Mechanistic understandings of membrane fouling in membrane filtration with particulate foulants

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**MECHANISTIC UNDERSTANDINGS OF
MEMBRANE FOULING IN MEMBRANE FILTRATION
WITH PARTICULATE FOULANTS**

**TRINH THIEN AN
SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING**

2019

**MECHANISTIC UNDERSTANDINGS OF
MEMBRANE FOULING IN MEMBRANE FILTRATION
WITH PARTICULATE FOULANTS**

TRINH THIEN AN

School of Chemical and Biomedical Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement 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 plagiarized material, and has not been submitted for a higher degree to any other University or Institution.

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SUPERVISOR DECLARATION STATEMENT

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A handwritten signature in blue ink, consisting of a stylized 'W' followed by a horizontal line and a vertical stroke, positioned above a dotted line.

Assoc. Prof. Chew Jia Wei

AUTHORSHIP ATTRIBUTION STATEMENT

This thesis contains material from 4 papers published and 1 manuscript submitted in the following peer-reviewed journals:

Chapter 3 is published as T.A. Trinh, W. Li, Q. Han, X. Liu, A.G. Fane, J.W. Chew, *Analyzing external and internal membrane fouling by oil emulsions via 3D optical coherence tomography*, Journal of Membrane Science, 548 (2018) 632-640.

The contributions of the co-authors are as follows:

- Professor Chew and Dr. Li provided the initial project direction.
- I performed the laboratory work at School of Chemical and Biomedical Engineering, NTU and Singapore Membrane Technology Centre, and analyzed the data.
- Dr. Li developed the OCT image analysis method.
- Dr. Liu and Han trained me to use the OCT and Han helped in some experiments.
- I prepared the manuscript draft. The manuscript was reviewed and revised by me, Dr. Li, Professor Fane and Professor Chew.

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The contributions of the co-authors are as follows:

- Professor Chew and I provided the initial project direction.
- I performed the laboratory work at School of Chemical and Biomedical Engineering, NTU and Singapore Membrane Technology Centre, and analyzed the data.
- I, Han and Ma performed characterization measurement.
- I prepared the manuscript draft. The manuscript was reviewed and revised by me and Professor Chew.

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The contributions of the co-authors are as follows:

- Professor Chew and I provided the initial project direction.
- I performed the laboratory work at School of Chemical and Biomedical Engineering, NTU and Singapore Membrane Technology Centre, and analyzed the data.
- Dr. Li developed the OCT image analysis method.
- I prepared the manuscript draft. The manuscript was reviewed and revised by me and Professor Chew.

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- Professor Chew provided the initial project direction.
- Dr. Li developed OCT image analysis method and gave suggestions about the data analysis.
- Han performed the laboratory work at School of Chemical and Biomedical Engineering, NTU and Singapore Membrane Technology Centre and analyzed the data.
- I conducted the zeta potential tests for the latex foulants and gave advices about the responses to reviewer's comments.
- Han prepared the manuscript draft. The manuscript was revised by Professor Chew and Professor Fane.

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- I revised the manuscript and improve the manuscript's logic.
- Professor Chew finalized the manuscript.

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MECHANISTIC UNDERSTANDINGS OF MEMBRANE FOULING IN MEMBRANE FILTRATION WITH PARTICULATE FOULANTS

ABSTRACT

Membrane filtration is an advance filtration technology that has been widely applied in many fields that requires separation. However, during membrane filtration, the process of deposition of components to the membrane that reduce the separation performance, i.e., membrane fouling, is inevitable. Despite many research studies that have been conducted, the full understanding of membrane fouling is still far from perfect due to the complication in the mechanism of the fouling process. In view of this gap of knowledge, a series of research studies were carried out to investigate the underlying mechanisms contributing to membrane fouling and provide with deeper understanding of membrane fouling as well as membrane fouling mitigation, using the advance in-situ and non-invasive three-dimensional (3D) optical coherence tomography (OCT) monitoring and characterization method.

The first chapter provides basic background of membrane filtration process and the objective of the studies. The working principle of a 3D OCT was discussed and the applications of OCT and other techniques in the past studied was reviewed. Specifically, compared to other techniques, OCT has the advantages of the full combination of real-time, non-invasive and capable of perform 3D scanning to monitor and characterize membrane fouling, which was used as the main novel method in the studies of this thesis. The literature review and gap of knowledge is discussed in Chapter 2, together with the Objectives of the studies in this Thesis and the outline of the Thesis.

Membrane fouling in practice is a phenomenon that involves many complex underlying mechanisms caused by different factors such as the surface charges, the polydispersity and the natural phase (i.e., solid or liquid) of the foulants in the feed. Therefore, the studies in this thesis aimed to provide more understandings of these effects. While Chapters 3 and 4 focused on investigating membrane fouling caused by oil-in-water emulsions, Chapters 5 focuses on

membrane fouling caused by solid droplets, emphasizing on internal fouling. The OCT monitoring and characterizing technique was applied in all of the studies with the aid of additional mathematical tools such as membrane fouling modeling or thermodynamic theories.

In Chapter 3, internal fouling by oil droplets monitored and analyzed by optical coherence tomography was reported for the first time. Both internal and external fouling by oil droplets were studied in comparison with solid glass particle. In the studied cases, compared with solid foulants, oil droplets tended to deposit onto one another to a greater extent, and capable of causing internal fouling even when the droplet size is of order of magnitude larger than the membrane pores. This was due to the nature of the liquid phase that allowed the droplets to deform to penetrate the pore or to wet the membrane. In Chapter 4, to study the effect of the stabilizing surfactants present in oil-in-water emulsions on fouling, thermodynamic models were employed together with OCT to describe and explain the interactions that lead to oil droplet deposition on the membrane surface. Oil emulsions stabilized by three surfactants with three different charges were studied (namely, positively, non-ionic and negatively charged). The repulsive energy, but not the attractive energy, predicted either by the DLVO or XDLVO model correlated well with the extent of fouling. In terms of surface charges, the oil emulsions stabilized by the non-ionic surfactant had the greatest fouling, characterized by the lowest peak of repulsive total Gibbs energy and the greatest increase of intensity in OCT images.

In practice, besides external fouling which accounts for the deposition of foulants on the membrane surface, internal fouling is evitable when the particles are smaller than the membrane pores. Compared to external fouling, studying internal fouling is more challenging due to the location of the deposition which is inside the membrane structure. Using OCT could overcome this issue and a study was conducted and reported as in Chapter 5. Specifically, polystyrene particles smaller than a quarter of the membrane pore was used as foulants, and three types of particles with different surface charges was used. The membrane used had negative surface charged too. In addition, a concept of “internal cake” which accounted for the cake formed inside the pores upon internal fouling was applied and developed into a mathematical model. The OCT results and the

model regression showed the least fouling by the most negatively charged particles which was described well by the pore constriction scheme alone, and the greater fouling in the case of the less negatively charged and the positively charged particles which was described well only by the combination of the pore constriction, pore blockage and internal cake fouling schemes. Besides, the parameters obtained from the model regression revealed the progressive cake growth perpendicular to the permeate flow which led to the higher cake resistance in the case of positively charged particles, and the less ordered deposition of the negatively charged particle which led to more pore blockage and more pore constriction but lower cake resistance. These deposition mechanics were attributed to the interaction between the membrane and the particles.

Chapter 6 concludes the findings in the Thesis and Chapter 7 compiles a list of publications. Chapter 8 provides additional co-authors works that studied membrane external fouling by solid particles using OCT.

Keywords: Membrane fouling; Regression; Membrane fouling models; Pore blockage; Cake filtration; Surface charge; Optical coherence tomography; Microfiltration; Bidisperse feeds; Cake formation; Membrane internal fouling; Membrane external fouling; Oil emulsions; Direct visualization; Interfacial energy; Surfactant; Oil-water separation.

Chapter 1. INTRODUCTION OF MEMBRANE TECHNOLOGY AND MEMBRANE FOULING

Membrane technology is an emerging field that has recently been applied in separation areas in many fields such as petroleum refining, food and metal processing [1]. A membrane is a selective semi-permeable barrier that allows certain components of a mixture in the upstream (i.e., the “feed”) to pass through to the downstream (i.e., the “permeate”) while the other certain components are retained (i.e., the “retentate”) [2] (Figures 1.1 and 1.2). In comparison to other separation techniques such as flotation [3,4], coagulation [5] and biotreatment [6], membrane-based separation has the advantages of ease of operation, no additional chemical requirements, high separation efficiency and low cost [7-9].

