouling mechanisms during membrane filtration, has not been undertaken yet. This thesis plan to bridge this gap by applying a new developed network model coupled with advanced OCT characterization method to reveal the underlying fouling mechanisms during microfiltration with different model foulants.

Figure 2-12 Diagram of summary of literature review.

Chapter 3 A Network-Based Approach to Interpreting Pore Blockage and Cake Filtration During Membrane Fouling

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Abstract

The efficiency of membrane-based separations is limited by various fouling phenomena, which necessitates a mechanistic understanding in order to improve such processes. This study proposes a network-based approach, in which the membrane is discretized and each particle is individually monitored, to explore the underlying fouling mechanisms leading to pore blockage and cake growth during a membrane filtration process. In particular, the network-based approach provides more spatial resolution than the continuum approach, thereby gives a more in-depth insight into membrane fouling. The network model developed involves the construction of a two-dimensional (2D) network of pores to represent the membrane, a series of probabilistic criteria to describe the fate of each individual particle, and finally a protocol for evaluating the fouling during either a constant flux or constant TMP (transmembrane pressure) filtration. Three fouling parameters can be obtained to characterize the fouling behavior, namely, the probabilistic factor for deposition in the dead zone (β), the initial cake resistance (R_{c0}), and the specific cake resistance with respect to cake thickness (R_c'), by best-fitting the experimental flux-decline data to the network model. The capability of the network model to account for the topological and stochastic aspects of a fouling process provides for a more mechanistic understanding of the complex interactions between the fluid flow, membrane, and foulant particles vis-à-vis a model based on the continuum assumption. Although limited fouling cases were examined in the current study,

it is expected that the network model developed here can be readily applied to study more complex phenomena involved in a membrane filtration process (e.g., shear-induced diffusion), and the associated insights would be significantly enhanced when coupled with more advanced fouling characterization techniques (e.g., Optical Coherence Tomography).

Keywords: Membrane fouling; Network modeling; Regression analysis; Pore blockage; Cake filtration

3.1 Introduction

Membrane fouling is a complex phenomenon that involves the interplay between fluid dynamics, foulants, and membrane materials during a membrane filtration process. Developing techniques for effectively mitigating membrane fouling to a great extent relies on an in-depth understanding of the mechanisms that underlies how the overall behavior of the filtration system, such as the variation in the permeation flow rate or trans-membrane pressure (TMP), responds to the dynamics of foulant deposition at multiple scales. Although experimental studies are the most direct way to explore the membrane fouling phenomena, mathematical modeling plays an essential role in interpreting various fouling mechanisms and extracting the intrinsic physics.

As reviewed by Sahimi *et al.* [13], mathematical models for describing the transport phenomena associated with a porous medium can be classified into continuum and discrete models. The continuum models have been extensively employed to study membrane fouling, including the classical fouling models (namely, the complete pore blockage model [53, 144], the intermediate pore blockage model, the cake filtration model [145], and the pore constriction model [52, 146]) and lately evolved into models that account for multiple fouling mechanisms, such as the combined fouling model (which coupled not only the complete and intermediate pore blockage model but also the cake filtration model) by Ho and Zydney [52] and the three-mechanism model by Duclos-Orsello *et al.* [53]. Despite having different focuses on the dominant membrane fouling mechanism, these fouling models assume that not only the spatial domains (e.g., the membrane and the fluid channel) but also the velocity and

concentration fields can be described by smooth functions. The dynamical processes are described by the phenomenological relations [14, 15], but the topological aspects of membrane fouling, such as the connectivity of the porous structure and the distribution of the deposits, are ignored owing to mathematical complexities.

Taking advantage of the advancement in computational capacity and algorithms, discrete models are getting more attention in the field of membrane process simulation. Instead of assuming a continuum, a discrete model represents the spatial domain as an array of unit cells and thereby adapts the species conservation law to the individual unit cells. The array of unit cells to represent the membrane topology is referred to as a network. Such network models are developed to accommodate random processes by establishing a series of probabilistic criteria [147], which is key to understanding and simulating membrane fouling as the local fouling behavior is stochastic in nature [148]. A network-based method has been proposed by Li [147] to investigate the effects of membrane asymmetry on membrane fouling, and further extended to account for the concentration polarization within the supporting structure of a forward osmosis (FO) membrane [60]. More recently, Griffiths *et al.* [61] employed a similar network model to theoretically interpret the flux-decline behavior during membrane fouling. A key advantage of network modeling highlighted by these studies is the much enhanced spatial resolution relative to the continuum model. The ability to account for the local fouling behavior at a scale defined by a unit cell allows for the accounting of the topological and stochastic aspects of a fouling process and is significant in the understanding of the fouling phenomenon on two counts. Firstly, it offers a tool for correlating the experimental observations from advanced characterization techniques for studying membrane fouling, such as the direct observation through the membrane (DOTM) [26], optical coherence tomography (OCT) [33], and electrochemical impedance spectroscopy (EIS) [149]. Secondly, it provides a highly flexible framework whereby each fouling mechanism can not only be readily extracted for a mechanistic understanding, but also readily combined to simulate practical fouling processes under various operating conditions.

The current study was aimed at developing a systematic approach to analyse membrane fouling via network modeling. In particular, the focus was on interpreting the pore blockage and cake growth on the membrane surface, both of which are categorized as external fouling in the literature [150-152]. The specific objectives in the overarching goal of developing the network model were to (i) determine the numerical stability and sensitivity of the model, (ii) compare the network model developed with the well-established continuum model [52], and (iii) validate the network model with experimental data. Accordingly, the steps taken in constructing the network model were: (1) to construct a two-dimensional (2D) network of pores to approximate a membrane having pores with specific distributions in size and location; (2) to establish a series of probabilistic criteria to describe the fates of each foulant particle; and (3) to develop a protocol for assessing both a constant flux and constant TMP (transmembrane pressure) filtration process.

3.2 Model Development

3.2.1 Constructing a network

The key basis of a network-based simulation is to approximate the porous structure or membrane with a hypothetical network that has two or three dimensions. Although the proposed method can be readily extended to account for more complicated membrane structures, it is expedient to restrict the current study to membranes having the simplest porous structure, i.e., uniform straight through cylindrical pores, so as to validate the model. Because the thickness of the membrane is very much smaller than the area of the membrane evaluated, a two-dimensional (2D) network can be used to approximate the membrane.

The 2D network is obtained by discretizing the membrane surface into square unit cells, whose area A_u is first estimated by assuming that a single pore is contained in each unit cell:

$$A_u \approx \pi \left(\frac{\bar{d}_{mp}}{2} \right)^2 / \varepsilon_m, \quad (3-1)$$

where ε_m is the membrane porosity and $\bar{d}_{mp}$ is the mean pore diameter. When the network area A_{nw} (i.e., the membrane area evaluated) is specified, the number of unit cells N_u is approximately equal to

$$N_u \approx \frac{A_{nw}}{A_u}. \quad (3-2)$$

On one hand, the network area A_{nw} should constitute a representative membrane surface whose area is large enough to encounter sufficiently many foulant particles such that the average fouling behavior is independent of the random behavior of any particle. On the other hand, increasing the network area A_{nw} markedly increases the number of the unit cells N_u as indicated by Eq. (3-2), thereby leading to a greater computational load in terms of a larger memory to store the data and a longer time for the calculation. Therefore, lower and upper limits exist for N_u . Regarding the lower limit, a strict definition is not possible, hence the recourse can be to perform uncertainty analyses to verify that N_u is sufficiently large to yield statistically meaningful outputs. As for the upper limit, a maximum $N_{u,\max}$ for the number of unit cells can be specified to limit the computational load; that is, when the number estimated with the single pore assumption is greater than $N_{u,\max}$, the value of N_u will be replaced by $N_{u,\max}$. In this study, $N_{u,\max}$ was set at 1,000,000. In the case of using $N_{u,\max}$ as the number of unit cells, the single pore per unit cell assumption does not hold and one needs to recalculate the number of pores in each unit cell using

$$N'_u = \frac{A_{nw} \varepsilon_m}{\rho \left(\frac{\bar{d}_m}{2} \right)^2} \bigg/ N_{u,\max} \quad (3-3)$$

Note that the value of N_u' may not be an integer. Instead of simply rounding N_u' to the nearest integer, a novel strategy for dealing with the non-integer cases is to employ the fractional part of N_u' as the probability of adding one more pore to each unit cell. In such a way, the difference between the porosities of the network and membrane is minimized. Specifically, there will be unit cells without any pores in the network if $N_u' < 1$. The fraction of the unit cells without pores ϕ_{ud} should be small since the single pore per unit cell assumption ensures that the fraction of the unit cells with pores ϕ_{uo} could not be significantly less than 1.

Figure 3-1 Flowchart illustrating the protocol employed for constructing a 2D network.

The key steps in constructing the network are summarized by the flowchart in Fig. 3-1 and described as follows. Firstly, assuming one pore per unit cell, the area of each unit cell (A_u) is calculated using Eq. (3-1) based on the membrane properties of porosity (ϵ_m) and mean pore diameter ($\bar{d}_{mp}$). Secondly, the number of unit cells (N_u) is derived using Eq. (3-2). The N_u

value obtained is compared against $N_{u,\max}$. If $N_u > N_{u,\max}$, N'_u is calculated using Eq. (3-3). Then, N'_u is used to replace N_u if N'_u is an integer, and the fractional component of N'_u was used to add more pores to the unit cells (i.e., the fraction corresponds to the number of additional pores divided by the total number of unit cells) if N'_u is not an integer. Thirdly, an array of pore diameters is generated and assigned to each pore to make up the pore-size distribution of the membrane. In this study, the pore diameters were assumed to be uniform. Finally, agreement of the porosity (ε_m) and mean pore diameter ($\bar{d}_{mp}$) values between the resulting network and the membrane of interest is ensured. It should be noted that the 2D network generated may not be unique, since probabilistic strategies are employed to determine not only the pore number but also the pore diameter d_u in each unit cell, whose deviation from the value of $\bar{d}_{mp}$ is assumed to be a normal distribution.

3.2.2 Describing the fouling behavior of individual particles

In contrast to fouling models based on the continuum approach whereby all the particles are treated as a continuous fluid, network-based simulations treat each particle discretely and require a numerical description of the process experienced by each particle. The crux of the numerical description is to establish a series of probabilistic criteria that determine the fates of individual particles, i.e., their final states after the filtration. For the external fouling of interest here, the particle movements outside the membrane structure are dictated by both the permeate flow (i.e., the flow whose direction is normal to the membrane surface) and the tangential flow (i.e., the flow whose direction is parallel to the membrane surface). Thereby, the network-based simulation allows for the behavior of each particle to be probabilistically interpreted while lumping the details of the complex flow-particle interactions.

Prior studies [150, 153] attribute the external fouling during membrane filtration to the gradual blockage of the membrane pores during the initial filtration and the cake growth dominating the longer term fouling. When considering the fouling behavior of a single particle, four scenarios are possible: the particle can (i) pass through the pore; (ii) deposit at the dead zone (i.e.,

region of membrane without pore); (iii) deposit at and block the pore; or (iv) deposit on the formed cake layer. Scenario (i) is the only one that does not lead to a flux decline. For scenarios (ii) and (iv), the probabilities P_m and P_c can respectively be defined for a particle that adheres to the dead zone of the membrane and for a particle that attaches to the particle layer. It should be noted that P_c and P_m are very similar in principle, since both relate to a particle depositing on a surface. The values of P_c or P_m are determined by the specific membrane or cake surface and the micro-hydraulic environment. Before the cake layer is formed, P_c equals to P_m , since the only surface the particle can deposit on is the membrane. When only some pores are blocked, we need to use P_m to determine if the particle will block the pore, so P_c is not relevant assuming reasonably that no significant cake layer has developed in the unit cell before all the pores are blocked. After all the pores are blocked, all particles inevitably deposit on the membrane dead zone or cake layer, so P_m or P_c equals 1. Therefore, the consideration of P_c is not needed, but the network model developed here does account for longer-term fouling, in particular cake deposition. Specifically, the cake characteristics is quantified by the two fouling parameters, namely, the initial cake resistance (R_{c0}) and the specific cake resistance (R_c').

The value of P_m is directly proportional to the membrane area not occupied by the membrane pores (i.e., $(1 - \varepsilon_m)$). In this case the proportionality constant is not simply the network area (A_{nw}), but is dependent on a number of factors associated with the complex flow dynamics and particle-membrane interactions, which can be lumped into a single parameter β . Specifically, β is a probabilistic factor for deposition in the dead zone of the membrane, whose magnitude reflects the affinity of the particle to the membrane material, thereby providing insights into such interactions. A larger and smaller β indicate respectively a higher and lower likelihood of the particle depositing on the dead zone of the membrane. One of the goals of the current study was to verify if the variation of the β values is capable of revealing the fluid-particle-membrane interactions in simple cases with model particulate foulants, the validation of

which would be useful for providing more mechanistic understanding of more complex systems. Therefore, P_m can be expressed as:

$$P_m = \beta(1 - \varepsilon_m). \quad (3-4)$$

When the membrane is approximated by a 2D network according to Fig. 1, the fate of a particle during the filtration then is determined by the interplay between the particle and unit cells, while the criterion based on P_m needs to be adapted to the network-based process at each decision-making step.

Fig. 3-2 shows a flowchart that illustrates the probabilistic strategy to determine the fate of a particle, with a diameter d_p within the diameter range of the feed, during dead-end filtration. Firstly, it is determined whether the particle would contact a unit cell without pores. When the number of unit cells without pores N_{du} is much less than the total number of unit cells N_u , the probability of the particle contacting a unit cell without pores P_d can be approximated in terms of β :

$$P_d \approx \beta \frac{N_{du}}{N_u}. \quad (3-5)$$

A randomly generated number X ($0 \leq X \leq 1$) is compared with P_d . The particle is assigned to the unit cell without pores if $X \leq P_d$, which physically means the particle deposits on the dead zone of the membrane (i.e., region without pore), and the evaluation ends. Secondly, if $X > P_d$, the probability (P_i) of the particle contacting a specific unit cell with pores is proportional to the flow rate within that unit cell and calculated as follows:

Figure 3-2 Flowchart illustrating the protocol employed for describing the stochastic fouling behavior of each individual particle in the 2D network.

$$P_i = \frac{Q_i}{Q_t} \quad (3-6)$$

where Q_i and Q_t are the flowrate through the pore in the current cell and the total flowrate, respectively. A random number Y ($0 \leq Y \leq 1$) is generated to determine which unit cell the particle will approach based on $P_1 + \dots + P_i < Y < P_1 + \dots + P_{i+1}$. Once the unit cell is determined, it is accessed if any open (i.e., unblocked) pore is present. If not, the particle deposits on the cake. Thirdly, in the event that an open pore is present in the unit cell, the probability of the particle being retained by the unit cell P_u is evaluated in terms of the porosity of this unit cell ε_u :

$$P_u \approx \beta(1 - \varepsilon_u) \quad (3-7)$$

A third random number Z ($0 \leq Z \leq 1$) is generated and compared with P_u . If $Z > P_u$, the particle passes through the pore if the particle is smaller than the pore,

or deposits on the pore otherwise. However, if $Z \leq P_u$, the particle deposits on the dead zone or the cake.

3.2.3 Simulating a membrane fouling process

The membrane fouling process is tied to whether the operating mode is of constant TMP or constant permeation flux. In contrast to the continuum approach that requires a major revision of the model to switch between the operating modes, the discrete description of a fouling process enables the network-based simulation to readily accommodate the different operating modes. The strategies for simulating fouling processes with the constant flux and constant TMP modes are illustrated by the flowcharts in Figs. 3-3 (a) and (b), respectively.

Both strategies are essentially based on the pseudo steady-state assumption. Specifically, the particle deposition should have negligible impact on the hydrodynamic environment of a unit cell if the period of evaluation is sufficiently short, which necessitates that the temporal discretization is appropriate. A finer temporal discretization would improve the accuracy of the simulation, but at the cost of increasing the computational load. Similar to the numerical method of solving an initial value problem [154], the evolution of the fouling process is resolved by sequentially evaluating the particle deposition in each time subdomain, although a stability analysis of the algorithm is not possible due to the complexity associated with the probabilistic approach.

The protocol for the constant flux algorithm in Fig. 3-3 (a) is described more explicitly as follows: (1) the time interval (Δt), flux and clean membrane resistance (R_m) are specified, and the time is initialized at $t = 0$; (2) the number of particles contacting the network (i.e., the membrane) in the time interval of Δt is calculated; (3) the fates of each of these particles are determined (Fig. 3-2), and then the resulting resistance and TMP increment are evaluated; and finally (4) the time t is increased by Δt , and if t is less than the duration assessed, the preceding step is repeated. For the constant TMP algorithm in Fig. 3-3 (b), the only differences are that the constant TMP instead of constant flux is specified in the first step, and the flux decrement instead of TMP increment is calculated in the third step.

Regarding step (2), as the effect of the tangential flow (i.e., parallel to the membrane) on the particles has been lumped into the probabilistic factor β , the number of the particles conveyed to the network during Δt_i is assumed to be proportional to the permeation flow rate through the network Q_{nw} :

$$N_{p,i} \approx \frac{C_f Q_{nw} \Delta t_i}{\frac{4}{3} \pi \left(\frac{\bar{d}_p}{2} \right)^3 \rho_p}, \quad (3-8)$$

where C_f is the weight-based concentration of the feed solution; $\bar{d}_p$ and ρ_p are the average particle diameter and density, respectively. Although Q_{nw} is a function of time for a constant TMP mode (Fig. 3-3 (b)), the pseudo-steady state assumption requires that Q_{nw} for the i^{th} period should be fixed at a constant value, which is determined by the state of each unit cell in the end of the $(i-1)^{\text{th}}$ period.

Regarding the calculation of resistances in step (3), there are various methods for estimating the cake resistance in a unit cell if the number of the particles rejected by this unit cell is given. As the network-based approach attempts to avoid the complexity arising from the subtle fluid-particle interactions, a simple way is employed to formulate the cake resistance R_c by defining a specific resistance R'_c in terms of the cake thickness, which is given by

$$R_c = R'_c \frac{V_{up}}{A_u (1 - \varepsilon_c)}, \quad (3-9)$$

where V_{up} is the total volume of the particles rejected in the unit cell and ε_c is the porosity of the cake layer. Therefore, the relationship between the fluid flux through a pore J_{mp} and the transmembrane pressure (TMP) can be given by

$$J_{mp} = \frac{\Delta p}{\mu (R_{mp} + R_c + R_{c0})} \quad (3-10)$$

where μ is the viscosity of the feed solution and R_{mp} is the hydraulic resistance of the cylindrical pore. In particular, R_{c0} is referred to as the initial cake resistance caused by a particle, which accounts for the pressure loss through the gap between the rejected particle and pore entrance. Note that Eq. (3-10) should be recast into the form with Δp as the dependent variable when the simulation is applied to the fouling process with a constant flux mode as indicated by the flowchart in Fig. 3-3 (a).

Figure 3-3 Flowcharts illustrating the protocol employed for simulating a membrane fouling process via the network-based method: (a) constant flux mode, and (b) constant TMP mode.

3.3 Experimental and Numerical Methods

3.3.1 Membrane fouling experiments

Membrane fouling experiments are not only a tool for directly studying fouling mechanisms but also essential in validating fouling models, which in

turn provide physical insights into the fouling process. In the current study dead-end filtration experiments were employed. The experimental data was first used to validate the network model, then regression analysis was carried out to extract the fouling parameters that shed light on the fouling mechanisms.

In the current study a track-etched membrane (catalog number WH-111111, Whatman, USA) having relatively uniform cylindrical pores each with a diameter of $2\ \mu\text{m}$ was employed for all the fouling tests. The membrane had a relatively low porosity ($\varepsilon_m \approx 0.05$), which could result in significant tangential flow in the dead zones, i.e., the inter-pore regions. Latex particles with two particle diameters ($\bar{d}_p$) of 3 and 5 μm (catalog numbers 79166 and 79633, Sigma Aldrich, USA) were used as the model foulant particles for the fouling tests.