Figure 1.1. Crossflow membrane filtration

Figure 1.2. Dead-end membrane filtration

There are many classifications of membrane separation based on the classifying criteria. Based on driving force, membrane separation can be

categorized into pressure-driven membrane filtration [10-15] and thermal-driven membrane filtration, where the latter is usually referred to as “membrane distillation” [16,17]. In membrane distillation process, a temperature difference is applied across the membrane instead of pressure. Due to the thermal gradient, the more volatile components in the feed will evaporated at the feed-membrane interface, enter and membrane pores and condense at the permeate-membrane interface, leaving the less volatile components being retained. In pressure-driven membrane filtration, a pressure difference is applied on two sides of the membrane with higher pressure on the feed side. The pressure difference across the membrane is termed “*trans-membrane pressure*” or “*TMP*”.

Base on the configuration of flows, membrane filtration can be categorized as “*dead-end*” (Figure 1.2) and “*crossflow*” (Figure 1.1) modes [2]. In dead-end mode, the feed direction is direct to the membrane surface without the presence of the retentate stream. Opposingly, in crossflow mode, the feed direction is tangent with the membrane surface and the retentate is usually recycled to the feed tank. Based on the size of the separated components, membrane filtration ranges from microfiltration (i.e., particle of diameter of micrometers such as yeast cells and bacteria) to as far as reverse osmosis (i.e., atomic or ionic size range such as ions of aqueous salt) [2].

Membranes used in membrane filtration could be classified into various types. There are track-etched polycarbonate or polyester membranes whose pores are straight-through cylindrical [18], and ceramic membranes made of aluminum oxide [19] that have pore that are non-interconnected. In contrast, there are membranes made by phase inversion [20,21] or stretching [22,23] with result in porous structure, i.e., pores are interconnected. These membranes are usually made of polyvinylidene fluoride (PVDF) [24] and polytetrafluoroethylene (PTFE) [25], polyethersulfone (PES) [26], etc.

Despite the advantages, in membrane filtration, a phenomenon where the deposition of the retained components onto the membrane surface or into the membrane structure, thereby reducing the throughput and selectivity of the separation [27], is inevitable. Such phenomenon is termed “*membrane fouling*” where the particle that deposit to the membrane is termed “*foulant*”. In-depth

understandings of the fouling mechanisms are crucial to mitigate the fouling's negative effects.

Membrane fouling is usually characterized by the “*flux*” [28-31] and rejection [32-34]. Flux is defined the volumetric flowrate per unit area of the membrane, denoted as “*J*” and usually having the metric unit of L/(m²h) – or “*LMH*” and is an important term in membrane filtration process. In addition to the conventional flux and rejection, more modern techniques can be used for membrane characterization such as scanning electron microscopy (SEM) [35,36], attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) [37,38], confocal microscopy [39-41], matrix-assisted laser desorption ionization mass spectrometry [42-44], atomic force microscopy (AFM) [40,45,46], surface force apparatus (SFA) [47-50], or acoustic methods [51-53].

Besides experimental methods, mathematically modeling has also been used to describe membrane fouling, which can be classified into continuum and discrete models [54]. The continuum models have been extensively employed to study membrane fouling, including the classical fouling models (namely, the complete pore blockage model [55,56], the intermediate pore blockage model, the cake filtration model [57], and the pore constriction model [58,59]) 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 [58] and the three-mechanism model by Duclos-Orsello et al. [56]. The complete pore blockage, intermediate pore blockage and the cake filtration account for the deposition of particle on the membrane surface, i.e., the “*external fouling*”, and the pore constriction model account for the deposition of particle into the membrane structure via membrane pores, i.e., the “*internal fouling*”. In contrast to the continuum models, network models have been developed to accommodate random processes by establishing a series of probabilistic criteria [60], which is key to understanding and simulating membrane fouling as the local fouling behavior is stochastic in nature [61]. Particularly, a network model divides a membrane into an array of unit cells and monitored each particle individually [10]. Besides modeling, theoretical methods such as application of thermodynamic theories DLVO and extended-DLVO [11,62,63] has also been

used to study membrane fouling. Specifically, these theories provide equations that calculate the interaction energies between the components in the membrane processes, such as foulant-foulant interaction or membrane-foulant interaction, via which the fouling behavior can be predicted.

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Chapter 2. LITERATURE REVIEW AND OBJECTIVES

The content of this chapter has been published under the titles of *Analyzing External and Internal Membrane Fouling by Oil Emulsions via 3D Optical Coherence Tomography* in Journal of Membrane Science, Volume 548, 15 February 2018, Pages 632-640 (<https://doi.org/10.1016/j.memsci.2017.10.043>), *Microfiltration of oil emulsions stabilized by different surfactants* in Journal of Membrane Science, Volume 579, 1 June 2019, Pages 199-209 (<https://doi.org/10.1016/j.memsci.2019.02.068>), and has been submitted to and accepted by Journal of Membrane Science under the title of *Internal fouling during microfiltration with foulants of different surface charges*.

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T.A. Trinh, Q. Han, Y. Ma, J.W. Chew, Microfiltration of oil emulsions stabilized by different surfactants, Journal of Membrane Science, 579 (2019) 199-209.

2.1. Three-Dimensional (3D) Optical Coherence Tomography (OCT) in Monitoring and Characterizing Membrane Fouling

The investigation of membrane fouling requires characterization methods which can monitor the filtration process and the membrane fouling phenomena non-invasively and in real time. Several techniques have been applied and reported in literature such as direct observation through the membrane (DOTM) [1-5], ultrasonic reflectometry [6] and electrical impedance spectroscopy (EIS) [7-11]; however, there are limitations associated with each of these methods. DOTM relies on an optical microscope to observe the feed-membrane interface and therefore requires transparent membranes and is limited to two-dimensional

(2D) imaging which are not as practical to monitor cases such as internal fouling. As for ultrasonic reflectometry and EIS, membrane fouling is detected via acoustic waves and alternating currents, respectively, where the fouling is inferred from signal changes rather than direct observation images.

The working principle of an OCT (Figure 1.3) involves low-coherence light beam emitted from a light source with a central wavelength of 905 nm and bandwidth of approximately 200 nm. The beam is split at the interference mirror into two beams, namely, reference and sample. The reference beam is reflected by a mirror, while the sample beam is backscattered by the sample. These two beams are recombined and collected at a spectrometer which generates the intensity versus depth profile. From synthesized the depth profile, the 3D images of the sample can be visualized. Based on the images, quantitative analysis of the growth of the fouling layer during membrane-based filtration can be achieved by analyzing a series of real-time OCT scans using image processing techniques based on background subtraction technique [12-15].

Optical coherence tomography (OCT) has been used to characterize membrane fouling in recent studies and has archived recognized results [12,13,16-20]. Specifically, OCT has been successfully used in detecting the fouling layers formed by solid particles (e.g., bentonite and silica particles [12,13,17]) or soft matter (e.g., a biofilm [14,18-23]). However, no study applying OCT to the characterization of the membrane fouling by oil emulsions is available to date. Compared with solid particles, oil droplets are unique in that they can coalesce and are deformable. Therefore, the inherent convolution effect of OCT imaging could prevent the detection of the initial deposition of oil droplets by background subtraction-based image analysis, especially when the oil droplets spread out on the feed-membrane interface (i.e., wetting) [24] or flow into the polymer network (i.e., internal fouling) [3,25]. Moreover, the visualization of a transparent particle depends on the discontinuity of the refractive index at the liquid-liquid interface, which could result in complex artifacts in the OCT images. In Chapter 3 of this thesis, the OCT was firstly applied to monitor and characterize membrane fouling caused by oil emulsions, revealing the capability of OCT to image the transparent liquid particulate foulant (e.g., the oil droplets) as well as the ability to capture the internal fouling of

membrane. These capabilities of the OCT were extended in Chapters 4 and 5. On one hand, Chapter 4 continued working on the ability of OCT to monitor and characterize membrane fouling caused by oil emulsion under the effects of different charges of the stabilizing surfactants. On the other hand, Chapter 5 employed OCT to investigate the internal fouling phenomena of membrane filtration under the effect of surface charge of solid foulants.

Figure 2.1. Schematic showing the working principle of an OCT in membrane filtration

2.2. Membrane Fouling by Oil-in-Water Emulsions under the effects of charges of stabilizing surfactants

The understanding of the fouling phenomenon is necessary to enhance the membrane filtration efficiency for oil-water separation. Despite that many studies have been done on membrane fouling by oil emulsions [3,5,26,27], the effect of the surfactants is not yet fully understood [28]. For produced water, the process chemicals such as corrosion inhibitors, biocides and extraction enhancers that are naturally present can act as surfactants which have great impacts on membrane fouling [28]. Lin and Rutledge [29] found that surfactant type affected membrane fouling in both dead-end and cross-flow systems, although surprisingly in different ways. Matos *et al.* conducted ultrafiltration and concluded that

surfactants with the similar charge type with the membrane increased the flux due to electrostatic repulsion that prevented cake formation, while that of opposite charge type with the membrane diminished the flux [30]. In contrast, Lu *et al.* found that the surfactants with the same charge type as the membrane had lower oil rejection due to the lack of adsorption and hence less pore blockage, while the surfactant with an opposite charge type improved the rejection [25]. Clearly these interesting findings appear tied to surfactant charge, which necessitates further understanding and thereby formed the goal of the current study.