A schematic of the dead-end filtration setup is displayed in Fig. 3-4. The dead-end filtration cell was composed of an upper and lower fluid chambers that sandwiched a membrane with an active area of $9.62\ \text{cm}^2$. The upper chamber was for the feed solution containing the foulant particles. In particular, the feed stream was split into four sub-streams, which entered the upper chamber through the holes uniformly distributed on the lateral wall; these holes were at a distance of approximately 2 cm from the membrane to minimize the entrance effect. A stainless-steel sintered plate was placed in the lower chamber to support the membrane. It was assumed that the pressure drop resulting from this porous plate was negligible.

The liquid flow was driven through the membrane by gravity. As shown in Fig. 3-4, feed container B was fixed at a position higher than the outlet tube for the permeation stream draining into permeate container C; the TMP then was proportional to the height difference of water column H_w . In order to maintain the TMP at a constant value during the filtration, the same feed solution was continuously pumped into container B from container A to maintain the same liquid height in container B. The TMP was fixed at different values around 6 kPa in order to maintain the permeation flow rate of DI water

at a value of 80 mL/min. The permeation flow rate (Q_m) was determined by measuring the change in the volume of liquid in container C per unit time.

Figure 3-4 Schematic showing the experimental setup for measuring the flux-decline curve during a membrane fouling process under the constant TMP mode. The TMP was proportional to the height difference of water column H_w ; the liquid surface in container B is maintained by continuously supplying the same solution from container A. The stream of the feed solution is split into four sub-streams that enter the upper chamber of the filtration cell from different directions (90° apart) to minimize secondary flows. The permeation flow rate is measured by weighing the liquid in container C and a representative flux-decline result is shown in the lower panel indicating the three key stages of each measurement.

Each fouling experiment consisted of three parts (namely, I, II and III) as indicated by a representative plot of the permeation flow rate (Q_m) versus time in Fig. 3-4. The filtration in Part I was performed using DI water as the feed solution to quantify the water permeability of the membrane. This served as a benchmark for comparison among different membranes, since variations in permeability are expected. For Part II, the filtration was intermittently stopped by closing valve B to ensure that the permeation flow rate (Q_m) became zero.

This was to ensure the robustness of the experimental setup. At the beginning of Part III, valve B was closed while the desired amount of concentrated solution containing the foulant particles was mixed into both containers A and B. Circulation of the foulant solution was carried out for about 2 minutes, which ensured uniform conditioning of the membrane by the foulants without initiating fouling, before valve A was closed and valve B opened. This was to initialize the fouling on the membrane and minimize the dilution effect in the upper chamber. The sampling interval was set at 0.5 min to yield approximately 80 sampling points for each fouling test (Part III). Each of the fouling tests was repeated at least three times to verify the reliability of the results.

3.3.2 Numerical experiments

The network modeling targeted at numerically duplicating the permeation flow rate $Q_m(t_i)$ during the fouling experiments in order to extract the fouling parameters (namely, probabilistic factor accounting for dead zone deposition β , initial cake resistance R_{c0} , and specific cake resistance R_c') via regression analysis. The first step of the network modeling was to construct a 2D network in terms of the characteristics of the track-etched membrane, as described in Fig. 3-1. A micrograph of the track-etched membrane is displayed in Fig. 3-5 (a). It is evident in Fig. 3-5 (a) that some pores were in contact with one another and appear as larger pores. The existence of such connected pores results in asymmetry of flows in the vicinity of the pores. It is reasonable to expect that this asymmetry would have little impact on the random events described by the network model, especially in the case considered in the current study in which the membrane had a relatively low porosity.

However, when a pore is connected with more pores, the probability of blocking the pore by a particle could be significantly changed. In such a case, more details of the membrane structure have to be included in the data structure that numerically describes the network and more criteria are required to determine the random events involved in the initial fouling. This is possible by the network model developed here, but beyond the current scope. When the area of the network was set at a value of $5 \times 5 \text{ mm}^2$, the spatial discretization based on the single pore per unit cell assumption, average pore diameter ($2 \mu\text{m}$) and membrane porosity ($\varepsilon_m \approx 0.05$) yielded an ensemble of 631×631 square unit cells whose width was approximately $8 \mu\text{m}$, as schematically illustrated in Fig. 3-5 (b). Specifically, Fig. 3-5 (b) superimposes the generated grid with the

Figure 3-5 (a) Representative image of the membrane with straight-through cylindrical pores (and) taken with a digital microscope (Keyence, USA); (b) Grids used to discretize the membrane based on the 2D network model; and (c) Resulting 2D network.

micrograph of the track-etched membrane (Fig. 3-5(a)) to illustrate that, even though the number of unit cells were calculated based on the single pore per unit cell assumption, the pores are randomly distributed such that some unit cells contain more pores while some have none. Nonetheless, on average, approximately a single pore is found in each unit cell, as shown in Fig. 3-5 (c). The generated network in Fig. 3-5 (c) indicates that a small fraction (0.7%) of the unit cells contained no pores so as to compensate for the minute difference between the calculated unit cell porosity ($\varepsilon_u \approx 0.0503$) and the actual membrane porosity ($\varepsilon_m \approx 0.05$); the unit cells without pores were randomly distributed in the network.

In the temporal domain the fouling process of 40 minutes in this study was discretized into at least 1000 time intervals (Δt) whose lengths were varied such that shorter intervals were used for the initial transient fouling period and longer intervals as a steady-state was attained. Then, the permeation flow rate (Q_m) was numerically evaluated at the times corresponding to the sampling points of the fouling experiment, as described in Fig. 3-3 (b). In the current work regression analysis [155] was carried out to obtain the best-fit fouling parameters that minimized the residual sum of squares (RSS), that is, the sum of $\left(\hat{Q}_m(t_i) - Q_m(t_i)\right)^2$, where $\hat{Q}_m(t_i)$ is the permeation flow rate evaluated by the network model and $\hat{Q}_m(t_i)$ denotes the permeation flow rate measured experimentally.

In contrast to a continuum fouling model, which usually accounts for the deterministic aspects of a fouling process, the network model interprets the fouling process using a series of probabilistic descriptions, which expresses the predicted quantities as random variables with unknown distributions, such as the permeation flow rates $\hat{Q}_m(t_i)$. The stochastic characteristic of the network modeling therefore entails special considerations when the network model is used as a regression function to fit the experimental data in a least squares sense.

Most importantly, one needs to fit the experimental data to the expectation of the modeling results rather than the results from a single simulation; mathematically, this requires performing the simulation with the same parameters infinite times. The current study balanced the trade-off between mathematical rigor and calculation efficiency by using the mean of the modeling results from finite number of simulations as the predicted value for the curve fitting. Specifically, the Gauss-Newton method [156] was employed to deal with the nonlinear regression, whereby the best-fit parameters were resolved by means of iteration. In this study, the iteration was carried out until the relative standard deviation (RSD, i.e., the ratio of the standard deviation to the mean) was of the order of 10^{-5} , which was the same criteria as that employed for the continuum model used here for comparison. As will be illustrated in the discussion section, analyzing the efficiency and stability of the adopted

Figure 3-6 Schematics comparing different modeling approaches used in accounting for the pore blockage and cake filtration phenomena: (a) a continuum modeling approach; and (b) a discrete modeling approach as per the network model developed here.

numerical algorithms offers a useful tool of studying the random fouling behavior during membrane filtration. All the simulations were implemented

using MATLAB codes developed in-house that enabled parallel computing for reducing the computation time.

3.4 Results and Discussion

3.4.1 Sensitivity and uncertainty analysis for the network model

As introduced in the section of model development, three fouling parameters are defined in the network model, namely, the probabilistic factor accounting for dead zone deposition β , the initial cake resistance R_{c0} , and the specific cake resistance R_c' . The probabilistic factor β plays the key role of characterizing the stochastic nature of external fouling. Although the initial cake resistance R_{c0} and the specific cake resistance R_c' are defined in a deterministic sense, their effects on the simulation results are to some extent of uncertainty owing to the intrinsic correlations between the three fouling parameters. Therefore, an important step in analyzing a fouling process via the network model is to determine the sensitivity ranges of the fouling parameters and verify the degree of uncertainty in the model predictions when varying the fouling parameters within the sensitivity ranges. Having reasonable initial estimates for the fouling parameters is important. When the track-etched membrane has a porosity of 0.05, the reasonable upper bound of β is approximately 1.05 per Eq. (3-4), while the lower bound is zero, which corresponds to the limiting case that pore blockage would definitely occur whenever a particle was conveyed into the vicinity of an open pore. According to the Kozeny-Carman equation [157], the order-of-magnitude of R_c' is 14 for the cake layer formed by the particles with a diameter of 3 μm if a random packing is assumed to yield a cake porosity of 0.38 [158].

Figure 3-7 Sensitivity and uncertainty analysis of the effect of the probabilistic factor β on permeate flux: (a) mean and (b) relative standard deviation of the normalized flux (Q_m/Q_{m0}). R_{c0} and R_c' were fixed in the network model, while the value of β was varied between 0 and 1. Each of the flux-decline curves was repeated five times. The 2D network was composed of 631×631 unit cells corresponding to a track-etched membrane ($A_m = 25 \text{ mm}^2$ and $L_m = 33 \text{ }\mu\text{m}$), whose pore diameter and porosity were $\sim 2 \text{ }\mu\text{m}$ and ~ 0.05 , respectively. The feed solution was assumed to contain spherical particles (0.005 g/L) with a diameter of $3 \text{ }\mu\text{m}$ and the TMP for the dead-end filtration was fixed at 6.56 kPa .

It should be noted though that the value of R_c' defined for a membrane pore by the network model could be significantly lower than the one estimated by the Kozeny-Carman equation that does not account for the tangential flows within the cake layer. Fig. 3-6 compares the flow profile associated with the continuum assumption (Fig. 3-6 (a)) to that based on a discrete approach (Fig. 3-6 (b)). For the continuum assumption (Fig. 3-6 (a)), the pore and non-pore areas are not distinguishable. Although the combined fouling model is able to account for the heterogeneity of the cake layer, the deposits form a continuous distribution on the membrane surface. Therefore, the tangential flow at each pore is not accounted for. In contrast, for the discrete approach (Fig. 3-6 (b)) in

the network model developed here, the differentiation of the impermeable dead zone and the straight-through cylindrical pores allows for the significant tangential flows near the membrane surface (i.e., impermeable dead zone) to be accounted for, thus leading to a significantly lower order-of-magnitude of R_c' . A filtration experiment carried out to estimate the total resistance of a membrane sample fouled by a known amount of the 3 μm particles indicated that the orders-of-magnitude of R_{c0} and R_c' were 8 and 13. These were used as initial estimates in the network model.

Flux-decline curves were first calculated using the network model for β varied from 0 to 1, while fixing R_{c0} and R_c' at $1 \times 10^8 \text{ m}^{-1}$ and $1 \times 10^{13} \text{ m}^{-2}$, respectively; each of the curves was calculated 5 times with the same fouling parameters to evaluate the mean and relative standard deviation (RSD, i.e., the ratio of the standard deviation to the mean). Figs. 3-7 (a) and (b) plots respectively the mean and RSD of the permeation flow rate normalized by the value at time zero (Q_m/Q_{m0}) as a function of time. Fig. 3-7 (a) clearly shows that (i) the mean of Q_m/Q_{m0} decreases as β increases, (ii) the differences in the mean of Q_m/Q_{m0} due to β become less as time progresses, and (iii) the effect of β on the mean of Q_m/Q_{m0} is more sensitive in the range of 0.5 and 1. As for the RSD of Q_m/Q_{m0} , three observations in Fig. 3-7 (b) are worth highlighting. Firstly, for the cases whereby β is smaller than 1, the RSD values decline sharply initially and the rate of decline decreases as β increases. This indicates that the system stabilizes quicker at lower β values. Secondly, in the case whereby $\beta = 1$, the RSD gradually increases with time. The increased degree of uncertainty could be attributed to the fact that, as the probability of particle capture is very high, only a very small fraction (5%) of the particles are directly rejected by the pores in each time interval of the network modeling, thereby substantially reducing the size of sample space.

Similar calculations were carried out for investigating the effect of R_{c0} , which characterizes the interaction between the particle and pore. The value of R_{c0} was varied from $0.2 \times 10^8 \text{ m}^{-1}$ to $2.2 \times 10^8 \text{ m}^{-1}$, while β and R_c' were fixed at 0.5 and $1 \times 10^{13} \text{ m}^{-2}$, respectively. The mean of the calculated normalized permeation flow rates (Q_m/Q_{m0}) is plotted as a function of time in Fig. 3-8 (a),

which shows that the flux decline rate increases as R_{c0} increases in the range of R_{c0} investigated. This is consistent with the scaling analysis results presented by Duclos-Orsello *et al.* [53]. The effect of R_{c0} on the uncertainty is exhibited by the plot of RSD versus time in Fig. 3-8 (b). Similar to the results for β , the RSD values are high initially but decrease with time.

Figure 3-8 Sensitivity and uncertainty analysis of the effect of the initial resistance R_{c0} on permeate flux: (a) mean and (b) relative standard deviation of the normalized flux (Q_m/Q_{m0}). β and R_c' were fixed in the network model, while the value of R_{c0} was varied between 0.2 and 2.2. Each of the flux-decline curves was repeated five times. The 2D network was composed of 631×631 unit cells corresponding to a track-etched membrane ($A_m = 25 \text{ mm}^2$ and $L_m = 33 \text{ }\mu\text{m}$), whose pore diameter and porosity were $\sim 2 \text{ }\mu\text{m}$ and ~ 0.05 , respectively. The feed solution was assumed to contain spherical particles (0.005 g/L) with a diameter of $3 \text{ }\mu\text{m}$ and the TMP for the dead-end filtration was fixed at 6.56 kPa.

Figure 3-9 Sensitivity and uncertainty analysis of the effect of specific cake resistance R'_c on permeate flux: (a) mean and (b) relative standard deviation of the normalized flux (Q_m/Q_{m0}). β and R_{c0} were fixed in the network model, while the value of R'_c was varied between 0.1 and 1.4. Each of the flux-decline curves was repeated five times. The 2D network was composed of 631×631 unit cells corresponding to a track-etched membrane ($A_m = 25 \text{ mm}^2$ and $L_m = 33 \text{ }\mu\text{m}$), whose pore diameter and porosity were $\sim 2 \text{ }\mu\text{m}$ and ~ 0.05 , respectively. The feed solution was assumed to contain spherical particles (0.005 g/L) with a diameter of $3 \text{ }\mu\text{m}$ and the TMP for the dead-end filtration was fixed at 6.56 kPa.

The plots in Fig. 3-9 display the simulation results for varying R'_c between $0.1 \times 10^{13} \text{ m}^{-2}$ and $1.4 \times 10^{13} \text{ m}^{-2}$, while fixing β and R_{c0} at 0.5 and $1 \times 10^8 \text{ m}^{-1}$, respectively. It is observed in Fig. 3-9 (a) that changing the value of R'_c has little impact on the flux decline initially, because R'_c characterizes the growth of a cake layer, whose resistance is negligible until it becomes comparable with the membrane resistance with time. The impact of R'_c therefore only manifests after the first few minutes such that the rate of flux decline increases as R'_c increases. Similar trends are observed in the plot of RSD versus time in Fig. 3-

9 (b) in that the variations of RSD for all the cases coincide in the initial period, but the RSD values are smaller as R_c' increases beyond 15 minutes.

It should be noted that the uncertainty in the model predictions can also be revealed by the stochastic fluctuations in the plots of RSD versus time for all three fouling parameters. In spite of these fluctuations, most of the values of RSD are confined in the range between 10^{-6} and 10^{-4} indicating the feasibility of approximating the expectation with the mean of finite samples, which is of critical importance in ensuring the stability of the numerical algorithm for the regression analysis.

3.4.2 Fitting the flux-decline data with the network model

Regression analysis [155] is a useful tool for validating the significance of correlation between the experimental data and model predictions. In the current study the network model was employed as the regression function to fit the flux-decline data measured by the fouling experiments. As discussed in the preceding section, the outputs of the network modeling are random in nature, thereby numerical stability could be a critical issue for the nonlinear curve fitting since the iteration may not be able to damp the stochastic disturbances resulting from the random events. Therefore, the experimental data from the case study of 0.005 g/L of the 3 μm latex particles using the 2 μm track-etched membrane were first fitted with the network model to analyze the convergence and stability of the curve fitting. In addition, the same flux-decline data were also fitted with the combined fouling model developed by Ho and Zydney [52], which employs a deterministic approach to describing the pore blockage and cake filtration based on the continuum assumption. The comparison of the best fitting results based on the network model and Ho-Zydney's model [52] was shown in the appendix. In view of the similarity between the network model and the combined fouling model, the fitting results will be compared in terms of validating the physical meaning of the fouling parameters defined in the network model. The magnitudes of the fouling parameters obtained for the two models cannot be compared directly, because while the network model provides β , R_{c0} and R_c' , the combined fouling model [52] gives three other fouling parameters, namely, pore blockage parameter α , initial resistance of the deposit

R_{p0} , and specific deposit resistance R_p' . Instead, because the accuracy of the parameters is reflected by the sum of the residuals, which indicates the difference between the experimental values and best-fit results, the two models are compared this way as described in the following.

The Gauss-Newton method was employed to iteratively seek the best-fit fouling parameters that minimized the RSS of the normalized permeation flow rate (Q_m/Q_{m0}). For the network model, the iteration for the curve fitting was started with a reasonable set of initial guesses of the fouling parameters, namely, $[\beta]_0 = 0.5$, $[R_{c0}]_0 = 1.0 \times 10^8 \text{ m}^{-1}$, and $[R'_c]_0 = 1.0 \times 10^{13} \text{ m}^{-2}$. As for the combined fouling model [52], the initial guesses for the iteration were set as $[\alpha]_0 = 1.0 \times 10^3 \text{ m}^2/\text{kg}$, $[R_{p0}]_0 = 1.0 \times 10^9 \text{ m}^{-1}$, and $[R'_p]_0 = 1.0 \times 10^{11} \text{ m/kg}$.

The residual sum of squares (RSS) serves as the criterion for determining the number of iterations required. The average RSS (i.e., averaged over the number of observations at each iteration) is plotted as a function of the number of iterations in Fig. 3-10 (a). It clearly shows that, for both models, the order-of-magnitude of RSS is substantially reduced from -2 to -5 after approximately 6 iterations. For the combined fouling model, the average RSS is stable at a value of 6.5×10^{-5} . In contrast, fluctuations in RSS are observed for the network model, indicating that the iteration is marginally stable per instability theory [159]; that is, the RSS values are not asymptotically convergent nor unbounded above. Although rigorous mathematical proof is not available, it is reasonable to infer that the marginal stability should be related to the probabilistic nature of the network modeling. The variations in $[\beta]_i$ and $[\alpha]_i$ with iterations are plotted in Fig. 3-10 (b). Although both β and α characterize pore blockage during the initial fouling, there are differences between their physical meanings. On one hand, β is a probabilistic factor accounting for the effect of the dead zone defined by Eq. (3-4). Therefore, the fitting result in Fig. 3-10 (b) indicates that the $3 \mu\text{m}$ particles hit an open pore with a probability of approximately 0.49 as the value of β is convergent to 0.52 in terms of marginal stability. On the other hand, α deterministically quantifies the surface area covered per unit mass of the particles. When the membrane is assumed to be a continuum as schematically illustrated in Fig. 3-6 (a), the value of α can be calculated as

$3/2d_p\rho_p = 476 \text{ m}^2/\text{kg}$, which is significantly smaller than the best-fit value of $2059 \text{ m}^2/\text{kg}$, i.e., the asymptotical value for α in Fig. 3-6 (a). This discrepancy of approximately fourfold is indicative of a substantial deviation from the continuum assumption that holds when the membrane has a relatively large porosity; for the cases in which dead zones are dominant on the membrane surface, as is the case here, a large amount of particles could be captured in the dead zones and thereby have little impact on the flux decline.

The initial deposit resistance R_{p0} defined in the combined fouling model is somewhat similar to the initial cake resistance R_{c0} for the network model. In particular, while both parameters account for the pressure drop resulting from the interaction between the foulant and membrane, the difference lies in the mathematical approaches to approximating the membrane structure, which give rise to different bases for evaluating the hydraulic resistance associated with the fouling. As indicated by the comparison in Fig. 3-6, the value of R_{p0} is based on the surface area of the membrane continuum (Fig. 3-6 (a)), whereas R_{c0} can be calculated with respect to the pore area (Fig. 3-6 (b)). Therefore, the ratio of R_{c0} to R_{p0} should be equal to the membrane porosity $\varepsilon_m = 0.05$ in the 2D membrane considered here, which is in good agreement with the best-fit results in Fig. 3-10 (c), i.e., $[R_{c0}]_\infty \approx 2.8 \times 10^8 \text{ m}^{-1}$ and $[R_{p0}]_\infty \approx 6.0 \times 10^9 \text{ m}^{-1}$.

Both R_c' in the network model and R_p' in the combined fouling model are defined to characterize the rate of change in the hydraulic resistance of the foulant layer. The former is the specific resistance with respect to the thickness of cake layer, which is a quantity more closely related to the cake morphology, whereas the latter measures the resistance resulting per unit mass of the deposits. It is evident that the relationship between the differential cake thickness (dL_c) and the differential deposit mass (dm_p) can be given by $dm_p = (1 - \varepsilon_c) \rho_p dL_c$; this relationship indicates that the ratio of R_c' to R_p' should be scaled by the factor $(1 - \varepsilon_c) \rho_p$ whose value is approximately 651 when assuming $\varepsilon_c \approx 0.38$ for a random packing. However, it should be noted that the flow profile, which is dependent on the connectivity of the porous structure as revealed by prior work [160], needs to be considered in estimating the cake resistance using the

network model, as schematically illustrated in Fig. 3-6 (b). When calculating R'_c/R'_p given in Fig. 3-10 (d), the factor accounting for the flow profile can be obtained as $(R'_c/R'_p)/(1-\varepsilon_c)\rho_p \approx 0.054$, which is a value very similar to the membrane porosity, indicating tangential flows could be dominant through the whole cake layer. Without tangential flow, this value should be 1.

Figure 3-10 Comparing the stability of the curve-fitting based on the combined fouling model and the network model for the same fouling process. The curve-fitting was implemented by employing the Gauss-Newton method for 20 iterations. The variations in the average RSS and the best-fit fouling parameters are presented as a function of the number of iterations. The experimental flux-decline data were measured during a

dead-end setup, whereby a feed solution of 3 μm Latex particles (0.005 g/L) was filtered through a track-etched membrane ($\bar{d}_{mp} = 2 \mu\text{m}$ and $\varepsilon_m \approx 0.05$) at a constant TMP ($\Delta p = 6.56 \text{ kPa}$). The 2D network composed of 631×631 unit cells corresponding to a membrane area of 25 mm^2 and the thickness was set at $33 \mu\text{m}$.

In addition to comparing the best-fit results from the network model with those from the combined fouling model, this study also assessed the significance of including the variable fouling parameter β in the model. An F-test, which is a statistical test used for the goodness of fit between a statistical model and a dataset [161], was employed to verify if the network model yields a significantly better fit to the flux-decline data in comparison with a ‘restricted network model’ in which β is a constant. In particular, β was fixed at zero for the restricted model to mimic the limiting case whereby all the open pores are deterministically blocked. The best-fit curves of Q_m/Q_{m0} for both the unrestricted (i.e., β is a best-fit parameter) and restricted (i.e., β is a constant) network models are compared with the experimental data in Fig. 3-11 (a), which shows that the restricted model gives rise to a greater deviation from the experimental observations. Fig. 3-11 (b) further presents the RSS/N_{exp} trends with respect to the number of iterations. It is evident that the restricted model incurs more error than the unrestricted one. Fluctuation of RSS values of these two models versus the number of iterations were observed, which were similar as the results showed in Fig. 3-10 and could be related to the probabilistic nature of the network modelling. In terms of the difference in RSS values, the value of the F statistic is approximately 620, which is much greater than the critical value 4.0 with (1, 83) degrees of freedom, thereby rejecting (at 5% significance level) the null hypothesis that the unrestricted model would not provide a better fit than the restricted model. This indicates that the unrestricted model performs better, which in turn affirms that the consideration of β as a best-fit parameter is important.

3.4.3 Interpreting the fouling process based on the best-fit parameters

As the network modeling is based on a more realistic discretized representation of the membrane, enhanced precision is expected of the fouling parameters defined in the network model, which would lead to enhanced resolution of the fouling mechanisms whose direct measurements are

challenging. Therefore, the regression analysis validated by the baseline case was further employed to interpret the external fouling by various foulants. Specifically, the current study focused on the effects of the foulant particle size and concentration on fouling behavior by fitting the network model to the experimental fouling data.

Figure 3-11 Comparison between a restricted ($\beta = 0$) and unrestricted model to understand the importance of including the probabilistic factor β : (a) regression curves compared with the experimental data; and (b) the variations in the average RSS as a function of the number of iterations. The experimental flux-decline data were measured during a dead-end setup, whereby a feed solution of $3 \mu\text{m}$ Latex particles (0.005 g/L) was filtered through a track-etched membrane ($\bar{d}_{mp} = 2 \mu\text{m}$ and $\varepsilon_m \approx 0.05$) with a constant TMP mode ($\Delta p = 6.56 \text{ kPa}$). The 2D network was composed of 631×631

unit cells corresponding to a membrane area of 25 mm² and the thickness was set at 33 μm .

Figure 3-12 Regression analysis for investigating the effects of particle size and concentration on the fouling parameters defined in the network model. The experimental flux-decline data were measured using a dead-end setup with the feed solutions of either 3 or 5 μm Latex particles (denoted in red and blue, respectively) and the particle number density was varied at two levels: (a) $3.37 \times 10^8 \text{L}^{-1}$ (solid dots) and (b) $1.68 \times 10^8 \text{L}^{-1}$ (void dots). The membrane was a track-etched membrane ($A_m = 9.62 \text{ cm}^2$, $\bar{d}_{mp} = 2 \mu\text{m}$ and $\varepsilon_m \approx 0.05$). The regression curves (solid lines) were obtained by fitting the network model to the experimental data. The 2D network was composed of 631×631 unit cells corresponding to a membrane area of 25 mm².

The experimental data are plotted in Fig. 3-12 (a) and (b) for the fouling tests with either the 3 or 5 μm latex particles at particle number densities (N_f) approximately equal to $3.37 \times 10^8 \text{ L}^{-1}$ and $1.68 \times 10^8 \text{ L}^{-1}$, respectively. The fouling test for each condition was repeated at least three times. Note that, at the same N_f , the mass concentrations (0.0116 and 0.0231 g/L) of the feed solutions containing the 5 μm particles were much higher than the ones (0.005 and 0.0025 g/L) for the 3 μm particles. The trends show that (i) when N_f was fixed at the same value, the variation in particle size (i.e., 3 and 5 μm particles) resulted in different flux-decline rates after approximately the first two minutes, though the differences in the initial flux decline were not significant at both N_f values; and (ii) the difference in N_f values impacted the 5 μm particles more than the 3 μm ones. The nonlinear curve fitting associated with the network model was applied to all these fouling cases and the obtained best-fit curves are compared with the experimental data in Fig. 3-12. The good agreement between all the regression curves and the corresponding experimental data indicates that the network model is able to correlate the flux decline with the variations in both particle size and concentration, which affirms that the best-fit fouling parameters obtained then can be employed to account for the fouling mechanisms reliably.

In order to provide evidence that the fouling parameters obtained from the network model developed here provides for a mechanistic understanding of the fouling process, model particulate foulants of different particle diameters (d_p) were investigated at different concentrations. Since the effects of these are well-known, they would affirm the validity of the network model. The variations of the best-fit fouling parameters, β , R_{c0} and R_c' , are presented in Fig. 3-13 (a), (b) and (c), respectively. The error bars represent the 95% confidence intervals from a t-test [162]. The filled bars represent the higher concentrations ($N_f = 3.37 \times 10^8 \text{ L}^{-1}$) investigated, while the unfilled bars the lower concentrations ($N_f = 1.69 \times 10^8 \text{ L}^{-1}$). The red and blue bars represent the particulate foulants whose particle diameters (d_p) are respectively 3 and 5 μm . Fig. 3-13 (a) clearly indicates that the 5 μm particles exhibited significantly lower β values, which indicate a much lower probability of depositing on the dead zone (i.e., area of the membrane not occupied by pores) than the 3 μm particles. Although a dead-end setup was used, local flows were still present near the membrane surface due to permeate drag,

which induced a greater shear-induced diffusion effect on the larger particles and caused them to be back-transported away from the membrane. In other words, the 5 μm particles exhibited a significantly higher probability ($P_b = 1 - \beta(1 - \varepsilon_m) \approx 0.94$) of blocking the open pores compared to the 3 μm particles ($P_b \approx 0.52$). As for the same particle size, the difference in the value of β between the two concentration levels is also statistically significant since the 95% confidence intervals do not overlap. Interestingly, whereas the probability of blocking the open pores (P_b) increased with concentration for the smaller 3 μm particles, P_b instead decreased with concentration for the larger 5 μm particles. For the smaller 3 μm particles, the increase in particle concentration caused more particles to be in the vicinity of the pores, hence increased the probability of blocking the pores. On the other hand, for the larger 5 μm particles, the increase in particle concentration may enhance the overall shear-induced diffusion effect, which caused more particles to be back-transported away from the membrane and resulted in a lower probability of blocking the pores.

Fig. 3-13 (b) compares the R_{c0} values for the four fouling cases. In contrast to the results for β , the difference in the value of R_{c0} between the two concentration levels is not statistically significant since the 95% confidence intervals slightly overlap. This implies that the impact of particle concentration on R_{c0} is negligible in this study. When the particle size increased from 3 μm to 5 μm , the value of R_{c0} decreased from approximately $2.6 \times 10^8 \text{ m}^{-1}$ to $1.1 \times 10^8 \text{ m}^{-1}$. This substantial difference in R_{c0} values can be explained by the more similar sizes between the 3 μm particle and the pore size of 2 μm leading to a tighter fit of the latex particle, which thereby results in a higher R_{c0} value for the smaller particle. Along the same vein, since the packing of the particles at the membrane surface is not too affected by the particle concentration in the bulk, R_{c0} was not affected by the change in particle concentration.

Figure 3-13 Comparing the fouling parameters best fitting the experimental flux-decline data for latex particles with various sizes and concentrations: (a) the probabilistic factor of particle capture β , (b) the initial cake resistance R_{c0} , and (c) the specific cake resistance R'_c . The fouling tests were performed by filtering the feed solution through a track-etched membrane ($A_m = 9.62 \text{ cm}^2$, $\bar{d}_{mp} = 2 \text{ }\mu\text{m}$, $\varepsilon_m \approx 0.05$, and $L_m \approx 30 \text{ }\mu\text{m}$). The 2D network was composed of 631×631 unit cells corresponding to a membrane area of 25 mm^2 . The error bars indicate the 95% confidence interval based on a t-test.

Three observations are worth highlighting in Fig. 3-13 (c). Firstly, R'_c was greater for the $3 \text{ }\mu\text{m}$ particles, due to the similar reason as that for R_{c0} , which is the denser packing of the smaller particles. Secondly, decreasing the particle concentration markedly increased the value of R'_c for the $3 \text{ }\mu\text{m}$ particles but had

negligible effect on the 5 μm particles. This is presumably because the lower concentration allowed for a denser packing of the smaller particles [163]. As revealed by Reising *et al.* [163], the particle-particle interactions could become more significant as the particle size decreases, which more likely prevent the slide of the particles, which in turn is important in forming a closely packed cake layer. Thirdly, the ratio of R_c' for the 3 μm particles to that for the 5 μm particles is approximately equal to 5, which is greater than the value of 3 predicted by the Kozeny-Carman equation [157, 158]. This discrepancy could be attributed to the different flow profiles above the cake layers, though further evidence is required.

3.5 Summary and Implications

A network-based approach, in which the membrane is discretized and each particle is individually monitored, was proposed to study the pore blockage and cake filtration phenomena during membrane fouling. Firstly, the steps involved in constructing a 2D network of pores to represent the membrane in terms of the key characteristics of porosity (ε_m) and mean pore diameter ($\bar{d}_{mp}$) were developed. Secondly, a series of probabilistic criteria was established to describe the fate of each individual particle, namely, deposit in the dead zone, deposit on the cake, deposit on the pore, or passes through the pore. Based on the four fates, three fouling parameters can be obtained to characterize the fouling behavior, namely, the probabilistic factor for deposition in the dead zone (β), the initial cake resistance (R_{c0}), and the specific cake resistance with respect to cake thickness (R_c'). Thirdly, protocols for evaluating fouling during both constant flux and constant TMP modes were laid out. The response of the modeling result to the variations in these fouling parameters was investigated to analyze the sensitivity and uncertainty of the network model; this theoretical study confirmed that small disturbances resulting from the random processes could be confined by averaging finite iterations, thereby ascertaining the efficacy of this model developed in evaluating membrane fouling.

Experiments involving a dead-end membrane filtration module operated in the constant TMP mode with particulate foulants were carried out to assess the model. An effective numerical algorithm was established to best-fit the

experimental flux-decline data to both the network model and also the earlier model based on the continuum assumption [52]. It should be noted that, compared to the continuum model, the network model provides more resolution to the fouling process since the membrane area is discretized and individual particles are tracked, which enables post-experiment analysis to identify the dominant fouling modality at each stage and monitor the particle deposition at the pore scale. A series of fouling experiments involving particulate foulants was performed to interpret the effects of particle size and concentration on fouling by comparing the best-fit fouling parameters (i.e., β , R_{c0} and R_c) obtained by the model. This study shows that the coupled theoretical and experimental effort is able to provide an enhanced mechanistic understanding of the complex interactions between the fluid, membrane, and foulant particles.

The combination of the network model and regression analysis essentially established a model-based measurement method for resolving parameters that characterize different aspects of a fouling process to provide for a more mechanistic understanding. Although limited fouling cases were examined in the current study, it is expected that this model can be readily extended to study more complex phenomena involved in a membrane filtration process, such as shear-induced diffusion [164] and the striping phenomenon in the concentration boundary layer [165]. Moreover, the utility of the network model developed here would be very much enhanced when coupled with the advanced fouling characterization techniques that are able to noninvasively detect the fouling process, such as DOTM [26], OCT [33], and EIS [118].

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3.7 Nomenclature

A_{nw}	The membrane area to be simulated	m^2
A_u	Area of a unit cell	m^2
c_f	The weight concentration of the feed solution	g/L
$\bar{d}_{mp}$	The mean of pore diameter	m
$\bar{d}_p$	Average particle diameter	m
d_u	The pore diameter	m
H_w	The height difference of water column	m
J_{mp}	The fluid flux through a pore	m/s
L_c	The thickness of the cake layer	m
m_p	The deposit mass	kg
N_{du}	The number of the unit cells without pores	
N_f	The number of particles in a unit volume	L^{-1}
N_u	The number of the unit cells	
$N_{u,max}$	Maximum number of the unit cells	
$\dot{N}_{up}$	The number of pores in each unit cell	
P_b	The probability of a particle blocked an open pore	
P_c	The probability of a particle being captured by the particle layer	
P_d	The probability of hitting a unit cell without pores	
P_i	The probability of the particle contacting a specific unit cell with pores	
P_m	The probability of a particle being captured by the membrane	
P_u	The probability of the particle being captured by a unit cell	

Δp	The pressure drop during filtration	Pa
$Q_m(t_i)$	The permeation flow rate measured by the fouling experiment	m^3/s
$\hat{Q}_m(t_i)$	The permeation flow rate evaluated at the times corresponding to the sampling points of the fouling experiment	m^3/s
Q_{nw}	Permeation flow rate	m^3/s
Q_t	The total flowrate	m^3/s
R_c	Cake resistance	m^{-1}
R'_c	A specific resistance in terms of the cake thickness	m^{-2}
R_{c0}	The initial cake resistance caused by a particle	m^{-1}
R_{mp}	The hydraulic resistance of the cylindrical pore	m^{-1}
R_{p0}	The initial resistance of the deposit	m^{-1}
R'_p	The specific deposit resistance	m/kg
Δt_i	Duration of the i^{th} simulation period	s
V_{up}	The total volume of the particles rejected in the unit cell	m^3
X	A randomly generated number to compare with specific probability	
Y	A randomly generated number to compare with specific probability	
α	Pore blockage parameter	m^2/kg
β	The effect of the area of the dead zone	
ε_c	The porosity of the cake layer	
ε_m	Membrane porosity	
ε_u	The porosity of a unit cell	

ϕ_{ud}	The fraction of the unit cells without pores	
ϕ_{uo}	The fraction of the unit cells with pores	
ρ_p	Particle density	kg/m^3
μ	The viscosity of the feed solution	$Pa \cdot s$

Chapter 4 Assessing fouling evolution during protein microfiltration

The content of this chapter has been published under the title of *Assessing internal fouling during microfiltration using optical coherence tomography and evapoporometry* in *Journal of Membrane Science*, vol. 595, 117588, 2020 (<https://doi.org/10.1016/j.memsci.2019.117588>).

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Abstract

The internal fouling of membranes is typically presumed and inferred, but the direct characterization of representative samples is challenging. This study targeted to assess internal fouling using the Optical Coherence Tomography (OCT) and Evaporimetry (EP) techniques for real-time monitoring during filtration and off-line measurement of the pore size distributions (PSDs) of the fouled membranes, respectively. The results were validated by atomic force microscopy (AFM) measurements and also the three-mechanism fouling model. The foulant used was the well-studied bovine serum albumin (BSA), while the membranes were three commercially available polymeric microfiltration membranes with similar nominal pore sizes and porosities. Although the OCT affirmed the progressive worsening of internal fouling in real-time, the quantitative comparison of the extents of internal fouling among the three membranes was not possible. As for EP, it was able to quantitatively compare the pore size distributions and average pore diameters to ascertain the different extents of internal fouling. The phenomenological model available was effective in quantitatively comparing the extents of pore-constriction among the three membranes, while AFM tied the worst internal fouling to the most attractive BSA-membrane affinity. More in-depth understanding of internal fouling is warranted to not only recommend better membranes but also facilitate the advancement of models.

Keywords: Membrane fouling; Internal fouling; Microfiltration; Pore-size distribution; Pore constriction

4.1 Introduction

Membrane-based separation has been valuable in addressing the critical water scarcity problem in modern society[1, 166]. However, one of the key factors limiting the more widespread application of membrane technologies remains the inevitable membrane fouling, which reduces permeation flux and increases energy consumption. Expectedly, many studies on membrane fouling have sprouted.

With respect to models on understanding membrane fouling, one of the first was by Hermia [9], in which four key fouling mechanisms have been presented, namely, complete pore blockage, intermediate pore blockage, pore constriction (also termed standard blocking) and cake filtration. Because multiple mechanisms occur concurrently, a combined fouling model that quantifies two external fouling mechanisms was proposed [52]. Subsequently, Duclos-Orsello et al. [167] established a three-mechanism model to describe both internal and external fouling behaviors. As described in Chapter 3, we recently developed a network model, which is a discretized rather than continuum model that allows for better spatial resolution, to reveal the external fouling mechanisms. Such phenomenological models are useful for advancing the understanding on membrane fouling. However, towards models based on first principles, more comprehensive experimental characterization is necessary.