The mechanistic study of membrane filtration requires (i) models to understand the physical underpinning; and also (ii) instruments that allow non-invasive and real-time monitoring of the filtration process, because offline, destructive methods are inadequate in providing information regarding the dynamic absorption and development of fouling layers on the membranes. Regarding instrument, OCT was applied. With respect to models, DLVO and extended-DLVO (i.e., XDLVO) models were employed since they have been validated for wide-ranging foulants [31], and have been shown to provide insights on foulant-foulant and foulant-membrane interactions not possible through experiments. In particular for oil, these two models have been applied to correlate with membrane fouling by oil emulsions stabilized by a single surfactant [32,33].

The DLVO and XDLVO models describe the interaction energies between an oil droplet and the membrane during the deposition. According to the classical DLVO model, the net interaction energy between an oil droplet and the membrane consists of contributions from Lifshitz van der Waals (LW) and electrostatic double layer (EL). The total interaction energy is a function of the separation distance between the oil droplet and membrane (d), expressed as:

$$\Delta G_{DLVO}^{total}(d) = \Delta G^{LW}(d) + \Delta G^{EL}(d) \quad (2.1)$$

Based off the classical DLVO model, van Oss *et al.* [34] proposed an extended DLVO model that has an additional contribution, termed Lewis acid-base (AB), due to the hydrogen bonding in polar solvents such as water:

$$\Delta G_{XDLVO}^{total}(d) = \Delta G^{LW}(d) + \Delta G^{EL}(d) + \Delta G^{AB}(d) \quad (2.2)$$

The net interaction between the oil droplet and membrane is repulsive if ΔG^{total} is positive and attractive if ΔG^{total} is negative.

2.3. Internal Fouling of Membrane Under the Effects of Surface Charges of Solid Foulants

Although membrane fouling has been widely researched, a complete mechanistic understanding of membrane fouling is still far from perfect, mainly due to the complexity of various factors that can affect membrane fouling. Among them, the surface charge of the foulants in the feed is well-acknowledged as important in influencing the extent of fouling and the underlying fouling mechanisms. McDonogh et al. [35,36] reported that the zeta potential of the colloidal foulants affect the specific cake resistance of the cake. Moreover, in our recent studies regarding the impact of foulant charge on membrane fouling by colloidal particles [37,38] and oil emulsions [39], the foulant-foulant and foulant-membrane interactions were found to significantly affect membrane fouling with respect to permeate flux and cake characteristics. Such results have been explained via modeling [37] or DLVO and extended-DLVO theories [38,39]. Delavari et al. [40] demonstrated that the membranes with net zero charge were more prone to fouling than those with strong negative charges, and Fu et al. [41] agreed that the zeta potential of the membrane governed membrane fouling. On the other hand, Liu et al. [42] found that zeta potential is poorly correlated with membrane fouling. Notably, most of the studies on the effect of surface charge have focused on external fouling (i.e., the foulants deposit on the membrane surface), while that on internal fouling (i.e., the foulants deposit within the membrane matrix) remains poorly understood, in part due to the challenges associated with monitoring the latter.

Regarding fouling models, the four key fouling mechanisms that are well-accounted for mathematically are pore constriction, intermediate pore blockage, complete pore blockage and cake filtration [43], whereby the first corresponds to internal fouling whereas the latter three represent external fouling. While earlier studies focused on each fouling mechanism individually [44-46], later studies have employed methods that combined a few fouling mechanisms to more accurately describe membrane fouling. Ho and Zydney [47] were among the first

to combine the cake filtration and pore blockage mechanisms to model external fouling, and subsequently Duclos-Orsello et al. [48] additionally incorporated pore constriction to also account for the concurrently occurring internal fouling. These combined fouling models have been valuable in understanding the membrane fouling mechanisms, though external fouling has always been presumed to be present. For cases wherein internal fouling is dominant, not only would the presence of the external fouling parameters cause over-fitting to the combined model, but the availability of only one internal fouling parameter may not be adequate to represent the internal fouling mechanisms at play. Therefore, a fouling model that focuses on internal fouling and also account for mechanisms other than pore constriction is necessary. To better understand internal membrane fouling, specifically with respect to the effect of foulant charge, a new combined internal fouling model that additionally accounts for internal cake filtration was developed and is reported in Chapter 5 of this thesis.

2.4. Outline

Specifically, this study was designed with three body chapters – Chapters 3, 4 and 5:

- i. Chapter 3: Study membrane external and internal fouling by liquid oil droplets in oil-in-water emulsions.
- ii. Chapter 4: Study membrane external fouling by oil-in-water emulsions under the effects of charges of the stabilizing surfactants.
- iii. Chapter 5: Study membrane internal fouling under the effects of surface charge of solid foulants.

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Chapter 3. MICROFILTRATION OF OIL-IN-WATER EMULSIONS

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Abstract

Membrane-based filtration is an emerging technique for processing oily wastewater. Improving the efficiency of oil-water separation via membranes entails novel techniques for studying the complex interactions between the oil droplets and membrane underlying fouling. This paper presents the first study that applies optical coherence tomography (OCT) to the characterization of membrane fouling by oil emulsions. A series of dead-end filtration experiments was performed to characterize the rejection of oil droplets ($\sim 10\ \mu\text{m}$; hexadecane) by the membrane structure ($0.45\ \mu\text{m}$ PVDF) via three-dimensional (3D) OCT scanning in real time. The experimental results were compared with the control experiments with $\sim 10\ \mu\text{m}$ glass beads to identify the optical artifacts. Both the external and internal fouling by the oil droplets were successfully revealed by analyzing the variation in OCT intensity at various layers that were mathematically defined in terms of the coordinate surfaces parallel to, and above and below, the feed-membrane interface. The evolution of membrane fouling was quantified by evaluating the fraction of fouling voxels as a function of time at varied depths. This study demonstrates that the OCT-based characterization has

the potential to shed light on the complex interactions occurring in oil-water separations via membrane filtration, particularly by providing real-time non-invasive monitoring of internal fouling, the understanding of which is valuable for both fundamental research and practical applications.

Keywords: Internal Membrane Fouling; External Membrane Fouling; Optical Coherence Tomography; Oil Emulsions; Direct Visualization

3.1. Introduction

Oily water, a by-product from many industries such as petroleum refining, food and metal processing [1], can cause severe health and environmental impacts in the absence of adequate treatment. In comparison with conventional treatment methods such as flotation [2,3], coagulation [4] and biotreatment [5], membrane-based separation is an emerging technology in this field due to its ease of operation, no requirement for additional chemicals, high separation efficiency and relatively low cost [6-8]. However, the performance of such membrane-based filtrations is inevitably compromised by fouling – a complex phenomenon whereby deposition of retained compounds such as oil droplets onto the feed-membrane interface occurs, thereby reducing the throughput and selectivity of the separation [9]. Therefore, an in-depth understanding of the fouling mechanisms is crucially important to mitigate the negative effects resulting from the fouling.

The investigation of membrane fouling by oil emulsions necessitates characterization methods which can non-invasively monitor the filtration process in real time. Several techniques have been reported for a range of foulants, such as direct observation through the membrane (DOTM) [10-14], ultrasonic reflectometry [15], and electrical impedance spectroscopy (EIS) [16-20]. However, some limitations are associated with each of these methods. DOTM, which relies on an optical microscope to observe the feed-membrane interface, requires transparent membranes which are not as practical and is limited to two-dimensional (2D) imaging which means the loss of depth information. As for ultrasonic reflectometry and EIS, they detect fouling via acoustic waves and

alternating currents, respectively, where the fouling is inferred from signal changes but direct high-resolution images are not possible.

Optical coherence tomography (OCT) has been used to characterize membrane fouling in recent studies [21-27]. Taking advantage of low coherence interference, OCT is able to obtain depth profiles of a semi-transparent sample by employing near-infrared light (wavelength from ~900 to ~1300 nm). The depth profiles can be synthesized to yield a three-dimensional (3D) image with a depth resolution of ~2 μm . Quantitative analysis of the growth of the fouling layer during membrane-based filtration has been achieved by analyzing a series of real-time OCT scans with image processing techniques based on background subtraction [21,23,28,29]. Despite the success in detecting the fouling layers formed by solid particles (e.g., bentonite and silica particles [21,23,24]) or soft matter (e.g., a biofilm [25-28,30-32]) using OCT, no study applying OCT to the characterization of the membrane fouling by oil emulsions is available to date. Compared with solid particles, oil droplets are unique in that they can coalesce and are deformable. Therefore, the inherent convolution effect of OCT imaging could prevent the detection of the initial deposition of oil droplets by background subtraction-based image analysis, especially when the oil droplets spread out on the feed-membrane interface (i.e., wetting) [33] or flow into the polymer network (i.e., internal fouling) [12,34]. Moreover, the visualization of a transparent particle depends on the discontinuity of the refractive index at the liquid-liquid interface, which could result in complex artifacts in the OCT images.

The current study was aimed at developing novel methods for quantitatively analyzing membrane fouling by oil emulsions via 3D OCT imaging. The proposed method was based on statistical analysis (e.g., averaging, standard deviation, 95% confidence interval) of the OCT data in a series of layers, above and below, parallel to the feed-membrane interface. Fouling experiments with hexadecane-in-water emulsions were compared with the control experiments with glass beads to validate the proposed method and assess the associated optical artifacts. It is shown that the mechanisms accounting for both the external and internal fouling by oil droplets can be revealed by statistically analyzing the variations in the OCT intensity as a function of time and space.

3.2. Experimental Procedures

3.2.1. Membrane Fouling Experiments

In the current study, dead-end filtration was employed to validate the OCT-based characterization of membrane fouling by oil. The filtration setup is schematically shown in Figure 3.1a. The membrane cell consisted of two chambers separated by a flat-sheet hydrophilic PVDF microfiltration membrane (Merck, product No. HVLP04700) with a nominal pore size of 0.45 μm and effective filtration area of 962 mm^2 . The feed entered the upper chamber (35 mm by 35 mm by 15 mm height) of the cell via four inlets located at the four side walls of the chamber and 14.5 mm above the feed-membrane interface. This configuration was to minimize the horizontal flows and the corresponding effects on the dead-end filtration process. The upper wall of the upper chamber had an optical window (35 mm by 35 mm quartz plate) for the OCT light to pass through. In the lower chamber (35 mm diameter by 15 mm height), a porous stainless steel plate (35 mm diameter by 2 mm height) was positioned flush with the membrane to provide mechanical support and stabilize the membrane during the filtration process.

The particulate foulants investigated were oil droplets and glass beads. The oil-in-water emulsion was prepared by blending (Waring, model No. 8010S) hexadecane (Merck, product No. 8.20633.1000) and DI water with a volume ratio of 1 : 2000 for 5 seconds at the speed of 18,000 rpm. The oil emulsion droplet size distribution (Figure 3.6, Appendix) was measured by the focused beam reflectance measurement (FBRM) technique (Lasentec, model No. PI-14/206), with the mean determined to be approximately 10 μm . The emulsions used as the filtration feed were prepared by dilution with DI water to 5 ppm by mass. Freshly prepared oil emulsions which were kept well-stirred throughout the experiment, were used for each experiment, and the distributions before and after each experiment were similar. Silica glass beads (Sigma Aldrich, product No. 440345-500G) with a particle size range of 9 - 13 μm and density of 1.1 g/mL were also used as foulants for comparison with oil droplets. Because the oil droplet size distribution (Figure 3.6, Appendix) indicated that the droplets in approximately the same size range of the glass beads was about 10% by mass of the total oil droplets, the feed concentration of glass beads was set at 0.5 ppm by mass, so

that the number concentrations of each of the two particulate foulants was approximately equal in the same size range. It should be noted that, although the fouling tendency between the two foulants cannot be directly compared in view of the different interfacial interaction energies despite the similar sizes, the key was that the glass beads were not able to cause internal fouling due to the homogenous size and rigidity whereas the oil emulsions could. Therefore, the glass beads served as a good reference to indicate the lack of internal fouling and thereby the incurrence of internal fouling by the oil emulsion.

The filtration experiments were operated under a constant trans-membrane pressure (TMP) of 40 kPa. The rotation speeds of the two gear pumps (Cole Palmer, model No. GJ-N23.PF1S.A) in series were regulated according to the readings of the pressure gauge to achieve constant TMP values. Prior to each experiment, the membrane was conditioned for 30 minutes with a DI water feed under the same TMP. Then, data logging was initiated for approximately 3 minutes with DI water, followed by the addition of the oil emulsion to achieve the desired concentration of 5 ppm. The volume and concentration of the feed during the filtration process was kept constant throughout each experiment. The filtration experiments with glass beads were conducted in a similar way. The flux measurement was recorded every 60 seconds, while the OCT scans were continuously performed at an A-scan rate of 30 kHz. Each fouling experiment was repeated at least three times to ensure the reliability of the analysis; it should be noted that the repeats were carried out to ensure the qualitative consistency of the trends, but quantitative consistency of the average intensities cannot be expected, since the optical field changed due to changes in the membrane and positioning of the filtration cell between repeats.

Figure 3.1. (a) Schematic showing the principle of a Fourier-domain OCT for characterizing dead-end filtration. (b) A 3D tomographic image with the coordinate system defined based on the scanned region. (c) The feed-membrane interface determined by analyzing the intensity gradient on the 3D tomographic image. (d) A layer constructed parallel to the determined feed-membrane interface.

3.2.2. Analysis of 3D OCT Images

OCT is an imaging technology based on low coherence interference. The basic principle of OCT is illustrated in Figure 3.1a. Low coherence light beam is emitted from a broadband light source and split into the sample and reference arms. In the sample arm, the light is backscattered by the scanned sample and recombined with the light from the reference arm, which is reflected by a mirror. The combined light is collected and measured by a spectrometer, generating the intensity versus depth profiles which are transformed into three-dimensional (3D)

images of the sample. More details of the basic principle of OCT can be found in prior studies [21,23].

A Fourier-domain OCT system (GANYMEDE-SP5, Thorlabs, USA) was used in the current study. The depth resolution of the system was 2 μm in water, determined by a light source with central wavelength of 905 nm and bandwidth of approximately 200 nm. The lateral resolution, on the other hand, was approximately 4 μm and determined by the scan lens (LSM03-BB). The filtration cell was slightly inclined at 5° to avoid strong reflection at the optical window.

The first step of the analysis was to determine the coordinates of the clean feed-membrane interface (i.e., at $t = 0$) from the 3D tomographic image obtained with OCT (Figure 3.1b). The same technique as our previous study [23] based on the variation in the intensity gradient was employed to estimate the coordinates of the feed-membrane interface. Specifically, a threshold gradient value was pre-determined, and the locations at which the OCT intensity gradients were greater than this threshold constituted the coordinate surface of the feed-membrane interface (Figure 3.1c). A new coordinate system (namely, x_m - y_m - z_m) was established based on the determined feed-membrane interface and a series of coordinate surfaces parallel to the feed-membrane interface was defined. For each coordinate surface, a corresponding layer was established such that it was constituted by all the voxels that intersected the coordinate surface. Each layer, which was parallel to the feed-membrane interface, had a thickness of approximately equal to the height of the voxels (Figure 3.1d).

In the current study, the series of coordinate surfaces parallel to the feed-membrane interface were uniformly spaced by a distance of 2 μm , which was approximately the depth resolution of the OCT system in water. It should be noted that the distances in the OCT images are the optical path lengths measured using the refractive index of vacuum, from which the real physical distance can be estimated only if the distribution of the refractive indices due to the different media (i.e., PVDF, oil or glass) is known. However, in view of water being the major medium, specifically because the PVDF membrane was 70% porous and the foulant concentrations were low (5 ppm oil or 0.5 ppm glass beads), the layers parallel to the feed-membrane interface were approximated to be 2 μm apart. A series of characteristic layers was established corresponding to the defined

coordinate surfaces. The layer corresponding to the feed-membrane interface was indexed as layer 0, from which the layers above the membrane-feed interface were indexed to be positive layers and those below the feed-membrane interface were indexed to be negative layers. The mean and standard deviation, along with the 95% confidence interval, of the OCT intensities were calculated for each layer evaluated. MATLAB was employed for the processing and analysis of the OCT datasets.

3.3. Results and Discussion

3.3.1. Visualizing Membrane Fouling by Oil Droplets

The OCT datasets were firstly used to generate two-dimensional (2D) images showing the feed-membrane interface to observe the progressive fouling by the oil droplets (Figure 3.2a) and glass beads (Figure 3.2b). Specifically, the sequential images shown in Figure 3.2 are about 3 - 5 minutes apart and up to a total of 28 minutes. Each image corresponds to an area of 300 μm by 300 μm .