In order to further understand protein fouling behaviours, various experimental techniques have been applied to characterize the fouling process, such as UTDR (ultrasonic time domain reflectometry)[168], EIS (electrical impedance spectroscopy) [25, 169] and CLSM (confocal laser scanning microscopy) [170-172]. Li et al. [168] employed the UTDR to reveal a more compact bovine serum albumin (BSA) gel layer during ultrafiltration at the pH near the isoelectric point, because of less electrostatic repulsion among the foulants. Sim et al. [25] utilized the EIS to characterize fouling by BSA and silica mixtures on RO membranes, and found that, at high BSA concentration, the nature of BSA changed and adsorbed on the surface of silica particles to form a BSA-filled cake of silica particles that increased the trans-membrane pressure (TMP) significantly. Zator et al. [172] investigated the membrane fouling mechanisms by ternary solutions of BSA, dextran and tannic acid with the aid of CLSM characterization and found the existence of tannic acid in protein-dextran feeds resulted in much more severe fouling than that for binary protein-dextran solutions. Tracey et al. [173] concluded that the effects of membrane pore diameter and foulant

concentration were dominant on fouling behaviours during microfiltration of protein. By comparing the experimental results with the internal and external fouling models [11, 173, 174], the fouling mechanism was found to change from internal pore blocking to cake formation with time. Huisman et al. [175] investigated the influence of protein-protein and protein-membrane interactions during the filtration of BSA by atomic force microscopy (AFM) measurements. It was reported that protein-membrane interactions played a more important role on the fouling behaviours during the initial period of filtration, while protein-protein interactions significantly affected the filtration performance subsequently as fouling worsened. Blatt et al. [176] found the membrane fouling was strongly dependent on the TMP in BSA ultrafiltration.

In spite of much information on BSA fouling obtained to date, the experimental investigation specifically on internal fouling remains limited due to the lack of adequate instrumentation in the past. The small angle neutron scattering (SANS) method has been applied to monitor internal fouling by BSA, but is restricted to ceramic membrane membranes, because of the requirement that the material has to be transparent to neutrons[177]. James et al. [178] employed the scanning electron microscopy (SEM) to visualize both pristine and fouled ultrafiltration (UF) membranes during the filtration of milk, and found protein colloids interacted with the pore walls of the membrane and formed agglomerates that narrowed and blocked the pores[178]; however, the pre-characterization treatment required may compromise the deposits and the sample size may be too small to be representative. For the popular method of liquid displacement porometry used to characterize pore size distribution, the high pressure required to displace the liquid may shear away the deposits that it is supposed to measure [179]. More recently, improved capabilities to better monitor internal fouling has been reported. As an offline method, Chen et al. [180] used the stimulated Raman scattering (SRS) microscopy to monitor offline the adsorption of foulants onto membrane surfaces and their aggregation within membrane pores. As another offline method, Akhondi et al. [81, 82] employed Evaporimetry (EP) to characterize the pore-size distribution of fouled membranes, which provide insights into the extents of internal fouling. In view of the necessity to monitor the evolution of internal fouling in real time for the conventional polymeric membranes, Trinh et al. developed an algorithm to enable the detecting of internal fouling by oil emulsions non-invasively during the filtration process [181].

In the current study, the objective was to enhance the understanding of internal fouling. The well-studied foulant, BSA, and three commercially available polymeric membranes (namely, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE) and mixed cellulose acetate (MCE)) with similar nominal pore sizes and porosities were used. The flux decline trends were obtained, and the combined fouling model, along with the EP, OCT and atomic force microscopy (AFM) techniques, were used to shed light on the internal fouling behaviours.

4.2 Material and methods

4.2.1 Materials

The bovine serum albumin (BSA), with a molecular weight of 67 kDa and purchased from Sigma-Aldrich (product number A7906), was dissolved in deionized (DI) water (Millipore, USA) to obtain the targeted concentration. The particle size distributions of the BSA feeds were characterized by the Zetasizer nano-zs (Malvern Instruments, UK). As shown in the appendix Figure 4-10A, BSA formed aggregates in the size range of 200 nm to 800 nm, which agrees with previous studies [68, 182]. Three flat-sheet membranes (Millipore Co., USA) of different materials, but similar nominal pore sizes of 0.1 μm and porosities of 70 – 80%, were assessed, namely, polyvinylidene fluoride (PVDF; product number VVLP04700), polytetrafluoroethylene (PTFE; product number JVWP04700) and mixed cellulose acetate (MCE; product number VCWP04700). The physical properties, including nominal pore size, porosity, DI water flux, wettability, thickness, porosity and surface potential (Anton Paar, Surpass, Austria), are listed in Table 4-1. The PTFE and MCE membranes had the highest and lowest DI water fluxes, respectively, which appears tied to the membrane thicknesses. Fig. 4-1 shows the scanning electron microscope (SEM; JSM-7200F, JEOL Ltd., Japan) images of the feed side and cross-section of the three virgin membranes. Specifically, the cross-sectional membrane samples were prepared by submerging the sample in liquid nitrogen to fragilize the sample, and then the sample was hit quickly in order to cause fracture. The cross-section surface of the fracture could be used in the SEM test. The SEM results in Fig. 4-1 indicate the three membranes are symmetric but the surface morphologies and pore structures are different despite the similarity in the nominal pore size and porosity.

4.2.2 Filtration experiments

A dead-end filtration cell, consisting of a feed chamber and a permeate chamber separated by a membrane (active filtration area = 9.62 cm^2), was used in all experiments. More details can be found in Chapter 3. The feed was driven by two gear pumps (Cole Parmer) employed in series in order to exert a transmembrane pressure (TMP) of 60 kPa. For each test, a new membrane was first used to filter DI water at the TMP of 60 kPa for 15 min, then the membrane permeability for DI water (Table 4-1) was measured for the next 5 min. The permeate flux data was recorded via a balance (Mettler-Toledo; ML4002E) every 60 s. Subsequently, the BSA stock solution was added to the feed to obtain the desired concentration of 0.5 g/L. The BSA concentrations on the feed and permeate sides were quantified using the UV-Vis spectrophotometer (UV-1800; Shimadzu, Japan) at the 280 nm wavelength to quantify the BSA rejection. Each filtration condition was tested three times.

Table 4-1 Physical properties of PVDF, PTFE and MCE membranes.

	PVDF	PTFE	MCE
DI water flux (ml/min·cm ²) *	4.51	9.78	1.91
Nominal pore size (μm)	0.1	0.1	0.1
Wettability	Hydrophilic	Hydrophilic	Hydrophilic
Thickness (μm)	97	30	103
Porosity	70%	80%	74%
Surface potential (mV)	-31.1 ± 1.2	-14.1 ± 0.3	-15.7 ± 0.03
Refractive index	1.426	1.356	1.50 ~ 1.52

* The DI water flux was measured through virgin membranes at the trans-membrane pressure (TMP) of 60 kPa.

Figure 4-1 FESEM images of feed side (left column) and cross-section (right column) of virgin membranes at magnifications of 5,000 times: (a) PVDF, (b) PTFE, and (c) MCE.

4.2.3 Three-dimensional OCT scan and image analysis

The optical coherence tomography (OCT; GANYMEDE-SP5, Thorlabs, USA) was utilized to monitor the evolution of membrane fouling through three-dimensional (3D) scans in-situ. Notably, OCT has been proven to be able to monitor internal fouling earlier [181]. Compared with the conventional time-domain techniques, the Fourier-domain OCT system had a higher scanning frequency (namely, 30 kHz) [30, 33]. The lateral and depth resolutions were respectively 4 μm and 2 μm in water [183], which is dictated by the light source (central wavelength = 905 nm; bandwidth = 200 nm). An

overview of the OCT technique is illustrated in Fig. 4-2. Part of the light beam emitted from a broadband light source reached the membrane filtration cell, and the light backscattered was combined with the light reflected from a reference mirror and collected by a spectrometer, which the OCT intensity as a function of optical distance was used to reconstruct the depth profiles at a certain point in the sample (A-scan). As depicted in Fig. 4-2b, 2D and 3D imaging were achieved by performing a series of A-scans along a single line and a set of parallel lines, respectively. For each test, 3D OCT scans (every 5 s; A-scan rate = 30 kHz) were performed during the filtration experiments, with DI water as the feed for the first 5 min followed by 0.5 g/L of BSA for the next 50 minutes. Each set of experimental condition was scanned via 3D OCT three times. However, since the optical fields for the repeat experiments are different primarily due to the variations in membranes and position of the membrane filtration cell, averaging the intensity values of repeats is inappropriate, thus only one representative OCT trend is presented for each case.

As described in a previous report [30], determining the coordinates of the feed membrane interface before the onset of fouling was the first step of the OCT image analysis. To achieve this, an intensity gradient was pre-determined as the threshold value, then the positions where the intensity gradients exceeded this threshold were designated as the feed membrane interface coordinates, which was indexed as Layer 0. After identifying the feed membrane interface, a new coordinate system (namely, x_m - y_m - z_m) was constructed, along with a series of parallel coordinate surfaces above (i.e., Layers 1, 2, etc.) and below (i.e., Layers -1, -2, etc.) the feed-membrane interface to monitor both external and internal fouling [30, 181]. The physical distance between two adjacent coordinate planes was 1.5 μm in the current study, which was the depth resolution of the OCT used. To quantify the evolution of membrane fouling extents on each layer (i.e., on the projected area of 1.3 mm by 0.3 mm), the mean and standard deviation of the intensities were derived before the onset of fouling, then a fouled voxel was identified as one whereby the intensity was at least two standard deviations greater than the mean [184, 185].

Figure 4-2 (a) Schematic depicting the principle of the 3D scan of dead-end membrane cell using the low-coherence Fourier-domain OCT; (b) Different scan modes of OCT.

4.2.4 Evaporoporometry characterization of pore-size distribution (PSD)

Evaporoporometry (EP) is an indirect technique used to measure the pore size distribution (PSD) of porous materials by applying the Kelvin equation, which derives pore diameter from the vapor pressure of a wetting liquid at the pore opening [80]. The Kelvin equation is given by the following:

$$\ln \frac{P_A}{P_A^\circ} = -\frac{4\gamma V \cos \theta}{dRT} \quad (4-1)$$

where P_A is the particle pressure of the vapor at the membrane surface when pores having a diameter d are draining; P_A° is the vapor pressure of a liquid layer on the liquid-saturated membrane at the beginning of the EP characterization (which also called as the ‘free-standing liquid’); γ is the surface tension of the liquid in the pores; V is the molar volume of the vapor; θ is the contact angle of the liquid at the membrane surface; R is the universal gas constant; and T is the absolute temperature. In the current study, the applied hydrophilic membranes, namely PVDF, PTFE and MCE were completely wetted by the liquid (DI water), so the contact angle (θ) was zero. The vapor phase is assumed to be an ideal gas since EP tests were carried out at atmospheric pressure. Eq. (4-1) could be casted in terms of the vapor-phase mole fractions that can be related to the evaporation rates [186]:

$$d = -\frac{4\gamma V}{RT \ln \frac{\chi_{A0}}{\chi_{A0}^\circ}} = -\frac{4\gamma V}{RT \ln \frac{W_{A0}}{W_{A0}^\circ}} \quad (4-2)$$

Where χ_{AO} and χ_{AO}^0 are the vapor-phase mole fractions at the liquid-gas interface during evaporation from the pores and from the free-standing liquid layer, respectively; and W_{AO} and W_{AO}^0 are the evaporation rates from the pores and the free-standing liquid layer, respectively. The schematic EP apparatus is shown in Fig. 4-3, which is reported previously [80]. Since larger pores have greater vapor pressure, the volatile wetting liquid will evaporate first from the largest pores, then from smaller and smaller pores. The key components of the EP apparatus are the test cell and the microbalance (Mettler-Toledo model XP205), which sit in an incubator (LE-150D, Yihder Technology) to keep the temperature constant at 29 °C.

The capability of EP to measure the PSDs of fouled membranes has been proven earlier [81, 82]. For each EP test, the membrane (either pristine or fouled) was first fully wetted with a volatile wetting liquid (in this case, DI water), then clamped in the test cell, which is then left on a microbalance to track the evaporation rate every 10 s. The pore size distributions (PSDs) of the three different membranes were tested before and after each filtration experiment. Each membrane was re-measured at least three times. The data-analysis protocol is briefly summarized as follows [80]: (i) the mass of the test cell was recorded every 10 s to give the evaporation rate (W_A); (ii) the evaporation rate of the free-standing liquid layer (W_A^0) was determined for the period over which W_A was approximately constant; (iii) the time instant at which pore-draining started was determined as when $W_A < W_A^0 - \delta$, where δ is the standard deviation of W_A ; (iv) the pore diameters (d) were calculated based on Eq.4-2 to give the mass-based PSD.

Figure 4-3 (a) Schematic of the EP apparatus used in the current study; (b) schematic of the test cell and sealing method; and (c) photograph of the Teflon test cell, the acrylic lid with PVC bolts and nuts [80].

4.2.5 AFM test

The atomic force microscope (AFM) (Park Systems, NX10, Korea) was used to measure the BSA-membrane adhesion force. Force measurements were conducted using colloid probes, namely, 5 μm microspheres made of SiO_2 with PEF- NH_3 surface chemistry on a silicon nitride (SN) cantilever (Novascan Technologies, Inc. USA). The spring constant of the cantilever was 0.06 N/m. The BSA-coated probe was prepared by adsorbing BSA onto the silica surface, as described in an earlier study [174]. Specifically, the colloid probe was immersed in a solution of 1 g/L BSA for 24 h at 4 $^\circ\text{C}$, which led to a single layer of BSA strongly bound on the probe surfaces. The membrane sample was soaked in the DI water for 15 min before AFM measurement, after which the force measurements were conducted in DI water in the AFM fluid cell. Of the 20 μm by 20 μm membrane area, three locations were randomly sampled to get at least 10 force curves per location. As described detailed in earlier study [187], the force is a function of probe displacement. Fig. 4-13A showed a typical AFM force curve measured over 1 μm . The deflection of the cantilever is monitored and converted into values of force using Hookes Law with calibration of the spring constant and deflection sensitivity. In the current study, the adhesion forces between the three different membranes and BSA were obtained by averaging the maximum force values from the force curves.

4.2.6 Fouling model

The flux decline has been modelled using the classical fouling models. The expressions for complete pore blockage, intermediate pore blockage, pore constriction and cake filtration [9, 11, 167] are summarized in Table 4-2. The definition of each variable was listed in the nomenclature.

Table 4-2 Classical fouling models [188].

Model	Governing equations	Normalized flow rate
Complete pore blockage	$\frac{dA_u}{dt} = -\alpha Q_u C_b$	$\frac{Q_m}{Q_{m0}} = \exp(-\alpha \frac{\Delta p}{\mu R_m} C_b t)$
Intermediate pore blockage	$\frac{dA_u}{dt} = -\alpha' Q_u C_b \frac{A_u}{A_0}$	$\frac{Q_m}{Q_{m0}} = (1 + \alpha' \frac{\Delta p}{\mu R_m} C_b t)^{-1}$
Cake filtration	$\frac{dR_p}{dt} = f R' J_b C_b$	$\frac{Q_m}{Q_{m0}} = (1 + f R' \frac{2\Delta p}{\mu R_m^2} C_b t)^{-1/2}$
Pore constriction	$\frac{d(N_0 \pi r_p^2 \delta_m)}{dt} = -\alpha_{in} Q_u C_b$	$\frac{Q_m}{Q_{m0}} = (1 + \alpha_{in} \frac{Q_{m0}}{\pi r_{p0}^2 \delta_m} C_b t)^{-2}$

A mathematical model to account for three of the classical fouling mechanisms during microfiltration, namely, pore constriction, pore blockage and cake filtration, is expressed as follows [167]:

$$\frac{Q_m}{Q_{m0}} = \frac{1}{(1 + \beta_{in} Q_{m0} C_b t)^2} \exp\left(-\frac{\alpha C_b J_0 t}{1 + \beta_{in} Q_{m0} C_b t}\right) + \int_0^t \frac{(\alpha C_b J_0 / (1 + \beta_{in} Q_{m0} C_b t_p)^2) \exp(-(\alpha C_b J_0 t_p) / (1 + \beta_{in} Q_{m0} C_b t_p))}{\sqrt{[(R_{p0}/R_m) + (1 + \beta_{in} Q_{m0} C_b t_p)^2]^2 + 2(f R' \Delta p C_b / \mu R_m^2)(t - t_p)}} dt_p \quad (4-3)$$

The fouling parameter α represents pore blockage, specifically the membrane area blocked per unit mass of protein filtrated (m^2/kg) [11]:

$$\alpha = \frac{f A_{agg}}{M_{agg}} \quad (4-4)$$

Where β_{in} represents pore constriction parameter defined as:

$$\beta = \frac{\alpha_{in}}{\pi r_{p0}^2 \delta_m} \quad (4-5)$$

Readers interested in the model details are referred to Duclos-Orsello et al.[167]. In the current study, this three-mechanism model was applied for the filtration of feeds containing BSA by three different commercial membranes to obtain an enhanced

understanding of the fouling mechanisms. In this study, the nonlinear least-squares solver in Matlab was used for the best-fitting. It should be noted that there may be more than one set of fouling parameters that fit the experimental data, and thus the initial guesses have to be chosen judiciously based both on the physical meaning of the parameter as well as with reference to previous studies. As an example, the initial guess of α was $2.9 \pm 2.6 \text{ m}^2 \text{ kg}^{-1}$ while the best-fit value determined from the filtration flux data was similar at $4.1 \pm 0.2 \text{ m}^2 \text{ kg}^{-1}$ in an earlier study [11] and here, an eightfold factor [189] was used for the initial guess for α (i.e., 23) since the membrane pores were half that in the earlier study (100 nm vs 200 nm).

4.3 Results and discussion

4.3.1 Permeate flowrate and rejection

The ratio of permeate flowrate (Q_m (g/min)) to the initial permeate flowrate (Q_{m0} (g/min)) versus filtration time, along with the best-fit curves based on the nonlinear curve-fitting per the three-mechanism model to obtain the fouling parameters (Eq. 4-3), are shown in Fig. 4-4(a). The most severe Q_m/Q_{m0} decline at the end of 50 min of filtration was PTFE, which could be tied to the highest permeability (Table 4-1). However, though PVDF gave the highest flux at the end of the 50 min, its permeability was higher than MCE. The decline of the normalized flowrates versus filtration volume is displayed in Fig. 4-10A, which indicates that the Q_m/Q_{m0} value declined the most for MCE, followed by PVDF then PTFE, indicating the worst fouling of the MCE membrane at the same filtration volume. Furthermore, Fig. 4-4(b) presents the rejection of BSA versus filtration time by the three membranes, showing that equilibrium values were attained by about 10 min of filtration. The rejections by all three membranes were less than 10%, with the highest by the MCE membrane at about 7%, indicating most of the BSA permeated through the membrane. The different flux declines and rejections are underlain by the different fouling mechanisms associated with the different membranes, which were evaluated by characterization techniques including OCT, EP and AFM and also the three-mechanism fouling model in this study. FESEM images in Figs. 4-11A and 4-12A demonstrate both internal and external fouling, though more in-depth probing was challenging.

Figure 4-4 (a) Ratio of permeate flowrate to initial permeate flowrate (Q_m/Q_{m0}) for the 0.5 g/L BSA feed through the PVDF, PTFE and MCE membranes. The discrete data points are experimental data while the black lines are the best-fit trend lines per the fouling model (Eq. 1); and (b) BSA rejection vs filtration time by the three different membranes. The feed was 0.5 g/L BSA and the TMP was 60 kPa.

4.3.2 Monitoring of membrane fouling by 3D OCT

The OCT was employed to reveal the underlying fouling mechanisms during BSA filtration by the three membranes. The plots of layer-averaged intensity with respect to layer index for feeds of 0.5 g/L BSA are shown in Fig. 4-5 for three membranes and three-time steps. The layer-averaged intensity profile of the pristine membrane (i.e., at $t = 0$ min) is included in every sub-figure to benchmark against the

progressive fouling. The intensities are unsurprisingly larger in the negative layers (i.e., below the feed-membrane interface) because of the opaqueness of the membrane. It should be noted that, although it is possible to display the intensities throughout the thickness of each membrane, the intensities deeper into the membrane may not be as meaningful due to the significant decay of the OCT light. Even though the light was expected to penetrate through the thinnest PTFE membrane (30 μm), the signal may be affected by the stainless-steel support beneath. Therefore, in this study, limited depth into the membrane was analysed.