In Figures 3.2a and b, the upper dark regions correspond to the feed liquid phase, whereas the bright regions mainly resulted from the changes in the refractive index because of the discontinuity of the media when the incident light penetrated the liquid-polymer boundaries. Beneath the feed-membrane interface, another horizontal bright region is apparent, which corresponds to the porous stainless-steel plate below the membrane that provides mechanical support. At $t = 0$ min, foulants were absent. The fouling process was initiated at $t = 3$ min by the addition of the oil emulsion or the glass beads to the feed, which led to the onset of flux decline at about $t = 5$ min (Figure 3.7, Appendix) and the appearance of bright spots corresponding to the deposition of the foulants on the feed-membrane interface from approximately $t = 10$ min (Figure 3.2). At TMP = 40 kPa, the fluxes (~ 8000 L/(m²h)) in both fouling cases should be able to override any buoyancy and settling effects [35]. As the filtration continued, the flux continued to decline (Figure 3.7, Appendix) and more bright spots are observed on the feed-membrane interface in the images (Figure 3.2). Note that the filtration with oil droplets had a more severe flux decline (Figure 3.7a, Appendix), indicating more extensive fouling that may involve wetting or adsorption of the oil droplets [12] and the entry of the oil droplets into the polymer network. The

sizes of these bright spots (i.e., deposited foulants) were around 10 μm (Figure 3.8, Appendix), which agree with the mean size of both the oil droplets and glass beads, and thereby affirm the capability of OCT to visualize such more transparent particulate foulants. Also, the similarity in the OCT patterns between Figures 3.2a and b provides evidence that the individual oil droplets of approximately 10 μm remained without coalescence or much deformation when being rejected by the membrane. In other words, in the time frame investigated, the fouling cake layer was formed non-homogenously by individual oil droplets rather than by the growth of a homogenous oil film. It should be noted that, as the refractive index of hexadecane ($n \approx 1.43$ [36]) and glass ($n \approx 1.46$ [37]) are closer to that of PVDF ($n \approx 1.4 - 1.45$ [38]), the OCT intensity reflected at the boundaries between the membrane surface and the oil droplets or the glass beads was relatively weak compared to the significant background intensity of the PVDF network at this region. As the result of the similar refractive indices, the boundaries between the membrane surface and the oil droplets or the glass beads in the OCT images were not distinct; however, this did not hamper the investigation of external and internal fouling, which was based on the increase in intensity at each layer due to the deposition of the foulants.

Interestingly, the bright spots in the images in Figure 3.2 are somewhat elongated in the direction of light propagation for both the deposited oil droplets and glass beads (scaled up in Figure 3.8, Appendix). The elongation in the spot pattern could be an OCT artifact arising from the variation in the light velocity when traveling through different media [39], since the construction of an OCT image is based on the assumption that the incident light travels at a constant velocity. Specifically, because the OCT measures the optical path length using the light velocity in vacuum, where the refractive index (n) is one, the distance between two interfaces could be significantly increased in the OCT image if the incident light travels through a medium sandwiched by the interfaces with a refractive index (n) greater than the surrounding media. Such is the case for both an oil droplet ($n \approx 1.43$ [36]) and a glass bead ($n \approx 1.46$ [37]) in water ($n \approx 1.33$ [40]).

(a)

100 μ m

(b)

Figure 3.2. Temporal sequences of the 2D cross-sectional images obtained using the OCT during the dead-end filtration (0.45 μm PVDF membrane, TMP = 40 kPa) of the feeds containing (a) 5 ppm oil droplets and (b) 0.5 ppm glass beads. The higher-intensity (i.e., brighter) bottom of each image represents the membrane while the lower-intensity (i.e., darker) top the feed, hence the interface between the lower-intensity and higher-intensity regions represents the feed-membrane interface. The progressive external fouling with time is shown as the appearance of higher-intensity spots above the membrane at the feed-

membrane interface, whereas internal fouling is not visually obvious due to the higher intensity associated with the membrane.

3.3.2. Analyzing the Fouling Phenomenon using Layer-Averaged OCT Intensity Profiles

Figure 3.2 shows that the OCT images provide direct observations of the external fouling process; however, further analysis of the growth of the cake layer as well as monitoring of internal fouling warrant study. The analysis is severely complicated by the deposition of the foulants near the membrane surface (in the case of external fouling) and inside the membrane's polymer network (in the case of internal fouling), because the OCT intensity of the PVDF membrane is so significant that the weak changes resulting from the deposition could be indistinguishable. A viable way to resolve this issue is to track the temporal variation in the intensity profile as a mathematical vector whose components correspond to the OCT intensities at various depths. However, the intensity profile at a specific location is susceptible to the random fluctuations arising from the background noise, while the deposition is also a random process which results in local inhomogeneity. Therefore, statistical analysis (e.g., averaging, standard deviation, 95% confidence interval) is needed in order to decipher the variation in the OCT data.

The OCT intensity was spatially averaged for each layer at each of the time steps depicted in Figure 3.2. Note that each layer is parallel to the feed-membrane interface and 2 μm apart, and layer 0 corresponds to the feed-membrane interface (Figure 3.1d). Figure 3.3 shows the layer-averaged intensity versus layer index at various time steps for the feeds containing oil droplets (Figure 3.3a) and glass beads (Figure 3.3b). The average intensity is expectedly larger below the feed-membrane interface (i.e., negative layers) than above (i.e., positive layers), but the change in intensity at the feed-membrane interface is smooth rather than abrupt. The gradual transition is due to the sponge-like porous structure of the PVDF membrane which averted a strong reflection at the feed-membrane interface, and the convolution of the original profile at the interface with the point spread function which is the inverse Fourier transform of the power spectrum of the OCT light source [41]. For layers below the feed-membrane interface, the

average intensity increased then decreased at around layer -10 due to the loss in the intensity of the incident light as it penetrated the polymer network.

The layer-averaged intensity profile at $t = 0$ min, which characterizes the clean membrane, is superimposed onto every sub-figure in Figure 3.3 to serve as a benchmark in order to monitor the progressive fouling. The intensity profile for the clean membrane at $t = 0$ min is shown in black, while that at subsequent time steps in red. Differences between the two profiles become clear at $t \geq 8$ min in Figure 3.3, which agrees with the observation of the onset of deposition on the feed-membrane interface in Figure 3.2. Notably, Figure 3.3a indicates that the average intensity significantly increased below the feed-membrane interface, specifically between layers -15 and -5, which is not observable in Figure 3.2a due to the higher intensity of the polymer network. Such an increase could either be due to internal fouling (i.e., the entry of the oil droplets into the porous membrane structure) or the convolution effect whose influenced region widens when the background intensity is relatively high [41].

A way of ruling out the convolution effect is to examine the fouling by glass beads, whereby only external fouling was expected since the glass beads were much larger than the nominal pore size of the PVDF membrane ($0.45 \mu\text{m}$). Figure 3.3b shows that, although the average intensity increased with time in the positive layers (i.e., above the feed-membrane interface), it remained unchanged in the negative layers (i.e., below the feed-membrane interface), except for a slight decrease at $t = 28$ min which is attributable to the loss in intensity of the incident light after penetrating the external fouling layer. Therefore, it is affirmed that the intensity increased in the negative layers for the feed with oil droplets (Figure 3.3a) indicates internal fouling by the oil droplets during the filtration. This was due to the ability of the oil droplets to deform and wet the membrane, and thereby enter the porous polymeric structure and foul the membrane internally, which was not possible by the rigid glass beads.

Moreover, the increase rather than decrease of the average intensity in the negative layers (Figure 3.3a) provides insights into the internal fouling phenomenon. Note that the refractive index of oil ($n \approx 1.43$ [36]) is closer to that of PVDF ($n \approx 1.4 - 1.45$ [38]) than water ($n \approx 1.33$ [40]); if the water in the polymer voids had been completely replaced by a uniform oil phase, the OCT

intensity would have been reduced owing to the decrease in the reflectance at the liquid-polymer boundaries. This is termed the index-matching technique [42] and has been exploited to enhance the quality of OCT imaging. Hence, the increase in the average intensity in the negative layers in Figure 3.3(a) further indicates that the oil droplets remained dispersed rather than coalesced within the porous structure of the hydrophilic membrane.

(a)

(b)

Figure 3.3. Temporal sequences of the layer-averaged intensity profiles during the dead-end filtration (0.45 μm PVDF membrane, TMP = 40 kPa) of the feeds containing (a) 5 ppm oil droplets and (b) 0.5 ppm glass beads. The intensity profile for the clean membrane at $t = 0$ min is shown in black, while those at subsequent time steps in red.

3.3.3. Quantifying the Evolution of Fouling via Layer-Oriented Segmentation

As revealed by an earlier study on characterizing heterogeneous tissue via OCT [43], there could be a highly non-linear response of OCT to the variation in the composition of the sample, which indicates that the quantification of the fouling process using the layer-averaged intensity profiles is inappropriate. In contrast to fouling by rigid solid particles, the deposition or adsorption of oil droplets onto the membrane involves more complex phenomena, such as wetting and coalescence of the oil droplets [12]. Therefore, applying the intensity-based segmentation developed in our prior studies for bentonite and silica particles [23]

to investigate the fouling by oil droplets is challenging. To circumvent this in the current study, the intensity-based segmentation algorithm was implemented layer-wise (i.e., for each layer at and away from the feed-membrane interface) to understand these complex fouling phenomena by oil droplets. In addition, a more rigorous criterion was established to identify the fouling voxels corresponding to the deposits as defined in a prior study [23]; although more sophisticated mathematical tools are available for de-noising signals, as have been achieved via for example wavelet decomposition [44,45], a single-value threshold has been shown to be adequate for detecting fouling. The mean and standard deviation of the OCT intensities were firstly calculated for each layer at $t = 0$, then a voxel in that layer was determined as a fouling voxel if its intensity was greater than the mean plus twice the standard deviation (i.e., 95% confidence interval) [46,47]. The fouling voxels at the 95% confidence level were determined for each layer and marked in red in the projected area of 1.3 mm by 0.6 mm (Figure 3.9, Appendix). The fraction of the fouling voxels for a specific layer (i.e., the ratio of the number of fouling voxels to the total number of the voxels in the same layer) then can be used to quantify the degree of fouling at various distances at and away from the feed-membrane interface.

The variation in the fraction of the fouling voxels evaluated over 30 minutes for four layers at and above the feed-membrane interface are displayed in Figures 3.4a and b for the feeds containing oil droplets and glass beads, respectively. In both cases, the steepest increase in the fraction with time is for the layer 4 (i.e., $\sim 8 \mu\text{m}$ above the feed-membrane interface), which agrees with Figure 3.2 in that the particulate foulant sized at approximately $10 \mu\text{m}$ deposited at the feed-membrane interface. It is interesting to note that at this layer, during the early stage of the fouling (approximately from $t = 5$ to 15 min), the fraction of fouling voxels curve was concave upwards (i.e., increasing rate) for the oil droplets while concave downwards (i.e., decreasing rate) for the glass beads. This difference suggests that some of the oil droplets may have penetrated into the polymer network (i.e., internal fouling) or spread out on the membrane (i.e., wetting) and thereby increased the rejection of the oil droplets although the permeate flux did not yet substantially decrease (Figure 3.7a, Appendix). Similar trends were also observed for the curves of layers 8 and 12 (i.e., ~ 16 and $24 \mu\text{m}$

above the membrane). This indicates that the oil droplets continued to deposit on other oil droplets, while glass beads were less inclined to deposit on other glass beads due to the repulsive Gibbs free energy of interaction between the glass beads [48].

For layer 0 (i.e., at the feed-membrane interface), the fraction of fouling voxels was relatively constant for the oil droplets but increased for the glass beads. It should be noted that the change in the intensity is not straightforward when a transparent particulate foulant deposits atop the feed-membrane interface, since it involves the introduction of a new liquid-foulant boundary and also the replacement of the liquid-polymer boundary by the foulant-polymer boundary when the foulant contacts with the membrane. On one hand, the new liquid-foulant boundary would increase the reflectance in this interfacial region and thereby give rise to higher OCT intensities. On the other hand, the substitution of the liquid-polymer boundary by the foulant-polymer boundary could have a relatively low reflectance if the refractive index of the particulate foulant is closer to that of the polymer than the liquid, which thereby may significantly lower the OCT intensity. In the case of fouling by glass beads, the increase in the fraction of fouling voxels for the layer 0 (i.e., feed-membrane interface) indicates that the substitution of part of the liquid-glass boundaries by glass-polymer boundaries due to external fouling increased the intensity and thereby the fraction of fouling voxels (Figure 3.4b). As for the case of fouling by oil droplets, the relatively constant fraction of fouling voxels with time (Figure 3.4a) appears to indicate that the degree of the boundary substitution could be much higher for oil droplets and thereby weakened the reflection from the liquid-polymer boundaries.

Figure 3.5 further presents the evolution of the fraction of fouling voxels for the layers below the feed-membrane interface for both the feeds containing oil droplets (Figure 3.5a) and glass beads (Figure 3.5b). A clear increase in the fraction of fouling voxels is observed for the layers -6, -8 and -12 (i.e., between ~12 to 24 μm below the feed-membrane interface) for the oil droplets (Figure 3.5a) but not the glass beads (Figure 3.5b). This is consistent with Figure 3.3, in which the layer-averaged intensity increased approximately between layers -5 and -15 (i.e., between ~10 to 30 μm below the feed-membrane interface) for oil droplets (Figure 3.3a), but was relatively unchanged for glass beads (Figure 3.3b).

Collectively, Figures 3.5a and 3.3a affirms not only internal fouling by the oil droplets but also the capability of OCT to monitor internal fouling. Notably, the decline in the intensity towards the end of the filtration could be caused by the attenuation of the incident light. Moreover, interestingly, Figure 3.5a indicates that the fraction of fouling voxels increased as the depth below the feed-membrane interface increased. This is presumably due to the wetting or adsorption of oil droplets at regions just below the feed-membrane interface ($< 10\ \mu\text{m}$ below the feed-membrane interface) which thereby reduced the reflectance in this region. As a result, the internal fouling had little impact on the OCT signals scattered from these regions, while the accumulation of the dispersed individual oil droplets in the regions further below the feed-membrane interface increased the OCT signal intensity due to the increase of the liquid-foulant (i.e., water-oil) boundaries.

Figure 3.4. Evolution of fouling in terms of the fractions of the fouling voxels in the various layers at and above the feed-membrane interface during the dead-end filtration ($0.45\ \mu\text{m}$ PVDF membrane, $\text{TMP} = 40\ \text{kPa}$) of the feeds containing (a) 5 ppm oil droplets and (b) 0.5 ppm glass beads. Note that 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 3.5. Evolution of fouling in terms of the fractions of the fouling voxels in the various layers below the feed-membrane interface during the dead-end filtration (0.45 μm PVDF membrane, TMP = 40 kPa) of the feeds containing (a) 5 ppm oil droplets and (b) 0.5 ppm glass beads. Note that 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.

3.4. Conclusions

The current study successfully applied 3D imaging to the investigation of membrane fouling by oil emulsions. The OCT could be used not only to generate images that allowed for the direct visualization of foulant deposition at the feed-membrane interface (i.e., external fouling), but also to provide a means for monitoring the entry of the foulant into the porous membrane structure (i.e., internal fouling). The ability to characterize both the external and internal fouling in real time is of critical importance to study more complex phenomena involved in the membrane fouling process by oil emulsions, such as the effects of various surfactants or salts on the interaction between the oil droplets and the membrane [34,49]. Although the OCT is not readily amenable for use on the large-scale practical applications, the insights obtained here are useful for ascertaining the fouling tendencies of oil emulsions and thereby formulating mitigation means accordingly. The analysis in this study also indicates that various optical artifacts could be involved in the OCT results, which reduced the spatial resolution of OCT and increased the difficulty in interpreting the fouling process. Also, the OCT analysis carried out here is limited to low concentrations of foulants (since the refractive index was assumed to be that of water) and cases whereby the oil coalescence is not too severe (since the intensity at the lower layers may decrease too significantly). Nevertheless, the current study confirms that comparing the OCT results from the fouling by oil droplets with those by glass beads is an effective way to identify the optical artifacts and retrieving useful information from the OCT datasets. This ability to monitor internal fouling in real time and non-invasively paves the way for more in-depth understanding of membrane filtration. Further studies shall be carried out to develop more effective algorithms to improve the accuracy of the quantitative analysis.

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Appendix

Figure 3.6. Number-based droplet size distribution of the oil emulsion, with a mean of approximately 10 μm and standard deviation of approximately 7 μm ; freshly prepared oil emulsions, which were kept well-stirred throughout the experiment, were used for each experiment, and the distributions before and after each experiment were similar. Droplets whose sizes are similar to that of the glass beads (in the range of 8 - 13.5 μm) accounted for approximately 10% by mass of the droplets in the emulsion.

Figure 3.7. Evolution of the permeate flux of the dead-end filtration processes (0.45 μm PVDF membrane, TMP = 40 kPa) with feeds containing (a) 5 ppm oil droplets and (b) 0.5 ppm glass beads.

25 μm

Figure 3.8. Magnified 2D cross-sectional images of deposited foulants during the dead-end filtration ($0.45\ \mu\text{m}$ PVDF membrane, $\text{TMP} = 40\ \text{kPa}$) with feeds containing (a) 5 ppm oil droplets and (b) 0.5 ppm glass beads. The red circles highlight the deposited foulants.

Figure 3.9. Evolution of the distribution of the fouling voxels (marked as red dots) in various layers during the dead-end filtration (0.45 μm PVDF membrane, TMP = 40 kPa) with feeds containing (a) 5 ppm oil droplets and (b) 0.5 ppm glass beads.

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Chapter 4. MICROFILTRATION OF OIL-IN-WATER EMULSIONS STABILIZED BY DIFFERENT SURFACTANTS

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Abstract

Membrane-based filtration is a promising technique to treat the enormous amounts of oily wastewater, specifically those with micron-sized oil droplets. However, the understanding on the effect of the surfactants, that are inevitably present to stabilize the oil emulsion, on the filtration performance remains poor. This study aimed to investigate the effect of surfactant type (namely, non-ionic Tween 20, positively charged CTAB, and negatively charged SDS) on filtration flux and membrane fouling during the microfiltration of the surfactant-stabilized oil emulsion with mean droplet sizes of approximately 20 μm . The Optical Coherence Tomography (OCT) was employed to quantify the evolution of fouling, and both the DLVO and XDLVO models were used to quantify the oil droplet-membrane and oil droplet-deposited layer interaction energies. Two key understanding on the correlation between the DLVO and XDLVO predictions with flux and fouling were obtained. Firstly, the steep flux enhancement vis-à-vis a DI water feed by the feed containing CTAB-stabilized oil emulsion was tied to the attractive interaction of the surfactant with the membrane, as evident from the DLVO model. This attraction was not related to the extent of membrane fouling, which was relatively lesser for the CTAB-stabilized oil emulsion.