OCT possesses the unique capability to survey the internal fouling non-invasively and in real-time [181]. As shown in Fig. 4-5, at the end of 50 min of filtration, significant increases of the average intensities were found for all the three membranes below the feed-membrane interface (i.e., negative layers), while only slight increases of the average intensities were observed for the PVDF and PTFE membranes above the feed-membrane interface (i.e., positive layers). This affirms the occurrence of internal fouling for the three membranes, and external fouling for PVDF and PTFE membranes. Regarding internal fouling, it is interesting to note that the intensities (i) did not change much just below the feed-membrane interface for all the three membranes (i.e., between Layers 0 and -5 for the PVDF and PTFE membranes, and between Layers 0 and -15 for the MCE membranes), which is because of the diminished reflectance of the polymer just below the feed-membrane interface due to the adsorption of BSA in this region [181]. but (ii) became significant deeper into the membrane (i.e., Layers -15 to -5 for the PVDF and PTFE membranes, and Layers -30 to -20 for the MCE membrane) due to the increase of liquid-foulant boundaries of the dispersed protein in the pores. The different internal fouling trends may be tied to different optical properties of different materials or different adhesion forces between the membrane and the foulant.

Figure 4-5 Layer-averaged intensity profiles at three-time instances during the filtration of 0.5 g/L BSA solution at TMP = 60 kPa by using the (a) PVDF, (b) PTFE and (c) MCE membranes. The intensity profiles for the clean membranes at $t = 0$ min are shown as empty circles for reference, while those at subsequent time steps are depicted as solid circles.

To further understand the evolution of BSA fouling on the three different membranes, the progressive fouling of each layer was investigated [181]. Fig. 4-6 illustrates for all three membranes the evolution of external and internal fouling, as reflected by variations of the fraction of fouling voxels for layers respectively above and below the feed-membrane interface (i.e., Layer 0). The fraction of fouled voxels increased with filtration time, indicating the expected increased extents of fouling as filtration progressed. For external fouling (left column of Fig. 4-6), the fraction of fouling voxels for the PVDF membrane increased most significantly and for the MCE membrane the least. The SEM images of the fouled membranes in Fig. 4-12A shows the thickest cake layer for the PVDF membrane, which is in agreement with the OCT results. Since the Q_m/Q_{m0} magnitude declined the most at the end of 50 min for the PTFE membrane (Fig. 4-4) but external fouling was intermediate (Fig. 4-6), internal

fouling played an important role in the flux decline tendencies of the different membranes.

With respect to internal fouling (right column of Fig. 4-6), the fouling voxels trends for PVDF and PTFE membranes were similar, while that of MCE exhibited the least increase, though a marked increment of the fraction of fouling voxels for the MCE membrane was found in Layer -26 (shown as grey dots in Fig. 4-6(c)). This is in agreement with Fig. 4-5, whereby a significant increase of the layer-averaged intensity was found from Layer -5 to Layer -15 for the PVDF and PTFE membranes, while that increase was observed approximately between Layer -20 and Layer -30 for MCE. Notably, whilst the occurrence and evolution of internal fouling of all three membranes could be monitored by OCT, quantitative comparison of the extent of internal fouling among different should be treated with caution due to the variation of the refractive indices of different materials (Table 4-1) and the complexity of the solid-liquid boundaries within the membrane matrices.

Figure 4-6 Evolution of the fractions of fouling voxels during the filtration of 0.5 g/L BSA at $TMP = 60$ kPa in the layers above (left column) and below (right column) the feed-membrane interface for the (a) PVDF, (b) PTFE and (c) MCE membranes. The grey dots in Fig. 4(c) represents the fraction of fouling voxels at layer -26 (corresponding to $39\ \mu\text{m}$ below the feed membrane interface) for the MCE membrane.

4.3.3 Assessment of pore-size distribution of internally fouled membranes by EP

Armed with the OCT results that showed progressive internal fouling, EP was employed to quantitatively compare offline the extent of internal fouling among the different membranes. Fig. 4-7 compares the pore-size distributions (PSDs) determined by EP of pristine and fouled (i.e., after the filtration tests) membranes. Clearly, for all three membranes, the average diameters of the fouled membranes were smaller than the virgin ones, which indicates the membranes were internally fouled. Comparing the fouled membrane with the unfouled ones, (i) the larger pores were diminished more,

which is due to the relatively higher flow-through causing greater internal fouling; and (ii) the greatest increase in percentage pore mass was for the intermediate pore sizes. Among the three membranes, the greatest reduction of the average pore diameter was that of the MCE membrane (Fig. 4-7(c)), which is consistent with the highest BSA rejection (Fig. 4-4(b)). Although the three membranes had similar vendor-given nominal pore sizes and porosity, the external fouling was the worst for the PVDF membrane (Fig. 4-6, Fig. 4-11A) and internal fouling worst for the MCE membrane (Fig. 4-6).

Figure 4-7 Pore-size distributions (PSDs) of virgin and fouled membranes: (a) PVDF, (b), PTFE, and (c) MCE. DI water was used as the volatile wetting liquid.

4.3.4 BSA-membrane interaction quantified by AFM

To further understand the different fouling behaviours, the adhesion force between BSA (i.e., the foulant) and the different membrane materials were measured by the AFM [76]. Fig. 4-8 shows the maximum relative force of adhesion for detachment of the BSA-coated colloidal probe from the different membranes. As shown in Fig. 4-8, the maximum retraction forces for BSA-PVDF and BSA-PTFE were -1.4 mN/m, while that for BSA-MCE was -2.8 mN/m. The significant BSA-MCE affinity is consistent with a previous study that ascribed it to the insufficient hydrophilicity, flexibility and chain mobility of the chemical function group of MCE [190]. The AFM force measurement results agree with the most extensive internal fouling demonstrated by EP (Fig. 4-7), and highest BSA rejection (Fig. 4-4(b)). This suggests that internal fouling was closely tied to the foulant-membrane affinity.

Figure 4-8 Maximum relative force of adhesion for detachment of the colloidal probe for BSA-PVDF, BSA-PTFE and BSA-MCE measured by AFM.

4.3.5 Fouling parameters via the three-mechanism model

Table 4-3 lists the fouling parameters obtained from the three-mechanism model (Eq. 4-3) from best-fitting the Q_m/Q_{m0} versus time trends of the three membranes (Fig. 4-4a). Notably, for the pore constriction parameter β_{in} associated with internal fouling, that for the MCE membrane was an order-of-magnitude larger than that for the PVDF and PTFE membranes, implying the most severe pore constriction for the MCE membrane. This is consistent with the dramatic reduction of the average pore diameter

of the fouled MCE membrane (Fig. 4-7) and highest BSA rejection (Fig. 4-4(b)), which was linked to the most attractive interaction of BSA-MCE (Fig. 4-8).

For the pore blockage parameter α , the value for the PTFE membrane was four orders of-magnitude lower than that for the PVDF and MCE membranes, which indicates least pore blockage for the PTFE membrane. The $f'R'$ parameter, which represents cake filtration, was smallest for the MCE membrane, while similar for the other two membranes. This is consistent with the OCT results (Fig. 4-6), which shows that external fouling was the least for the MCE membrane. By using the resistance-in-series model [191] and DI water flux listed in Table 4-1 to derive R_m (which is related to the DI water permeability), it was deduced that the values of initial deposit resistance R_{p0} (Table 4-3) were similar for the PVDF and PTFE membranes, but that of the MCE membrane was four times smaller. The highest R_{p0} value for the MCE membrane agrees with the AFM measurement results whereby the BSA-MCE adhesion force was the greatest, and also with a previous study that found the effect of protein-membrane interactions was dominant on the fouling behaviours during the initial period of filtration [175].

Table 4-3 The fouling parameters from the three-mechanism model [188] by best-fitting the experimental flux data.

	α (m ² /kg)	β_{in} (kg ⁻¹)	$f'R'$ (m/kg)	R_{p0}/R_m
PVDF	23.4 ± 3.5	$5.0 \pm 0.2 \times 10^2$	$8.0 \pm 0.2 \times 10^{10}$	0.18 ± 0.02
PTFE	$1.0 \pm 0.01 \times 10^{-3}$	$5.0 \pm 0.2 \times 10^2$	$8.0 \pm 0.2 \times 10^{10}$	0.35 ± 0.05
MCE	15.2 ± 2.88	$5.0 \pm 1.3 \times 10^3$	$1.0 \pm 0.3 \times 10^{10}$	0.31 ± 0.12

4.4 Conclusion

The experimental characterization of internal fouling is challenging, primarily because direct visualization is difficult due to the typical opaqueness of membranes, and pre-characterization sample preparation (e.g., coating requirement for scanning electron microscope) or characterization conditions (e.g., high pressure requirement of liquid displacement porometry) may compromise the deposits. To provide more understanding on internal fouling, this study was targeted at assessing this using a well-studied foulant (namely, BSA) and three commercially available microfiltration membranes (namely, PVDF, PTFE and MCE).

Despite having similar vendor-given nominal pore sizes and porosity, the three membranes (namely, PVDF, PTFE and MCE) investigated here gave distinctly different flux decline trends, which is linked to the different fouling tendencies. For the same filtrate volume, MCE gave the greatest decline in the normalized flux, which was associated with the worst internal fouling, that was in turn tied to the most attractive BSA-MCE affinity.

OCT was able to quantitatively compare the extents of external fouling. Among the three membranes, OCT showed that external fouling was the most and least extensive for the PVDF and MCE membranes, respectively, which agrees with the cake filtration parameters ($f'R'$) of the fouling model previously developed. For internal fouling, although the current algorithm allowed for monitoring in real-time, it was challenging to implement quantitative comparison among the membranes, owing to variations of membrane material and complex liquid-foulant-membrane boundaries. Although the pore constriction parameter β_{in} for the MCE membrane was an order-of-magnitude larger than that for the PVDF and PTFE membranes, and the rejection rate was the highest for MCE, OCT intensities did not reflect this.

EP was able to quantify the extent of internal fouling off-line by characterizing the change in pore-size distribution of the fouled membranes. The most drastic decrease in the average pore diameter of the fouled MCE membrane relative to the pristine one agrees with the order-of-magnitude higher pore constriction parameter β_{in} relative to the other two membranes.

A more in-depth understanding of internal fouling is warranted to not only recommend better membranes but also facilitate the advancement of models. The OCT and EP are valuable tools in this respect.

4.5 Acknowledgements

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4.6 Nomenclature

A_u	area of unblocked membrane (m^2)
A_0	initial area of unlocked membrane (m^2)
C_b	bulk concentration (g/L)
f'	fractional amount of total foulant contributing to deposit growth
J_b	filtrate flux within the blocked area (m/s)
J_0	initial filtration flux of clean membrane (m/s)
Δp	pressure drop during filtration, Pa
Q_u	volumetric flow rate through the unblocked area (m^3/s)
Q_m	volumetric flow rate measured during the fouling experiment (m^3/s)
Q_{m0}	Initial volumetric flow rate of clean membrane (m^3/s)
r_p	radius of membrane pore (m)
R_m	resistance of the clean membrane (m^{-1})
R_p	resistance of the deposit (m^{-1})
R_{p0}	initial resistance of the deposit (m^{-1})
R'	specific protein layer resistance (m/kg)
t	filtration time (s)
t_p	the time at which that particular region was first covered or blocked by a protein aggregate (s)

Greek letters

α	pore blockage parameter (m ² /kg)
α_{in}	specific pore constriction parameter (m ³ /kg)
β	pore constriction parameter (kg ⁻¹)
δ_m	membrane thickness (m)
μ	fluid viscosity (Pa·s)

4.7 Appendix

Figure 4-9A Particle distribution for BSA feed.

Figure 4-10A Evolution of the ratio of permeate flowrate to initial permeate flowrate (Q_m/Q_{m0}) for the three different membranes versus filtration volume.

Figure 4-11A FESEM images of surface of virgin membranes (left column) and fouled membranes (right column) at magnifications of 5,000 times: (a) PVDF, (b) PTFE, and (c) MCE.

Figure 4-12A FESEM images of the cross-section of virgin membranes (left column) and fouled membranes (right column) at magnifications of 5,000 times: (a) PVDF, (b) PTFE, and (c) MCE. The red squares referred to the external fouling of the membranes.

Figure 4-13A Typical force-distance measurement curve [187].

Chapter 5 Effect of the Surface Charge of Monodispersed Particulate Foulants on Cake Formation

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Abstract

In microfiltration and ultrafiltration, particulate foulants are inevitably deposited on the membrane surface, forming a cake whose structure and behavior play crucial roles in the subsequent filterability of the suspensions. This study investigated the impact of fouling by three types of latex particulate foulants, which were of the same size (3 μm) but with different surface charges. Surprisingly, although the positively charged aminated latex was expected to perform the worst in the flux-decline experiments due to attractive electrostatic interaction with the negatively charged membrane, this latex displayed the best performance relative to the two negatively charged latex. To understand these counter-intuitive results, the network model and three-dimensional (3D) optical coherence tomography (OCT) image analysis were employed to reveal the underlying reasons for the different fouling behaviors. Two mechanisms were found to contribute to the worse performance of the negatively charged latex. Firstly, these particles tended to deposit on the pore rather than non-pore region of the membrane due to the repulsive particle-membrane electrostatic interactions, which led to a more complete pore blockage and thereby greater initial cake resistance. Secondly, these particles had a greater tendency to cluster and deposit on other deposited latex due to similarly repulsive particle-membrane and particle-particle interactions, which led to a more inhomogeneous cake and thereby greater specific cake resistance.

Keywords: Membrane fouling, surface charge, network model, optical coherence tomography, microfiltration

5.1 Introduction

Membrane fouling is almost inevitable for all membrane filtration processes, but such filtration applications continue to grow because they offer key advantages like operation without a phase change, without the need for high temperatures or additives, and their potential for low energy consumption. In particular microfiltration is an attractive membrane filtration process due to its relatively lower operating pressures and higher permeation fluxes, which has motivated many studies dedicated to understanding and mitigating the fouling issue [192].

Experimentally, a variety of techniques have been used to study the onset and evolution of fouling [20, 193, 194] in order to shed light on the fouling mechanisms by different foulants. Examples of such techniques that allow for the monitoring of membrane fouling non-intrusively and in real time include electrical impedance spectroscopy (EIS) [25], direct observation through the membrane (DOTM) [26], confocal laser scanning microscopy (CLSM) [27] and optical coherence tomography (OCT) [30]. Many interesting observations and understandings have been obtained with the aid of these techniques. The evolution of fouling by colloidal particles and organic macromolecules has been characterized by the EIS [25], the effect of particle size and crossflow on critical flux has been revealed by DOTM [195], biofilm formation on a membrane in a membrane bioreactor has been studied by CLSM [196], and the velocity profile and changes in cake thickness have been observed using OCT [33]. In parallel with the experimental efforts, various models have been proposed to enhance the understanding of the fouling mechanisms during the filtration of colloids, as reviewed in Belfort et al. [192]. In addition to the hydrodynamic factors that account for particle size, particle concentration and shear rate, Bacchin et al. [8] factored into their model the contribution of the interfacial foulant-membrane interactions due to its non-negligible influence. Furthermore, based on the various pore-blocking phenomena proposed by Hermia [197], Ho and Zydney [52] extended such models by accounting for the various phenomena concurrently rather than each individually, which allowed for understanding the effect of foulant-membrane interactions through pore blockage parameters and initial cake resistances. Charfi et al. [51] proposed a mathematical model considering three fouling mechanisms to successfully assess the scouring effect of GAC particles on membrane fouling control. This continuum model subsequently led to discretized models with better spatial resolution to further improve the

understanding of fouling particularly with respect to the topological aspects, such as the connectivity of the porous structure and the distribution of the deposits on the membrane [12, 60, 61]. Coupling the novel discret network model developed in Chapter 3 in the current study with the experimental results could be very useful for obtaining a more mechanistic understanding of the fouling mechanisms.

Although many studies have been carried out to investigate a variety of foulants during the membrane filtration process, a question that remains not fully answered is the effect of colloidal surface charge on membrane fouling. Colloidal particles are ubiquitous in natural waters which cover a wide size range from a few nanometers to a few micrometers. In the pH range of natural waters, most colloids carry a negative surface charge [50, 198]. Previous studies found that the negatively charged natural organic matter (NOM) would become positively charged when overdose a coagulant [40, 199]. Some of the industrial textile wastewater were found carrying positively charged in acid aquatic condition [200]. Since membrane filtration process is widely used to treat these kinds of wastewater, deep understanding of particle surface charge on membrane fouling formation is of great importance.

Some inroads have been made with regards to revealing the impact of the surface charges of particulate foulants. McDonogh et al. [201, 202] found that, regardless of dead-end or cross-flow filtration, as the zeta potential of monodisperse silica colloids increased beyond about 10 mV, the specific resistance of the cakes decreased monotonically; for potentials < 10 mV the trend was opposite due to colloid aggregation. The decreasing specific cake resistance trend was explained by a model of charged colloid interaction based on the classical DLVO theory. Similar trends, with more highly charged colloidal particles tending to give more porous cakes, were reported by other groups [203-205]. However, on the contrary, Huisman et al. [206] found that neither the zeta potential of the membrane nor the zeta potential of the particles influenced the observed critical flux. Since the zeta potential was changed by adjusting the pH, this may be explained by the results presented by Faibish et al. [205] in which solution pH had a negligible effect on flux decline. Recently [207], our group have investigated two types of negatively charged particulate foulants and found significantly different fouling behaviors, which was attributed to the attractive and repulsive particle-membrane and particle-particle interactions quantified by Gibbs free energy [208]. However in this work the electrostatic component (which factors in zeta

potential) of the Gibbs free energy was reported to be minor, relative to the other two components of Lewis acid-base and Lifshitz-van der Waals in the XDLVO theory, which agrees with previous reports [209, 210]. In summary, prior work have revealed both qualitative and quantitative differences in the observed effects of particle surface charge on membrane fouling, but the understanding remains incomplete because the zeta potential values have been limited to the negative range. As a result this study builds on the knowledge base to date and applies deadend flow (to minimise tangential shear effects) to the filtration of particles that are identical except for their surface charges which span positive and negative zeta potentials. The evaluation is made using a novel non-continuum model and noninvasive observation using OCT.

Thus, the objective of this work is twofold: (i) investigate the effect of surface charges of particulate foulants on flux-decline trends; and (ii) understand the differences in the fouling mechanisms via a network model and OCT image analysis [30]. Latex particles of the same size but of different surface charge (namely, one positively charged and two with different negative charges) were investigated. The flux decline data were obtained under deadend filtration, and fitted to the network model to obtain the fouling parameters (namely, probability to deposit on non-pore regions of the membrane, initial cake resistance and specific cake resistance). The OCT technique allowed for 3D imaging of the fouling process non-intrusively and in real-time, which provided an understanding not only of the progress of fouling on the membrane surface but also the cake growth.

5.2 Experimental Procedure

5.2.1 Membrane fouling experiments

In the current study, dead-end filtration was employed to investigate the effect of three different surface charges of particulate foulants on membrane fouling. The membrane used was a polycarbonate track-etched (PCTE) membrane (catalog number WH-111111, Whatman, USA), with relatively uniform cylindrical pores each with a diameter (d_{mp}) of 2 μm and relatively low porosity (ε_m) of 0.05. The zeta potential (Malvern Zetasizer nano-zs, UK) of the PCTE membrane was measured in the presence of 1mM KCl at pH 6.2 using 300 nm latex particles as the tracer particles, indicating that the membrane had a negative surface charge of -35.3 mV. A new membrane was used in each experiment. The three particle types were all latex particles with uniform

particle diameters (d_p) of 3 μm : one was non-modified (catalog number 79166, Sigma, Aldrich, USA), and two had surfaces modified with functional groups, namely, aminated (catalog number AM003UM, Magsphere, USA) and carboxylated (CA003UM, Magsphere, USA). The zeta potentials (Malvern Zetasizer nano-zs, UK) of the three particle types, as listed in Table 5-1, indicated that the surface charges span -31.0 to 10.5 mV, and two were negatively charged while one was positively charged. The concentration of the latex particles was constant for every experiment at 0.005 g/L.