Secondly, the extent of membrane fouling was tied to the repulsive energy magnitudes rather than attractive ones, specifically in that the least repulsive energy values of the Tween 20-stabilized oil emulsion was linked to the most extensive fouling.

Keywords: Membrane Fouling; interfacial energy; Oil Emulsion; Surfactant; Oil-water Separation

4.1. Introduction

Adequate, efficient treatment of oily wastewater before discharge into the environment is of critical importance, especially in view of the vast volumes from the oil and gas industry [1-4], which has been estimated at more than 88 billion barrels worldwide annually [5]. Several treatment methods have been studied and applied, such as coagulation [6], flotation [7,8], biotreatment [9] and membrane filtration [1,10-12]. Among these, membrane filtration is a promising method with significant advantages including relatively lower cost, ease of scalability and no need for additional chemicals [11,13-16]; hence, it has become increasingly popular for applications in various industries such as food, metal processing and petroleum refining [17,18]. Unfortunately, membrane-based oil-water separation is inevitably compromised by membrane fouling, i.e., the deposition of components in the feed onto the membrane that causes a reduction in the filtration throughput [11,19]. Correspondingly, the understanding of the fouling phenomenon is necessary to enhance the membrane filtration efficiency for oil-water separation.

Much has been reported on membrane fouling by oil emulsions [20-23], but the effect of the surfactants that are naturally present to stabilize the oil droplets is not fully understood [24]. In particular for produced water, the process chemicals typically present such as corrosion inhibitors, biocides and extraction enhancers can act as surfactants, which not only determines emulsion stability but also influences membrane fouling [24]. Matos *et al.* conducted ultrafiltration using ceramic membranes and concluded that surfactants with the same charge type as the membrane increased the flux due to electrostatic repulsion that prevented cake formation, while that of opposite charge type with the membrane

diminished the flux [25]. On rejection, Lu *et al.* found during the ultrafiltration of oil emulsions using ceramic membranes that the surfactants with the same charge type as the membrane had lower oil rejection due to the lack of adsorption and hence less pore blockage, while the surfactant with an opposite charge type improved oil rejection [26]. Lin and Rutledge [27] found that surfactant type affected membrane fouling in both dead-end and cross-flow systems, although surprisingly in different ways. Clearly these interesting findings appear tied to surfactant charge, which necessitates further understanding and thereby formed the goal of the current study.

The mechanistic study of membrane filtration requires (i) models to understand the physical underpinning; and also (ii) instruments that allow non-invasive and real-time monitoring of the filtration process, since offline, destructive methods are inadequate in providing information regarding the dynamic absorption and development of fouling layers on the membranes. With respect to models, DLVO and XDLVO models have been validated for wide-ranging foulants [28], and have been shown to provide insights on foulant-foulant and foulant-membrane interactions not possible through experiments. In particular for oil, these two models have been applied to correlate with membrane fouling by oil emulsions stabilized by a single surfactant [29,30]. Regarding instruments, popular examples of such techniques include the Direct Observation Through the Membrane (DOTM) [20,21,31-33], Ultrasonic Reflectometry [34], Electrical Impedance Spectroscopy (EIS) [35-38], and Optical Coherence Tomography (OCT) [39-43]. Each of these methods, however, possess certain disadvantages. DOTM requires transparent membranes and is limited to two-dimensional (2D) observation, which means only the information at a planar layer can be obtained and thereby that depth information is not clear. Ultrasonic reflectometry and EIS, which employ respectively acoustic waves and electrical signals to monitor membrane fouling, do not provide direct visual observations. OCT is advantageous as a non-invasive, real-time technique that can provide three-dimensional (3D) observation. Employing low coherence interference, OCT uses near-infrared light (wavelength ~ 900 to ~ 1300 nm) to obtain the depth profile of the scanned sample, hence generating 3D images. The images can then be processed using background subtraction technique [39,43-45] to analyze the

growth of the fouling layers. Recently, OCT has been successfully applied in membrane filtration with foulants like bentonite [39,40], glass [43], latex [41], biofilm [46-49], oil emulsion [50] and mixture of foulants [51,52]. OCT was further employed here to understand the effect of surfactant type on membrane fouling by oil.

The current study aimed to further contribute towards the understanding on the effect of surfactant type on membrane fouling in the microfiltration of surfactant-stabilized oil emulsions. Three surfactants of different charges, namely, non-ionic, positively charged and negatively charged, were investigated. 3D OCT imaging technique was used to evaluate the evolution of the fouling layer. Furthermore, DLVO and XDLVO models, which have only been applied for oil emulsions stabilized by a single surfactant [29,30], were used to provide insights on the underlying thermodynamics of interactions governing membrane fouling by oil emulsions stabilized by different surfactants.

4.2. Materials and Method

4.2.1. Membrane Fouling Experiments

4.2.1.1. Experimental Setup

Dead-end filtration was implemented in this study to focus on the interfacial interactions in the absence of shear effects, since the interfacial interactions have been shown to be diminished as hydrodynamics effects increase [53]. The schematic of the experimental setup is shown in Figure 4.1. The membrane cell had feed and permeate chambers partitioned by a flat-sheet hydrophilic PVDF membrane (Merck; product No. GVWP04700; nominal pore size of 0.22 μm). The effective filtration area was 9.62 cm^2 (circular; 35 mm diameter). The upper feed chamber (35 mm by 35 mm by 15 mm height) had four feed inlets located at the mid-points of the four side walls and 0.5 mm below the upper wall of the chamber. The feed inlets were so designed to minimize unilateral flows across the chamber during the filtration. An optical window (quartz, 35 mm by 35 mm) at the upper wall of the feed chamber allowed the light source from the optical coherence tomography (OCT) to enter. In the permeate chamber (35 mm diameter by 15 mm height), the membrane was

mechanically supported by a porous plate (stainless-steel; 35 mm diameter by 2 mm height) positioned flush below.

Figure 4.1. Overview of the principle of a Fourier-domain OCT scanning dead-end filtration.

The filtration experiments were operated at a constant trans-membrane pressure (TMP) of 0.2 bar. The TMP was monitored by a pressure gauge (BD Sensors, Baroli 02) and kept constant by regulating the rotation speed of two gear pumps (Cole Palmer, GJ-N23.PF1S.A) in series. Before each experiment, the membrane was conditioned for 30 minutes with DI water at 0.2 bar. The permeate flux was measured using a digital balance (Mettler Toledo, ME4002E) and recorded every 60 seconds. The OCT scans were performed continuously at an A-scan rate of 30 kHz.

4.2.1.2. Materials

Three surfactants with different charges were employed, namely, non-ionic Tween 20 (Sigma-Aldrich, P1379-1L), positively charged cetyltrimethylammonium bromide (CTAB; Sigma-Aldrich, 52365-50G) and negatively charged sodium dodecyl sulfate (SDS; Sigma-Aldrich, 75746-250G). The similarity among these surfactants is that the carbon chains in the hydrophobic tails are all linear.

The same oil and surfactant concentrations were used in each case to provide a common basis for comparison, as with a previous study [27], since the concentrations of both oil [20] and surfactant [23] have been reported to affect membrane fouling. Each surfactant solution was prepared by dissolving the specific surfactant in DI water at a mass ratio of 1:5,000. The concentrated stock of oil-in-water emulsion, which was prepared to improve consistency of the sizes of the oil droplets among repeated experiments, was made by blending (Waring, model No. 8010S) hexadecane (Merck; product number 8.20633.1000) and the surfactant solution at a volume ratio of 1:2,000. The droplet size distributions of the oil emulsions were measured by the focused beam reflectance measurement (FBRM) (Lasentec, model PI-14/206). The means of the distributions of the oil emulsions stabilized by all three surfactants were similarly in the range of ~ 19 - $22\ \mu\text{m}$ (Figure 4.10, Table 4.5, Appendix), which were two orders-of-magnitude larger than the nominal pore diameter of the membrane. The feed used was composed of 50 ppm of oil and 50 ppm of the targeted surfactant, which was prepared by diluting the high-concentration stock solution, DI water and surfactant solution at a volume ratio of 1:7.5:1.5.