Table 5-1 Zeta potential values of the PCTE membrane ($d_{mp} = 2 \mu\text{m}$ and $\varepsilon_m \approx 0.05$) and the three particulate latex foulants with uniform particle diameters of 3 μm .

	Zeta potential (mV)	Standard deviation (mV)	Feed medium
PCTE Membrane	-35.3	0.75	1 mM KCl
Aminated Latex	10.5	2.38	DI water
Non-modified Latex	-20.8	0.88	DI water
Carboxylated Latex	-31.0	0.53	DI water

The dead-end filtration cell was the same as the one used for the filtration experiments as described in Chapter 3. Gravity was used as the driving force across the membrane, which provided a constant trans-membrane pressure (TMP) to result in the permeate flux. The TMP was fixed at different values around 6 kPa in order to maintain the permeation flow rate of DI water at a value of 80 ml/min. More details of the dead-end setup could be found in Chapter 3. The permeation flow rate (Q_m) was measured by the change in the permeation volume over 30 s. For each experiment, 0.005 g/L (5 ppm) of latex particles of a particular charge was used and each test for each condition was repeated at least three times.

5.2.2 Network model

In order to obtain a mechanistic understanding of the complex interactions involved during fouling, the network model was employed to extract the fouling parameters (namely, probabilistic factor accounting for dead zone deposition β , initial cake resistance R_{c0} and specific cake resistance R_c') by best-fitting the experimental flux-decline data via regression analysis. More details about the network modeling and the best-fitting methods could be found in Chapter 3. The application of the network model allowed for the accounting of the topological and stochastic aspects of the fouling process and provided a more in-depth understanding of the effect of particle surface charge on the complex interactions between the fluid flow, membrane, and foulant particles.

5.2.3 Optical coherence tomography (OCT)

The optical coherence tomography (OCT; GANYMEDE-SP5, Thorlabs, USA) technique was used to carry out three-dimensional (3D) scans of the membrane filtration cell during fouling. More details of the principles of OCT can be found in Chapter 4. For each experiment, the 3D OCT scan was initially performed for 5 minutes with DI water, after which 0.005 g/L of latex particles of a particular charge was added and the scans continued for another 35 minutes. In this study, the OCT scans were continuously performed via an A-scan, which provides a depth profile [211], at the rate of 30 kHz and the time interval between two consecutive scans was 1.5 s.

Figure 5-1 (a) side view of the virgin membrane via 3D OCT scanning, with the red line denoting the membrane-fluid interface obtained via resolving the OCT data; and (b) side view of the used membrane showing the deposition of the non-modified latex particles ($t = 35$ min, $\text{TMP} \approx 6$ kPa, foulant concentration = 0.005 g/L) via 3D OCT scanning.

The analysis of the OCT signals relied on the method first proposed by Li et al. [30], whereby the coordinate surface of the feed-membrane interface was determined by comparing the intensity gradients with a pre-determined threshold gradient value, and the positions at which the OCT intensity gradients were greater than the threshold value were designated as the surface of the feed-membrane interface. As representative examples, Figs. 5-1a and b display the side views of the virgin and used membranes (after filtering the non-modified latex particles), respectively, with the red lines denoting the feed-membrane interfaces determined. The Li et al. [30] method then was further developed to analyze the topological aspects of particle deposition on the membrane. Specifically, a new coordinate system (namely, x_m - y_m - z_m) was established based on the determined feed-membrane interface, after which a series of coordinate surfaces parallel to the feed-membrane interface was defined in order to monitor the progressive growth of the cake layer. The coordinate surfaces were uniformly spaced apart by 2 μm in vacuum, which was approximately the depth resolution of the OCT system. Because the distances in the OCT images are the optical path lengths measured using the refractive index of vacuum, the real physical distance in pure water is

approximately equal to $1.5\ \mu\text{m}$, as indicated in Fig 5-2a. Fig. 5-2a shows that the layer corresponding to the feed-membrane interface was indexed as layer 0, and each layer above was progressively numbered.

Figure 5-2 (a) Schematic indicating the layers identified from the analysis method for interpreting the OCT data; and (b) snapshots showing the evolution of fouled voxels during membrane filtration.

After the layers were identified, the evolution of the cake layer could be monitored by distinguishing the voxels that reflect that particles have deposited (i.e., fouled), as reported in an earlier study [30]. Specifically, the means and standard deviations of the OCT intensities were first calculated for each layer at $t = 0$, then a voxel in that layer was determined as a fouled voxel if its intensity was greater than the mean plus twice the standard deviation (i.e., 95% confidence interval [184, 185]). The fouled voxels determined at the 95% confidence level were determined for each layer at each time point, and marked in red in the projected area of $0.9\ \text{mm}$ by $0.15\ \text{mm}$, which was chosen to be large enough to be representative (about 2200 pores in the area captured) and yet small enough to allow for reasonable scan rates (1.5 s per image; a larger image requires more time per scan), as depicted in Fig.5-2b. To quantify the extent of fouling, the number fraction of fouled voxels with respect to the total number of voxels were quantified for each layer at each time step. Furthermore, to have a qualitative understanding of the topology of the deposits, the deposit patterns at each layer were also analyzed.

5.3 Results and discussion

5.3.1 Evolution of permeate flux for latex particles of three different surface charges

Because the membrane was negatively charged (Table 5-1), it was expected that the positively charged aminated latex would lead to the worst fouling due to attractive foulant-membrane interactions. Surprisingly, Fig. 5-3, which displays the evolution of the permeate flow rate normalized with respect to the initial permeate flow rate (Q_m/Q_{m0}) for feeds containing the latex particle with three different surface charges, indicates instead that the more negatively charged carboxylated latex gave the worst performance, whereas the positively charged aminated latex gave the best performance. The same trends were observed for repeated tests. This counter-intuitive behaviour was further probed by the network model and OCT.

Figure 5-3 Evolution of the permeate flow rate normalized with respect to the initial permeate flow rate (Q_m/Q_{m0}) for feeds containing the latex particle with three different surface charges investigated, with the discrete points denoting the experimental data and the solid lines being the results of the regression analysis for obtaining the fouling parameters defined in the network model. R_a^2 , R_n^2 and R_c^2 represents the coefficient of determination for experiment-model fitting of aminated latex, non-modified latex and carboxylated latex, respectively.

5.3.2 Interpreting the fouling process based on the best-fit parameters via network modeling

The non-linear curve-fitting associated with the network model was implemented on all three experimental permeate flux trends, as denoted by the solid lines in Fig. 5-3. Satisfactory coefficient of determination for aminated latex (0.9935),

non-modified latex (0.9879) and carboxylated latex (0.9902) implies good agreement was obtained between all three regression trendlines (solid lines) and the corresponding experimental data (discrete points). The fitting results indicates that the network model was able to account for the variation in the surface charges of particulate foulants, and thereby that the best-fit fouling parameters obtained from the network model could be harnessed to understand the fouling mechanisms reliably.

The variations of the best-fit fouling parameters, β , R_{c0} and R_c' , are presented in Figs. 5-4a, b and c, respectively, for the three particle types. The error bars represent 95% confidence intervals from the t-test [212]. Fig. 5-4a clearly shows that the aminated latex particle exhibited the greatest β value, which indicates the highest probability of depositing on the dead zone (i.e., area of the membrane not occupied by pores). The probably reason is the attractive electrostatic interactions between the negatively charged membrane and the positively charged aminated latex. Analogously, the least value of β for negatively charged carboxylated latex may possibly be due to the repulsive electrostatic interactions between the particle with the membrane. In terms of probability of blocking the open pores ($P_b = 1 - \beta(1 - \varepsilon_m)$), the carboxylated particles exhibited a significantly higher P_b value ($P_b = 0.94$) compared to that of the non-modified latex ($P_b \approx 0.52$) and aminated latex ($P_b \approx 0.43$). Since the membrane used in the current study had symmetric straight-thorough pore structures and low porosity ($\varepsilon_m \approx 0.05$), the highest P_b value of the carboxylated latex led to the severe flux decline seen in Fig. 5-3.

Figure 5-4 Comparison of the fouling parameters obtained by best-fitting of the experimental flux data via regression analysis to obtain the fouling parameters in the network model: (a) the probabilistic factor for deposition in the non-pore regions of the membrane (β), (b) the initial cake resistance R_{c0} , and (c) the specific cake resistance R'_c .

Regarding cake resistance, Figs. 5-4b and c indicate respectively that R_{c0} and R'_c values increased as the zeta potential values decreased, which agrees with a previous crossflow study [213]. Since hydrodynamics effects were similar in view of all three particulate foulants being of the same sizes ($d_p = 3 \mu\text{m}$), the variations were presumably related to the foulant-membrane and/or foulant-foulant interfacial interactions. With respect to R_{c0} (Fig. 5-4b), the different foulant-membrane interactions among the three particulate foulants would have played a key role. Figure 5-5 depicts hypothesized pore interactions and cake morphologies for a range of scenarios. For the positively charged aminated latex, because of the attractive interactions with the negatively charged

membrane, the preferential deposition on the dead zone (i.e., membrane surface without pores; Fig. 5-4a) may led to lesser alignment of the particle to the pore, as depicted in Fig. 5-5a. For the more negatively charged carboxylated latex, due to the lesser affinity to the membrane, the alignment of the particle to the pore could be more complete, as illustrated in Fig. 5-5b. Correspondingly, the incomplete pore blockage by the aminated latex would give a lower R_{c0} value than the more complete pore blockage by the carboxylated latex. Regarding R_c' (Fig. 5-4c), the aminated and carboxylated latex gave respectively the least and greatest cake resistance as the cake developed because of the nature of the cake layer. Figs. 5-5c and d illustrate the hypothesized cake morphologies for the different cakes. Because the positively charged aminated latex had greater affinity to the negatively charged membrane, they preferentially deposited on the membrane rather than other deposited aminated latex, thereby forming a more uniform cake layer (Fig. 5-5c) with relatively less resistance (R_c'). On the other hand, because the negatively charged carboxylated latex particles were approximately equally deposit either on the negatively charged membrane or other negatively charged carboxylated particles deposited, an inhomogeneous cake (Fig. 5-5d) was likely formed, which conferred greater cake resistance (R_c') partly due to the thicker cake. Such differences in the distribution of the particulate foulants constituting the cake layers and the corresponding differences in the resistances have been proposed by Ethier et al. [214].

Figure 5-5 Schematic of the hypothesized cake morphology based on the fouling parameters (namely, R_{c0} and R_c') of the network model: (a) the ‘incomplete pore blockage’ refers to initial particle deposition when particle-membrane electrostatic interactions are attractive, resulting in a low R_{c0} ; (b) the ‘complete pore blockage’ refers to initial particle deposition when particle-

membrane electrostatic interactions are repulsive, resulting in a high R_{c0} ; (c) the ‘uniform cake’ refers to a uniform deposition of foulants due to attractive particle-membrane electrostatic interactions, resulting in a smooth cake layer on the membrane surface and a low R_c' ; and (d) the ‘inhomogeneous cake’ refers to clusters of foulants due to repulsive particle-membrane electrostatic interactions, resulting in localized uneven cake layers on the membrane surface and a high R_c' .

5.3.3 Analyzing the fouling phenomenon using OCT

Armed with the understanding from the network model, the OCT was used to provide further evidence of the mechanistic picture given by the network model of the different fouling phenomena by the latex particles of different surface charges. Fig. 5-6 illustrate the evolution with respect to filtration volume of the fraction of fouled voxels of four different layers (namely, 1, 3, 5 and 7) above the feed-membrane interface, which reflect the extents of fouling at different distances from the membrane. Regardless of surface charge, Fig. 5-6 indicates that the fraction of fouled voxels increased as filtration progressed, which reflect the extent of fouling increasing with the filtration volume, with the layers closer to the membrane generally increasing more. Three observations are worth highlighting. Firstly, the fractions of fouled voxels were the greatest for the carboxylated latex, which corresponds to the most severe flux decline (Fig. 5-3), followed by the non-modified latex and lastly the aminated latex. The evolution of the fraction of fouled voxels with respect to time is displayed in Fig. 5-9 A in the appendix; these plots have more data points because the OCT data were taken every 1.5 s while the filtration volume was taken every 30 s. Secondly, among the three surface charges, the trends of the four layers were most distinctive from one another for the positively charged aminated latex (Fig. 5-6a), whereas the trends for Layers 1 and 3 were closer to each other for the non-modified latex (Fig. 5-6b) and carboxylated latex (Fig. 5-6c). This agrees with the mechanistic picture of the different cake layers in Figs. 5-5c and d, and thereby the R_c' trends in Fig. 5-4c. The distinctive trends of the four layers for the aminated latex (Fig. 5-6a) suggests the sequential build-up of the cake layers, which suggests uniform cake layers (Fig. 5-5c). On the other hand, the less distinctive trends between Layers 1 and 3 for the other latex imply the deposition of the particulate foulants at the same rates in both layers, which indicates inhomogeneous cakes (Fig. 5-5d). Thirdly, the significantly greater fraction of fouled voxels in Layers 5 and 7 for the carboxylated latex particles relative to that of the

aminated was likely due the growth of the clusters (Fig. 5-5d), which became rapidly taller than the uniform cake (Fig. 5-5c). In particular for Layer 7 (which was 10.5 μm above the feed-membrane interface), the final fractional blockage for the carboxylated latex was more than 10%, whereas that for the non-modified latex and aminated latex were approximately 5% and 0%, respectively. This provides affirmation of the hypothesis proposed in Fig. 5-5.

Figure 5-6 Comparison of the evolution of the cake layer with filtration volume when the feed contained 0.005 g/L of (a) aminated latex particles, (b) non-modified latex particles, and (c) carboxylated latex particles. Each error bar represents the 95% confidence interval based on a t-test; note that error bars are included in Fig. 6(c), but too small to be clearly visible.

5.3.4 Topology of the deposits

The OCT data also provided more information on the topology of the deposits. The patterns of the fouled voxels in each layer (Fig. 5-2b) were further analyzed based on the techniques described by Dixmier [215]. Specifically, the fouled voxels appeared either as individual voxels (i.e., no adjacent fouled voxel) or as groups (i.e., a few adjacent fouled voxels). To study the topology, these patterns were classified into four categories using Matlab: Category A represents individual fouled voxels; Category B represents groups of 2 to 5 adjoining fouled voxels; Category C represents groups of 6 to 10 adjoining fouled voxels; and Category D represents groups of more than 10 adjoining fouled voxels. For each layer, the fractions of fouled voxels in each category with respect to the total number of fouled voxels were analyzed. Figs. 5-7 and Fig. 5-8 illustrate this fraction at various filtration volumes for respectively Layer 1 (i.e., ~ 1.5 μm above the feed-membrane interface) and Layer 3 (i.e., ~ 3 μm above the feed-membrane interface).

Regarding Layer 1 (Fig. 5-7), the change in the deposit patterns as the filtration volume increased is clear. At the filtration volume (V_f) of 200 mL (Fig. 5-7a), the deposits were more dispersed and thereby largely classified as Categories A and B. The difference among the three particle types was negligible, which indicates that the effect of surface charge was insignificant in dictating the fouling patterns at this initial phase of fouling. As the filtration volume (V_f) increased to 500 mL (Fig. 5-7b), larger clusters of deposits corresponding to Categories C and D appeared as fouling became more extensive and the effect of the different surface charges became significant. The positively charged aminated latex had the greatest fractions in Categories A and B, whereas the more negatively charged carboxylated latex had the greatest fraction in Category D. This indicates that the positively charged aminated latex preferentially deposited individually or in smaller clusters compared to the negatively charged latex. The tendency of the non-modified latex to cluster rather than form a more dispersed layer of deposits agrees with our previous study, and was attributed to the attractive Gibbs free energy of interaction [216]. As the filtration volume (V_f) further increased to 800 mL (Fig. 5-7c), the fractions in Category D increased while those in Categories A and B decreased, signaling the evolution of the fouling. The effect of the different surface charges was consistent in that the positively charged aminated latex displayed

the most dispersed deposits, as evident in the highest fractions in Categories A – C and lowest fraction in Category D. Conversely, the more negatively charged carboxylated latex had the lowest fractions in Categories A – C and highest in Category D, which indicates the most clustered deposits. Therefore, Fig. 5-7 shows that, for the first layer of deposition on the membrane, the positively charged aminated latex tended to deposit as individual particles or as small clusters of particles due to foulant-membrane attraction but foulant-foulant repulsion, whereas the negatively charged carboxylated latex exhibited greater tendency to form larger deposited clusters due to more similar foulant-membrane and foulant-foulant affinities and the drag force by permeate flow. With respect to Layer 3 (Fig. 5-8), similar trends as Layer 1 (Fig. 5-7) were observed. Collectively, the results in Figs. 5-7 and 5-8 are consistent with the hypothesized cake morphology resulting from the network model results, in that the aminated latex tended to form a more uniform cake (Fig. 5-5c) while the carboxylated latex a more inhomogeneous cake (Fig. 5-5d).

The results obtained show clear effects of particle charge on fouling evolution. However it is recognized that the membranes used are idealized and further work is planned to assess the effect of membrane type on fouling by charged foulants using the Network Model and OCT analysis.

Figure 5-7 Comparison of the contribution of each category of deposition on Layer 1 for the three particle types with different surface charges at filtration volumes of (a) 200 mL, (b) 500

mL, and (c) 800 mL. Category A represents individual fouled voxels, while Categories B, C and D represent groups of fouled voxels consisting of 2 – 5 adjoining fouled voxels, 6 – 10 adjoining fouled voxels and greater than 10 adjoining fouled voxels, respectively.

Figure 5-8 Comparison of the contribution of each category of deposition on Layer 3 for the three particle types with different surface charges at filtration volumes of (a) 200 mL, (b) 500 mL, and (c) 800 mL. Category A represents individual fouled voxels, while Categories B, C and D represent groups of fouled voxels consisting of 2 – 5 adjoining fouled voxels, 6 – 10 adjoining fouled voxels and greater than 10 adjoining fouled voxels, respectively.

5.4 Conclusions

The current study employed a network model and 3D OCT image analysis [30] to understand the impact of the surface charge of particulate foulants on cake formation. Low-porosity PCTE membranes were used, and the model particulate foulants used were latex, which were of the same sizes (3 μm) but had different surface charges (namely, positively charged aminated, and negatively charged non-modified and carboxylated).

Surprisingly, although the positively charged aminated latex was expected to perform the worst in the flux-decline experiments due to attractive electrostatic interactions with the negatively charged membrane, this latex displayed the best performance relative to the two negatively charged latex. This counter-intuitive

behaviour was examined by the network model and OCT image analysis to understand the underlying reasons for the different fouling behaviors.

The network model indicated that the positively charged aminated latex exhibited the greatest probability for deposition in the dead zones (i.e., non-pore membrane region β), and the lowest initial cake resistance (R_{c0}) and specific cake resistance (R_c'). The initial pore-blocking phenomenon and subsequent cake morphologies were then hypothesized. Regarding pore-blocking, the 'incomplete pore blockage' results from attractive particle-membrane electrostatic interactions and leads to a lower R_{c0} value, while the 'complete pore blockage' results from repulsive particle-membrane electrostatic interactions and leads to a higher R_{c0} value. As for cake morphology, the 'uniform cake' results from attractive particle-membrane electrostatic interactions leading to a smooth cake layer on the membrane surface and a lower R_c' value, while the 'inhomogeneous cake' refers to clusters of foulants above pores due to repulsive particle-membrane electrostatic interactions, resulting in uneven cake layers on the membrane surface and a higher R_c' value.

3D OCT characterization further affirms the hypotheses on the different fouling behaviors by the particulate latex foulants of different surface charges. Specifically, the progressive cake buildup on the feed-membrane interface was analyzed in terms of the fraction of fouled voxels at each incremental layer. Three observations were obtained. Firstly, the fractions of fouled voxels were the greatest for the carboxylated latex, which corresponds to the most severe flux decline, followed by the non-modified latex and lastly the aminated latex. Secondly, the trends of the four layers were most distinctive from one another for the positively charged aminated latex, which suggests the progressive growth of the uniform cake layer; on the other hand, the trends for Layers 1 (i.e., 1.5 μm above the feed-membrane interface) and 3 (i.e., 3 μm above the feed-membrane interface)) were closer to each other for the non-modified latex and carboxylated latex, which suggests the growth of an inhomogeneous cake. Thirdly, the significantly greater fraction of fouled voxels in Layers 5 and 7 for the carboxylated latex particles relative to that of the aminated was likely due the growth of an inhomogeneous cake, which became locally taller more rapidly than the uniform cake.

The coupling of the network model and OCT characterization affirmed the counter-intuitive filtration performance of the three particulate latex foulants (3 μm) of different surface charges. It should be noted that membrane porosity[214], different

operating mode and different initial permeate flux [217] would also have significant effects on charged particle deposition which needs to further investigate.

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5.6 Appendix

Figure 5-9 A Comparison of the evolution of the cake layer with time when the feed contained 0.005 g/L of (a) aminated latex particles, (b) non-modified latex particles, and (c) carboxylated latex particles. The dead-end filtration was carried out at $\text{TMP} = 6 \text{ kPa}$ and membranes used were PCTE membranes ($d_{mp} = 2 \text{ }\mu\text{m}$ and $\varepsilon_m \approx 0.05$).

Chapter 6 Cake formation of bidisperse suspensions in dead-end microfiltration

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Abstract

The evolution of the cake during dead-end microfiltration of different compositions of bidisperse feeds was investigated using network modeling and three-dimensional (3D) optical coherence tomography (OCT) imaging. The foulant particles were latex of two different sizes (namely, 3 and 5 μm) and the membrane was polycarbonate track-etched with nominal diameter of 2 μm . The results from the network model indicate that (i) the deposition of the smaller particles on the non-porous area was reduced when sufficient amount of larger particles existed, whereas that of the larger particles was only affected when the mass concentration ratio of the smaller ones is high; and (ii) monodisperse small particles gave a greater specific cake resistance than monodisperse large particles, and the specific cake resistance of the bidisperse mixture can only be reduced with a sufficient concentration of larger particles. OCT results substantiated the model by revealing that (i) bidisperse feeds tended to form homogeneous cakes, but the presence of a higher concentration of large particles led to heterogeneous cakes; (ii) the presence of a lower concentration of larger particles enhanced clustering, while a higher concentration reduced that; and (iii) in the longer-term filtration, the monodisperse feed of small particles dynamically deposited and detach continuously, while the bidisperse feed with the highest concentration of larger particles exhibited negligible deposition and detachment.

Keywords: Microfiltration; membrane fouling; bidisperse feeds; cake formation

6.1 Introduction

Microfiltration is widely implemented in industry to improve the purity of either the feed or permeate [57]. Unfortunately, the key drawback is that the suspensions in the feed lead to membrane fouling that not only reduces productivity but also compromises with membrane functionality, which makes the process less efficient [218] and increases operating cost [219]. Developing effective techniques for mitigating membrane fouling relies on an in-depth understanding of the fouling mechanisms. Although the mechanisms leading to fouling during filtration are complex and not yet fully understood, macroscopic laws have been developed for well-acknowledged phenomena like pore clogging and cake formation [14, 145]. Sahimi et al. reviewed the mathematical models for describing the transport phenomena with porous media and found these models could be classified into continuum and discrete models [13]. The continuum models, which assumed that not only the spatial domains (e.g., the membrane and the fluid channel) but also the velocity and concentration fields can be described by smooth functions, have been extensively applied to investigate membrane fouling mechanisms, including the classical fouling models describe by Hermia [9]. Based on these classical models, Ho and Zydney [52] proposed a combined fouling model accounting for various phenomena occurring concurrently rather than exclusively, which allowed for understanding the effect of foulant-membrane interactions through pore blockage parameters and initial cake resistances. Bacchin et al. investigated particle size, particle concentration and shear rate in the fouling models to gain further understanding of the fouling mechanisms [8]. While such models are able to reveal some fouling mechanisms, the continuous models failed to account for the topological aspects of membrane fouling, such as the connectivity of the porous structure and the distribution of the deposits. Taking advantage of the development in computational capacity and algorithms, discrete models were developed in recent studies to describe the membrane filtration process and fouling mechanism. Different from the continuum assumption, a discrete model represents the spatial domain as an array of unit cells and thereby adapts the species conservation law to the individual unit cells. Li et al. proposed a network based method to study the effects of membrane asymmetry on membrane fouling [12]. Griffiths et al. employed a network model to theoretically interpret the flux decline behavior during membrane fouling [220].

In parallel with the modeling efforts, a variety of characterization techniques have been applied to study the evolution of the cake layer in real time, such as ultrasonic time domain reflectometry (UTDR) [21, 22], electrical impedance spectroscopy (EIS) [23-25], direct observation through the membrane (DOTM) [26], confocal laser scanning microscopy (CLSM) [27-29] and optical coherence tomography (OCT) [30]. Many interesting observations and understandings have been obtained with the aid of these techniques. For examples, Xu et al. monitored the kaolin particle deposition and cake formation on a single hollow fiber membrane by using UTDR [22], and Sim et al. employed EIS to characterize the evolution of the silica and protein fouling on reverse osmosis membrane [25]. The effect of particle size and crossflow rate on critical flux has been revealed by DOTM [221, 222]. The 3D structure of monodisperse and bidisperse cakes have been characterized by CLSM [28, 29].

Despite the availability of much information on the behaviour of a variety of foulants during the membrane filtration, the cake formation characteristics of polydisperse particles still lack understanding. In practical feeds that employ microfiltration, the suspensions contain a mixture of particles of different sizes (fermentation broth, wastewater, juices, alcoholic beverages, etc.) [223]; therefore the influence of polydispersity on cake formation warrants more investigation in order to optimize the operating condition and mitigating. Some valuable findings have been achieved with regards to revealing the impact of bidisperse suspensions on critical flux and cake formation. Zhang et al. found the critical fluxes of the mixed suspensions increased in the presence of the larger particles [222]. Tanudjaja et al. investigated the effect of spacer and crossflow velocity on the critical flux of bidisperse suspensions, and found bidispersity was more effective in enhancing critical flux at lower crossflow velocities [221]. Ngene et al. visualized cake formation with bidisperse feeds and found the specific cake resistance was higher than the theoretical values obtained from the Kozeny-Carman relation, which implied better ordering or compaction of the cake formed by bidisperse particles [224]. Klaver et al. reviewed the shear-induced particle migration for filtration and fractionation process and found that, in a bidisperse system, small particles hinder migration of large particles in all the reviewed cases [225]. In summary, prior work have revealed some effects of the bidisperse particles on filtration performance and cake evolution. However, the bidisperse cake characteristics and dynamics are still not well understood.

The current work aims to study more realistic situation such as hose encounter in various applications where suspensions containing different sizes of particles are filtered. The objectives of this study were to understand the fouling mechanisms and cake formation process of bidisperse feeds via network modelling and 3D OCT image analysis. Four feeds (namely, one monodisperse to serve as the benchmark, and three bidisperse feeds of varying compositions) were investigated with the same membrane. The flux decline data obtained were data-fitted to the network model to obtain three fouling parameters, and real-time in-situ 3D OCT characterization was applied to provide detailed information on cake morphology and evolution.

6.2 Experimental and analysis methods

6.2.1 Membrane fouling experiments

In the current dead-end filtration study, the membrane used for each test was a polycarbonate track-etched (PTFE) membrane (Whatman, USA), which had approximately uniform cylindrical pores each of diameter 2 μm , was negatively charged and had a low porosity (ϵ_m) of 0.05. The zeta potential (Anton Paar, Surpass, Austria) of the PTFE membrane was measure in electrolyte solution with 1mM KCl. The feed composed of monodisperse latex particles with the same particle density of 1.05 g/cm³ but different mean diameters (d_p) of 3 μm and/or 5 μm (SigmaAldrich, USA). The zeta potentials (Malvern Zetasizer nano-zs, UK) of particles and membrane were listed in Table 6-1.

Table 6-1 Zeta potential values of two latex foulants with uniform particle diameters of 3 μm and 5 μm and the PCTE membrane ($d_{mp} = 2 \mu\text{m}$ and $\epsilon_m \approx 0.05$).

	Zeta potential (mV)	Standard deviation	Feed medium
3 μm Latex	-20.8	0.88	DI water
5 μm Latex	-26.5	1.86	DI water
PTCE membrane	-37.8	1.5	1 mM KCl

Armed with the goal of understanding the cake characteristics of bidisperse particle systems, four different feeds of latex particles were investigated, as summarized in Table 6-2 and described as follows:

- Case I, which served as the benchmark, consisted of 5 mg/L of monodisperse 3 μm particles.
- Case II was a bidisperse suspension of 2.5 mg/L of 3 μm and 2.5 mg/L of 5 μm particles. The total mass concentration was the same as Case I. In terms of number concentration, the number of 3 μm particles was 4.64 times higher than that of the 5 μm ones.
- Case III was a bidisperse suspension of 5 mg/L of 3 μm and 2.5 mg/L of 5 μm particles. The mass concentration of 3 μm particles was the same as Case I. In terms of number concentration, the number of 3 μm particles was 9.3 times higher than that of the 5 μm ones.
- Case IV was a bidisperse suspension of 2.5 mg/L of 3 μm and 11.6 mg/L of 5 μm particles. In terms of number concentration, the number of 3 μm particles was equal to that of the 5 μm ones. The number of smaller particles was the same as that in Case II, and the total number concentration in Case IV was the same as that in Case I.

The four cases were carefully chosen to shed light on the following: (1) comparing Cases I and II allows for understanding the difference between bidisperse and monodisperse systems at the same total mass concentrations; (2) comparing Cases I and IV reveals the difference between bidisperse and monodisperse systems at the same total number concentrations; (3) comparing Cases I and III unveils the effect of the addition of larger particles when the concentrations of the smaller particles were the same; and (4) comparing Cases II, III and IV elucidates the effect of varying the ratios of the constituents in each bidisperse mixture.

Table 6-2 Summary of the four different feeds investigated in the current study. Cases A*, B* and C* were from the results in Chapter 3 and used here for comparison. M_f and N_f represent the mass concentration and number concentration, respectively.

	Polydispersity	Total mass concentration of the feed (mg/L)	Total number concentration of the feed ($\times 10^8 \text{ L}^{-1}$)	3 μm		5 μm	
				M_f (mg/L)	N_f ($\times 10^8 \text{ L}^{-1}$)	M_f (mg/L)	N_f ($\times 10^8 \text{ L}^{-1}$)
Case I	-	5	3.37	5	3.37	-	-
Case II	0.84	5	2.054	2.5	1.69	2.5	0.364
Case III	0.80	7.5	3.734	5	3.37	2.5	0.364
Case IV	0.64	14.1	3.37	2.5	1.69	11.6	1.69
Case A*	-	2.5	1.69	2.5	1.69	-	-
Case B*	-	2.5	0.364	-	-	2.5	0.364
Case C*	-	11.6	1.69	-	-	11.6	1.69

The dead-end filtration cell consisted of two chambers separated by the membrane with an effective filtration area of 9.62 cm^2 . Gravity was used as the driven force by providing a constant TMP to drive the permeation through the membrane. The permeation flow rate was obtained by measuring the change in the permeation volume per unit time. More details of the dead-end filtration setup can be found in Chapter 3. The fouling test for each condition was repeated at least three times.

6.2.2 Network model

In order to obtain a mechanistic understanding of the complex interactions involved during fouling, the network model was employed. For better understanding of the fouling mechanism, the three fouling parameters defined in Chapter 3 (namely, probabilistic factor accounting for deposition on the non-pore regions of the membrane β , initial cake resistance R_{c0} and specific cake resistance R'_c) were calculated by best-fitting the experimental flux-decline data associated with the network model via regression analysis.

In the current study, the network model comprised of 1010×1010 unit cells corresponding to a membrane area of 64 mm^2 . Since two sizes of latex particles were involved in the current study, two dead zone deposition probabilities (i.e., β_1 for $3 \text{ }\mu\text{m}$ and β_2 for $5 \text{ }\mu\text{m}$) and two initial cake resistances ($R_{c0,1}$ for $3 \text{ }\mu\text{m}$ and $R_{c0,2}$ for $5 \text{ }\mu\text{m}$) were defined. In particular, $R_{c0,1}$ and $R_{c0,2}$ were assigned with pre-determined values of respectively 2.75×10^8 and 1.26×10^8 obtained from Chapter 3 by best-fitting the experimental flux-decline data from monodisperse latex filtration with different particle concentrations. The initial cake resistance was found varied with particle size but was independent of particle concentration. Therefore, three fouling parameters, namely, β_1 , β_2 and R'_c , were obtained from best-fitting the experimental flux-decline data.

6.2.3 3D OCT imaging

To further understand the membrane fouling mechanism, the optical coherence tomography (OCT; GANYMEDE-SP5, Thorlabs, USA) was used for non-invasive, in-situ membrane fouling characterization in real time. The OCT, which was based on the Fourier-domain [30, 33] that had a relatively higher scan rate (30 kHz) compared to those based on the time-domain technique [124], was used to perform three-dimensional (3D) scans. The principles of OCT have been detailed in Chapter 4.

For each experiment, the feed for the first 5 minutes was DI water, then the targeted latex particles (Table 6-2) were added, after which filtration continued for 35 minutes. Throughout the experiment, the permeation flux was recorded every 30 s while the 3D OCT scans were continuously performed at an A-scan rate of 30 kHz every 1.5 s. Each experiment was repeated at least three times to ensure the reliability of the analysis. Only one representative result of the three repeated tests was shown for each case in the OCT results since it was inappropriate to average the intensity values and indicate error bars from repeats due to the different optical fields arising from changes in membranes, positioning of the filtration cell, etc.

6.2.4 Statistical analysis of the 3D OCT images

The identification method of the coordinates of the feed-membrane interface was shown in Chapter 4. As illustrated in Fig. 6-1a, the plane identified as the feed-membrane interface was indexed as layer 0, and the adjacent parallel planes above were indexed successively. Once the planes were established, a rigorous criterion was used to distinguish between the unfouled and fouled voxels in order to monitor the evolution of membrane fouling. Specifically, the mean and standard deviation of the OCT image intensities were first calculated for each layer at $t = 0$, then a fouled voxel in each layer was determined as one whose intensity was greater than the mean plus twice the standard deviation (i.e., 95% confidence interval) [184, 185]. Accordingly, the fouling voxels were identified for each layer and marked in red in the projected area of 0.9 mm by 0.15 mm (Fig. 6-1b), which gives the number fraction of fouled voxels with respect to the total number of voxels and thereby the extent of fouling for each layer at each time step.

Furthermore, the patterns of the fouled voxels (Fig. 6-1b) can be further analyzed to provide more detailed topological information of the deposits, per that described by Dixmier [226]. Specifically, a fouled voxel can appear either as an individual voxel (i.e., no adjacent fouled voxel) or as part of a cluster of voxels (i.e., a few adjacent fouled voxels). These patterns were classified into four categories using Matlab, namely, Category A representing individual fouled voxels, Category B representing groups of 2 – 5 adjoining fouled voxels, Category C representing groups of 6 – 10 adjoining fouled voxels, and Category D representing groups of more than 10 adjoining fouled voxels. Moreover, the dynamic behaviour of the foulants can also be obtained in terms of the change in the fraction of fouling voxels per unit time.

Figure 6-1 (a) Schematic illustrating the feed-membrane interface and corresponding parallel planes identified from the analysis of the OCT images, with yellow spheres representing the 3 μm latex particles and blue spheres the 5 μm latex particles; and (b) snapshots depicting the evolution of the fouled voxels at three time points (namely, 30 s, 100 s and 1800 s) of membrane filtration.

6.3 Results and discussion

6.3.1 Understanding the fouling mechanisms using the network model

Fig. 6-2 shows the evolution of flux decline for the four feeds (Table 6-2). The fouling test for each condition was repeated at least three times. Clearly, while three of the feeds gave similar trends, Case IV gave the least flux decline. Two notes are worth highlighting about Case IV. Firstly, Case IV was the bidisperse system with the smallest mass ratio ($M_{f,3\mu\text{m}}/M_{f,5\mu\text{m}} = 0.216$) and number ratio ($N_{f,3\mu\text{m}}/N_{f,5\mu\text{m}} = 1$), which agrees with an earlier study on bidisperse feeds that the permeability reduction was the least for the case with smallest smaller particle/large particle mass ratio [29]. Secondly, surprisingly, despite Case IV having the greatest total mass concentration, the flux decline was the least. This highlights the dominant influence of the larger particles in alleviating fouling [221, 222].

Nonlinear curve-fitting based on the network model was applied to all four flux-decline trends, with the good agreement between the best-fit curves and experimental data in Fig. 6-2 affirming that the network model is amenable for interpreting fouling by feeds containing bidisperse suspensions.

Figure 6-2 Evolution of the permeate flow rate normalized with respect to the initial permeate flow rate (Q_m/Q_{m0}) for four different feeds. The discrete points represent the experimental data and the solid lines the results of the regression analysis carried out to obtain the fouling parameters defined in the network model.

Fig. 6-3 presents the best-fit fouling parameters (namely, β_1 , β_2 and R'_c) for the various feeds, with the error bars representing 95% confidence intervals from a t-test [212]. Other than the four feeds experimentally investigated in this study (Table 6-2), results from Chapter 3 involving three other feeds, namely, 2.5 mg/L of monodisperse 3 μm latex particles (Case A), 2.5 mg/L of monodisperse 5 μm latex particles (Case B) and 11.6 mg/L of monodisperse 5 μm latex particles (Case C), are also presented in Fig. 6-3.

Regarding deposition by bidisperse particles, the effect of gravitational settling of both particles were ignored since the settling velocities [227] for the two particles were several orders of magnitude smaller than the permeate flux. Previous studies have shown that the critical flux increased in the presence of the larger particles, which was linked to the enhancement of shear-induced diffusivity of the smaller particles by the larger particles [221, 222]. Another study on bidisperse systems concluded that smaller particles hinder the migration of large particles [225]. This study provides further insights on the fouling phenomena by bidisperse suspensions through the β parameter. Fig. 6-3a shows that (i) at the same concentration of 3 μm particles (Cases A, II and IV), the β_1 value for the bidisperse systems (Cases II and IV) was smaller than that for the monodisperse (Case A); and (ii) for the bidisperse systems, at the same concentration of 3 μm particles (Cases II and IV), β_1 decreased when the concentration of the 5 μm particles increased. Regarding β_2 , Fig. 6-3b shows that (i) at the higher concentration of 5 μm particles of 11.6 mg/L (Cases C and IV), both monodisperse and bidisperse systems gave similar β_2 values; (ii) at the lower concentration of 5 μm particles of 2.5 mg/L (Cases B, II and III), both bidisperse systems gave much higher β_2 values than the monodisperse case regardless of the concentration of the 3 μm particles; and (iii) the two distinctly different β_2 values of about 0.4 and 0.1 in the bidisperse system appear to be tied respectively to the lower and higher concentrations of the 5 μm particles.

In summary, Figs. 6-3a and 6-3b indicate that (1) the probability of the smaller particles being retained on the non-porous area (β_1) would only be reduced with sufficient larger particles in the bidisperse system (Case II and Case IV) and the reduction augmented as the concentration of the larger particles increased; and (2) the deposition of the larger particles (β_2) was increased significantly only when the mass ratio of small particles was high in the bidisperse system (Case II and III) probably due to the existence of small particles prevented the occurrence of large particles rolling to the membrane pore. These results agree with the conclusion in an earlier review that smaller particles hinder the migration of large particles in bidisperse systems [225]. Although dead-end filtration was implemented in this study, local tangential flows were

still present near the membrane surface due to low membrane porosity and permeate drag, which was similar as the laminar flow in a pipe with sudden contraction of cross sectional area [228]. The magnitude of lateral force induced by the tangential flow increases with particle size [229] thus leading larger particles more likely to be transported to the membrane pores. For Cases I and A, the monodisperse small particles with lesser lateral force were more likely retained on the membrane surface, which agrees with the highest β_1 value and also the numerical study by Schmitz [230]. Regarding Case IV, the low β_1 and β_2 values imply the particles tended to be transported to the membrane pores that were distributed sparsely in view of the low porosity of the track-etched membrane, thus resulting in a lower particle concentration near the membrane surface.

Figure 6-3 Comparison of the fouling parameters obtained via the network model: (a) probabilistic factor for deposition in the non-pore regions of the membrane by the 3 μm latex particles (β_1); (b) probabilistic factor for deposition in the non-pore regions of the membrane by the 5 μm latex particle (β_2); and (c) specific cake resistance (R_c). The error bars represent 95% confidence intervals based on t-tests. Results of three other feeds (namely, 2.5 mg/L monodisperse 3 μm latex, and 11.6 mg/L and 2.5 mg/L monodisperse 5 μm latex) from Chapter 3 are also displayed.

Fig. 6-3c illustrated the effect of varying concentrations of the constituents in the bidisperse feed on cake resistance. Four observations are worth highlighting: (i)

Comparing Case I with Case III, it is obvious that at the higher 3 μm particle concentration of 5 mg/L, the presence of 2.5 mg/L of 5 μm particles increased R'_c (Case III) significantly; (ii) at the lower 3 μm particle concentration of 2.5 mg/L (Cases A, II and IV), adding 2.5 mg/L of 5 μm particle changed R'_c negligibly, but the higher 5 μm particle concentration of 11.6 mg/L reduced R'_c drastically, which agrees with the results shown in Chapter 3; (iii) at the higher 5 μm particle concentration of 11.6 mg/L (Cases C and IV), both monodisperse and bidisperse systems gave similar R'_c values; and (iv) at the lower 5 μm particle concentration of 2.5 mg/L (Cases B, II and III), the bidisperse systems gave much higher R'_c values than the monodisperse one. In summary, Fig. 6-3c indicates that the relative concentrations of the constituents of the bidisperse feed affected the resultant cake resistance, specifically in that (1) R'_c values were the lowest for the monodisperse 5 μm particles (Cases B and C) and also for the bidisperse system with the higher concentration of 5 μm particles (Case IV); and (2) R'_c values were the highest for the cases of lower concentration of monodisperse 3 μm (Cases A) and lower concentration of 5 μm particles for the bidisperse systems (Cases II and III). This suggests that the cake resistance R'_c for bidisperse systems will only decrease when sufficient 5 μm particles existed [231].

As for R'_c , results from Chapter 3 already demonstrated that a higher concentration of monodisperse 3 μm particles gave a lower R'_c (Case I). When the particle concentration was high, larger voids in the cake formed due to the high interparticle cohesion [163] and relatively high deposition rate, thereby giving rise to a cake layer with a lower hydraulic resistance. Similar result was also revealed by Reising who found concentrated slurries favor the formation of larger void in packing [163]. Comparing Case B with Case I, lower particle concentration with lower deposition rate allowed the rearrangement of the particle deposition thus resulting in higher cake resistance. The addition of 2.5 mg/L 5 μm particle at higher 3 μm particle concentration (Case III) increased the cake resistance of the bidisperse system probably because the presence of larger particle decreased the interparticle cohesion of small particles thus allowing the rearrangement of the particles and form a better ordered cake with higher resistance. Similar result was reported in previous study that the specific cake resistance increased due to better packing in the presence of bidispersity, with the experimentally

measured resistance being higher than the theoretical one predicted by the Kozeny-Carman correlation [224].

6.3.2 Analyzing the fouling phenomena using OCT

6.3.2.1 Layer-by-layer cake growth

The OCT was used to provide further understanding on the evolution of the cake formed by the bidisperse latex feed. Fig. 6-4 illustrates the evolution of the cake layer formed with respect to filtration time for the four feeds investigated (Table 6-2). Each sub-figure in Fig. 6-4 displays the fractions of fouled voxels on four layers above the feed-membrane interface, namely, layers 1, 3, 5 and 7, which correspond respectively to 1.5, 4.5, 7.5 and 10.5 μm above the feed-membrane interface. Note that the x -axes range for the sub-figures are different because filtration was terminated when 4 ± 0.1 mg of particles in the feed, determined by the product of permeation volume and feed concentration, has deposited.

Figure 6-4 Comparison of the evolution of the cake layer with filtration time; note that the x-axes' ranges are different because the durations for 4 ± 0.1 mg of particles to deposit onto the membrane were different. The error bars are not shown despite three repeats carried out for each test condition, because although the trends were consistent, it was inappropriate to average the intensity values and indicate error bars from repeats due to the different optical fields arising from changes in membranes, positioning of the filtration cell, etc.

Overall, Fig. 6-4 indicates that the fraction of fouled voxels in every layer increased as filtration progressed, which reflect that the extent of fouling expectedly increased with time, with the layers closer to the membrane generally having higher fractions. Two interesting observations that highlight differences in the cake characteristics should be noted. Firstly, while the trends of the four layers were distinctive from one another in Cases II and III (Figs. 6-4b and 6-4c), overlaps of the

trends were clear in Case I (Fig. 6-4a) and also to some extent in Case IV (Fig. 6-4d). The distinctive trend in each layer in Case II and Case III implied the gradually growth of the cake layer in terms of cake thickness whereas the higher fraction of fouling voxels in Layer 3 compared with Layer 1 in Case I and Case IV implied higher particle concentration in the central region of the cake. Therefore, despite Cases I, II and III having similar flux decline trends, Case I displayed an inhomogeneous (non-uniform) cake whereas Cases II and III exhibited uniform cakes. Secondly, the shortest time range for Case IV indicate that deposition of 4 ± 0.1 mg of particles was the fastest, followed by Case III, then Cases I and II. This fastest cake growth seems to contradict the flux decline trends in Fig. 6-2 in which flux declined the slowest for Case IV and fluxes declined at similar rates for Cases I, II and III. The contradiction can be explained by different cake porosity resulting from the different feed mixtures [28, 29, 230]. As evident in Figs. 6-3a and b, Case IV gave lower β_1 and β_2 values relative to the other bidisperse mixtures, which indicates that the particles deposited more sparsely on the membrane surface and thereby implies lower cake porosity.

6.3.2.2 Topology of the deposits

It should be noted that the OCT technique used here was unable to differentiate between $3 \mu\text{m}$ and $5 \mu\text{m}$ particles from the fouled voxels due to the limit of lateral resolution ($\sim 4 \mu\text{m}$), but can nonetheless provide insights on the cake patterns. Due to high OCT scan rate (1.5 s) applied in current study, three sequential images corresponding to relative deposit mass in each case were analyzed and the values were averaged to minimised the experimental errors. Figs. 6-5 and 6-6 illustrate the clustering of the deposits respectively on Layers 1 (i.e., $\sim 1.5 \mu\text{m}$ above the feed-membrane interface) and 3 (i.e., $\sim 4.5 \mu\text{m}$ above the feed-membrane interface) as filtration proceeded. The extent of clustering was depicted through categorizing the deposits into four categories, namely, Category A that represents individual fouled voxels, and Categories B, C and D that represent groups of fouled voxels consisting of 2–5 adjoining fouled voxels, 6–10 adjoining fouled voxels and greater than 10 adjoining fouled voxels, respectively.

Regarding both Layers 1 (Fig. 6-5) and 3 (Fig. 6-6), generally larger clusters formed as fouling progressed. More specifically on Layer 1 (Fig. 6-5), the effect of bidispersity was apparent on two counts. Firstly, Cases II and III had the largest clusters

throughout filtration, which implies that the presence of a lower concentration of the larger particles enhanced clustering, while a higher concentration of the larger particles eliminated that (Case IV) due to the dominance of the augmented shear-induced diffusivity [221, 222]. This is in sync with the uniform cake formation by Cases II and III seen in Fig. 6-4 and the highest specific cake resistance (R_c') shown in Fig. 6-3. Secondly, the monodisperse Case I had the highest fractions of Categories A and B, which indicates that bidispersity promoted clustering. Similar clustering patterns by bidisperse feeds have been observed, whereby the smaller particles tended to deposit around the larger particles [29].

With respect to Layer 3 (Fig. 6-6), Cases II and III persisted to have more dominant clustering initially (Fig. 6-6a), which is similar to that in Layer 1 (Fig. 6-5). However, particularly regarding Category D at the deposited mass of 2 mg, the fractions of larger clusters were greater in Layer 3 relative to Layer 1 for Cases I and IV, but approximately similar for Cases II and III. This reaffirms the heterogeneous cakes for Cases I and IV, and the homogenous cakes for Cases II and III presented in Fig. 6-4, which resulted in higher cake resistance (R_c') for Cases II and III (Fig. 6-3c).

Figure 6-5 Comparison of the contribution of each category in Layer 1 (i.e., $\sim 1.5 \mu\text{m}$ above the feed-membrane interface) when the total deposit mass (D_m) was (a) 0.5 mg, (b) 1 mg, and (c) 2 mg for the four cases. Category A represents individual fouled voxels, while Categories B, C and D represent groups of fouled voxels consisting of 2–5 adjoining fouled voxels, 6–10 adjoining fouled voxels and greater than 10 adjoining fouled voxels, respectively.

Figure 6-6 Comparison of the contribution of each category in Layer 3 (i.e., $\sim 4.5 \mu\text{m}$ above the feed-membrane interface) when the total deposit mass (D_m) was (a) 0.5 mg, (b) 1 mg, and (c) 2 mg for the four cases. Category A represents individual fouled voxels, while Categories B, C and D represent groups of fouled voxels consisting of 2–5 adjoining fouled voxels, 6–10 adjoining fouled voxels and greater than 10 adjoining fouled voxels, respectively.

6.3.2.3 Analyzing the fouling phenomenon via fouling incremental/removal rate

Figs. 6-7 and 6-8 present the evolution of the change in the fraction of fouling voxels with respect to time in Layers 1 and 3, respectively, to understand the dynamic fouling behaviors. The data were obtained by detecting the appearance and disappearance of fouling voxels between successive OCT images. It should be noted that the slightly higher values in Fig. 6-8a relative to Fig. 6-7b and Fig. 6-8a relative to Fig. 6-8b give the extent of fouling at each time point, as seen in Fig. 6-4. A few general observations are highlighted. Firstly, regardless of monodisperse or bidisperse, the fractions of deposited and removed fouling voxels both increase for between 200 – 1000 s before decreasing with time. This indicates that, as filtration progressed, the rates of deposition and removal increased more quickly initially, then decreased more gradually. Secondly, the fractions were greater in Fig. 6-9 than Fig. 6-8, implying that the rate of deposition and removal were greater at the higher layer due to the larger degree of freedom for movement.

Compared to the monodisperse feed (Case I), the bidisperse feeds (i.e., Cases II – IV) (i) shortened the initial duration over which the fractions increased; (ii) caused faster rates of decrease beyond the peak magnitude of the fractions; and (iii) had higher fractions before the peak fractions were attained and lower fractions beyond. This indicates the significant influence of the enhanced shear-induced diffusion associated with larger particles in affecting deposition and removal dynamics, which agrees earlier reports of enhanced particle movements due to the larger particles in bidisperse systems [29, 221, 222]. A closer inspection of the bidisperse compositions reveals that, for Case IV that had the greatest concentration of large particles, the fractions peaked the earliest and were the lowest after the peak. Between Cases II and III that had the same concentrations of large particles, the trends were quite similar, with the latter having lower magnitudes due to the higher concentration of smaller particles causing it to behave more like the monodisperse system (Case I).

Figure 6-7 Evolution of the change in the fraction of fouling voxels with respect to total number of voxels in Layer 1: (a) deposited fouling voxel; and (b) removed fouling voxel. The error bars are not shown despite three repeats for each test condition, because although the trends were consistent, it was inappropriate to average the intensity values and indicate error bars from repeats due to the different optical fields arising from changes in membranes, positioning of the filtration cell, etc.

Figure 6-8 Evolution of the change in the fraction of fouling voxels with respect to total number of voxels in Layer 3: (a) deposited fouling voxel; and (b) removed fouling voxel. The error bars are not shown despite three repeats for each test condition, because although the trends were consistent, it was inappropriate to average the intensity values and indicate error bars from repeats due to the different optical fields arising from changes in membranes, positioning of the filtration cell, etc.

6.4 Conclusion

The current study applied network modeling and 3D OCT imaging to understand cake formation by feeds containing bidisperse particles. Low-porosity polycarbonate track-etched membranes and latex particles of two sizes (namely, 3 μm and 5 μm) were used. Four different feeds were investigated, namely, a monodisperse feed of 3 μm particles to serve as a benchmark and three bidisperse feeds with varying compositions of the two constituents (Table 6-2). Of the four feeds, the flux decline was the least for the bidisperse feed with the greatest concentration of large particles despite having the greatest overall concentration, while the flux trends were similar for the other three feeds.

The network model indicates that: (1) the probability of the smaller particles being retained on the non-porous area (β_1) was reduced by the presence of larger particles, with the reduction augmented as the concentration of the larger particles increased; (2) the deposition of the larger particles (β_2) was affected only by the concentration of the larger particles, regardless of the concentration of the smaller ones; and (3) the specific cake resistance (R'_c) of the bidisperse feed can only be lowered with a sufficient concentration of large particles.

OCT results indicate that: (1) the monodisperse feed and the bidisperse feed with the greatest concentration of large particles gave heterogeneous cakes, while the bidisperse feeds with lower concentrations of large particles gave homogeneous cakes due to the interaction between the two constituents; (2) the presence of a lower concentration of the larger particles enhanced clustering, while a higher concentration of the larger particles reduced that; and (3) bidisperse feeds shortened the initial duration over which the fractions of deposited fouling voxels increased and caused faster rates of decrease beyond the peak magnitude of the fractions.

This study therefore provides more detailed mechanistic understanding of cake formation by bidisperse particles, which is valuable in advancing the knowledge on the microfiltration of feeds that are inevitably polydisperse. Further studies on the effect of different membranes, different polydispersities, different operating modes are warranted.

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Chapter 7 Conclusion and Future Perspectives

7.1 Overall Conclusions

This thesis firstly presents the development of a two-dimensional novel network fouling model to analyse fouling mechanism by interpreting the pore blockage and cake growth on the membrane surface and three fouling parameters were defined in this model, namely the probabilistic factor for deposition in the non-porous area (β), the initial cake resistance (R_{co}), and the specific cake resistance with respect to cake thickness (R_c'). Secondly, optical coherence tomography (OCT) characterization technique was applied in BSA protein microfiltration to monitor the fouling evolution in real time and the layer-based 3D OCT image analysis method was employed to analyse the OCT data. Two offline characterization techniques, namely evapoporometry (EP) and atomic force measurement (AFM) and a well-developed classical three mechanism fouling model were also used to get further information about the BSA fouling behavior. The results showed that OCT was able to characterize the fouling behavior and the layer-based analysis method helped to gain more detail information about fouling evolution, which implied the potential to couple network modeling with the OCT technique to obtain a deeper understanding of fouling mechanism. Thirdly, the network model and 3D OCT image analysis were employed to investigate the impact of the surface charge of monodisperse particulate foulants on cake formation. The results affirm the availability to combine network model and OCT characterization to study external fouling caused by monodisperse particulate foulant. Fourthly, the network model was modified and improved to account for the external fouling by bidisperse particulate foulants. The fouling parameters obtained from best fitting revealed different fouling mechanisms for different combination of bidisperse particles. 3D OCT results helped to affirm the theoretical results obtained from network model as well as provide more detailed information about the cake formation in the experimental way.

The major findings and conclusions are summarized as follows:

- Network modeling proposed in current study is a discrete fouling model in which the membrane is discretized and approximated as a network contains a set of unit cells and each particle approach to the membrane was monitored individually. Three fouling parameters were defined in this model, namely the probabilistic factor

for deposition in the dead zone (β), the initial cake resistance (R_{c0}), and the specific cake resistance with respect to cake thickness (R'_c).

- Compare to the continuum model, the network model provides more resolution to the fouling process since the membrane area is discretized and individual particles are tracked, which helps to provide an enhanced mechanistic understanding of the complex interactions between the fluid, membrane and the foulants.
- Assessing the fouling evolution during BSA microfiltration by three different kinds of membrane with same vendor-provided nominal pore size and similar porosity, OCT showed the ability to quantitatively compare the extents of external fouling. For internal fouling, OCT can provide the variation of light intensity to monitor the internal fouling versus time but failed to implement quantitative comparison among the membranes.
- Evaporimetry was able to quantify the extent of internal fouling off-line by characterizing the variation in pore-size distribution of the fouled membranes.
- The availability of coupling of the network model and OCT characterization to study the counter-intuitive filtration performance of the monodispersed particles with different surface charges helped to understand the underlying reasons for the different fouling behaviors.
- The application of improved network modeling in the bidisperse particle solution reveals the high flexibility of the network model framework which is able to combine different mechanisms to simulate fouling processes with various operating conditions.
- 3D OCT image analysis employed in investigating the cake formation of bidisperse feeds not only presented different cake morphology formed by different combinations of the bidisperse feeds but also is able to reveal different dynamic fouling behaviors above the membrane surface for different bidisperse cases.

7.2 Future Perspectives

Due to the complexity of the particle-fluid-membrane interaction during membrane filtration, more studies could be done to shed light on the fouling mechanism in the future. To optimize the network modeling and the analysis method of OCT data, the followings could be taken into consideration:

- The network model developed in the current study is a two-dimensional network which can only account for the external fouling. In most of the practical membrane filtration processes, both external fouling and internal fouling will occur. In order to account for the internal fouling, new algorithm should be developed to illustrate the internal fouling process: The two-dimensional network should be expanded into three-dimensional one contained a set of cubic unit cells. The structure of the network should be able to simulate the geometrical characteristics of the membrane, like the membrane hydraulic permeability, and adaptable to estimate the distribution of flow within the network. A series of probabilistic criteria could be applied to simulate the transportation and rejection of foulants in the network.
- The operating condition in the current study is limited to constant pressure dead-end filtration mode. Network model combined with OCT could also be employed in the membrane processes with different operating condition such as constant flux crossflow mode as well as to investigate more complex foulants such as nanoparticles, oil-emulsion, polydisperse particles etc. In order to apply the network modeling in crossflow filtration mode, more criteria should be required to describe the transportation of foulants from one unit cell to another unit cell as a result of complex crossflow-particle-membrane interaction.
- The current study combined network modeling with OCT characterization to understand fouling mechanism during microfiltration. As a discrete fouling model which could monitor the fouling behavior for each particle, network model could also couple with other advanced fouling characterization techniques, such as EIS, CLSM, UTDR etc.
- OCT is an advanced characterization technique to detect the fouling evolution during membrane filtration and able to implement quantitatively comparison for the extents of external fouling for different cases. However, quantitatively comparison for internal fouling was challenged with the current data analysis method due to the variation of membrane material and complex liquid-foulant-membrane boundaries. Therefore, optimizing the OCT analysis algorithm could be done to obtain more meaningful information about internal fouling.
- The limitation of OCT characterization on quantitatively compare the extent of internal fouling could be solved by coupling OCT with EP, which implied the availability of combining different characterization techniques to reveal the

underlying fouling mechanisms. Also, in the same membrane filtration process, comparing the OCT results with the results obtained from other characterization techniques could help to understand the differences between different characterization techniques as well as to validate the findings from the characterization result.

- OCT characterization as well as other characterization techniques could be applied in other membrane processes such as forward osmosis or membrane distillation as well as applied in the membrane cleaning process, which could potential help to optimize the fouling mitigation methods.

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