The zeta potentials of the three feeds were measured to be -25.97, 61.87 and -38.53 mV respectively for the Tween 20-stabilized, CTAB-stabilized and SDS-stabilized oil emulsions (Malvern, Zen3600, Zetasizer Nano) (Table 4.1), and -12.55, 18.92 and -19.97 mV respectively for the membranes submerged in 50 ppm of Tween 20, CTAB and SDS (Anton Paar, SurPass 3) (Table 4.2).

Table 4.1. Zeta potential values of oil emulsions stabilized by Tween 20, CTAB and SDS (50 ppm oil, 50 ppm surfactant).

	Mean (mV)	Standard Deviation (mV)
Tween 20-stabilized oil emulsion	-25.97	0.62
CTAB-stabilized oil emulsion	61.87	7.49
SDS-stabilized oil emulsion	-38.53	3.00

Table 4.2. Zeta potential values of the membrane submerged in 50 ppm Tween 20, CTAB and SDS solutions, and the corresponding pH values.

	Zeta Potential (mV)		pH	
	Mean	Standard Deviation	Mean	Standard Deviation
Membrane in Tween 20 solution	-12.55	1.75	5.14	0.04
Membrane in CTAB solution	18.92	1.33	5.76	0.12
Membrane in SDS solution	-19.97	1.31	5.50	0.07

4.2.2. DLVO and XDLVO Models

According to the classical DLVO model, the net interaction energy between an oil droplet and the membrane consists of contributions from Lifshitz van der Waals (LW) and electrostatic double layer (EL). The total interaction energy is a function of the separation distance between the oil droplet and membrane (d), expressed as:

$$\Delta G_{DLVO}^{total}(d) = \Delta G^{LW}(d) + \Delta G^{EL}(d) \quad (4.1)$$

Based off the classical DLVO model, van Oss *et al.* [54] proposed an extended DLVO model that has an additional contribution, termed Lewis acid-base (AB), due to the hydrogen bonding in polar solvents such as water:

$$\Delta G_{XDLVO}^{total}(d) = \Delta G^{LW}(d) + \Delta G^{EL}(d) + \Delta G^{AB}(d) \quad (4.2)$$

The net interaction between the oil droplet and membrane is repulsive if ΔG^{total} is positive and attractive if ΔG^{total} is negative.

According to van Oss *et al.* [55], the total surface tension of a substance (γ) is the sum of the dispersive (γ^{LW} ; i.e., non-polar) and polar (γ^{AB}) surface tensions of the substance:

$$\gamma = \gamma^{LW} + \gamma^{AB} \quad (4.3)$$

where γ_{AB} is composed of an electron acceptor (γ^+) and an electron donor (γ^-) component:

$$\gamma^{AB} = 2\sqrt{\gamma^+\gamma^-} \quad (4.4)$$

In addition, in the extended Young's equation (Equation 4.5), the total surface tension of a liquid (γ) and the contact angle (θ) between the liquid (l) and a solid (s) surface in air are related to the surface tension components of each substance such that:

$$\gamma(1 + \cos \theta) = 2 \left(\sqrt{\gamma_l^{LW} \gamma_s^{LW}} + \sqrt{\gamma_l^+ \gamma_s^-} + \sqrt{\gamma_l^- \gamma_s^+} \right) \quad (4.5)$$

In Equation 4.5, the three unknown surface tension components of the solid surface ($\gamma_s^{LW}, \gamma_s^+, \gamma_s^-$) could be calculated by measuring the contact angles of the solid surface with three probe liquids with known surface tension (γ) and surface tension components ($\gamma_l^{LW}, \gamma_l^+, \gamma_l^-$). When two planar surfaces approach each other, the contact happens at the minimum equilibrium cut-off distance $d_0 = 0.158$ nm [56]. Assuming the membrane (m) and an oil droplet (o) to be two infinite planes approaching each other in a surfactant solution (l), the adhesion energy components ($\Delta G_{mlo}^{LW}, \Delta G_{mlo}^{EL}, \Delta G_{mlo}^{AB}$) can be calculated as:

$$\Delta G_{mlo}^{LW}(d_0) = -2 \left(\sqrt{\gamma_m^{LW}} - \sqrt{\gamma_l^{LW}} \right) \left(\sqrt{\gamma_o^{LW}} - \sqrt{\gamma_l^{LW}} \right) \quad (4.6)$$

$$\Delta G_{mlo}^{EL}(d_0) = \frac{\varepsilon_0 \varepsilon_r \kappa}{2} (\xi_m^2 + \xi_o^2) \left[1 - \coth(\kappa d_0) + \frac{2\xi_o \xi_m}{(\xi_o^2 + \xi_m^2)} \operatorname{csch}(\kappa d_0) \right] \quad (4.7)$$

$$\Delta G_{mlo}^{AB}(d_0) = 2 \left[\sqrt{\gamma_l^+} (\sqrt{\gamma_o^-} + \sqrt{\gamma_m^-} - \sqrt{\gamma_l^-}) + \sqrt{\gamma_l^-} (\sqrt{\gamma_o^+} + \sqrt{\gamma_m^+} - \sqrt{\gamma_l^+}) - \sqrt{\gamma_o^- \gamma_m^+} \right] \quad (4.8)$$

where ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of water, ξ is the zeta potential, κ is the reciprocal Debye length calculated by Equation 4.9:

$$\kappa = \sqrt{\frac{e^2 \sum n_i z_i^2}{\varepsilon_0 \varepsilon_r kT}} \quad (4.9)$$

where

e is the electron charge, n_i is the number concentration, z_i is the valence of ion i , k is the Boltzmann's constant, T is the temperature [28,54,57,58]. Equations 4.6, 4.7, 4.8, however, are only applicable to planar surfaces. For a spherical oil droplet approaching a planar membrane surface, the Derjaguin approximation

can be applied to calculate the adhesion energy components at separation distance d :

$$\Delta G_{mlo}^{LW}(d) = 2\pi\Delta G^{LW}(d_0) \frac{d_0^2 a}{d} \quad (4.10)$$

$$\Delta G_{mlo}^{EL}(d) = \pi\epsilon_0\epsilon_r a \left[2\xi_o\xi_m \ln\left(\frac{1+e^{-\kappa d}}{1-e^{-\kappa d}}\right) + (\xi_m^2 + \xi_o^2) \ln(1 - e^{-2\kappa d}) \right] \quad (4.11)$$

$$\Delta G_{mlo}^{AB}(d) = 2\pi a \lambda \Delta G^{AB}(d_0) \exp\left(\frac{d_0 - d}{\lambda}\right) \quad (4.12)$$

where a is the radius of the oil droplet and $\lambda = 0.6 \text{ nm}$ is the characteristic decay length of the AB interaction [28,59].

4.2.3. Contact Angle and Surface Tension Measurement

The surface tension components of the membrane were calculated using the extended Young's equation (i.e., Equation 4.5, Table 4.4). Ultrapure water, formamide and diiodomethane were used as the probe liquids (Table 4.3) as suggested by van Oss *et al.* [60]. The surface tension components of hexadecane are shown in Table 4.3 [60].

Table 4.3. Surface tension and surface tension components of the probe liquids and hexadecane [60]

	γ (mN/m)	γ^{LW} (mN/m)	γ^{AB} (mN/m)	γ^+ (mN/m)	γ^- (mN/m)
Water	72.8	21.8	51	25.5	25.5
Formamide	58	39	19	2.28	39.6
Diiodomethane	50.8	50.8	0	0	0
Hexadecane	27.5	27.5	0	0	0

The surface tension γ of each of the surfactant solutions, i.e., Tween 20, CTAB and SDS, was measured (Dataphysics, OCA 15EC). As per the previous study [61], parafilm ($\gamma^{LW} = 25.5 \text{ mN/m}$ [61]) was employed as the planar surface due to its apolarity (i.e., the AB component equals zero). The contact angle of each surfactant solution on parafilm was measured (Dataphysics, DCAT 11), and Equation 4.5 was used to calculate the corresponding γ^{LW} values.

Furthermore, the contact angle of each surfactant solution on the membrane was measured (Dataphysics, DCAT 11), and Equations 4.3, 4.4 and 4.5 were used to calculate respectively γ^{AB} , γ^+ and γ^- (Table 4.4).

Table 4.4. Contact angle with parafilm, contact angle with membrane, surface tension, and surface tension components of the membrane and of the surfactant solutions. Contact angle with parafilm, contact angle with membrane, surface tension, and surface tension components of the membrane and of the surfactant solutions

	θ (°) with parafilm	θ (°) with membrane	γ (mN/m)	γ^{LW} (mN/m)	γ^{AB} (mN/m)	γ^+ (mN/m)	γ^- (mN/m)
Membrane	-	-	32.31	23.32	9.00	3.46	5.85
Tween 20 (50 ppm)	94.28	55.08	60.13	30.36	29.77	4.68	47.37
CTAB (50 ppm)	104.91	71.74	70.52	26.89	43.63	60.78	7.83
SDS (50 ppm)	108.91	74.56	72.33	23.43	48.90	15.20	39.34

The DLVO and XDLVO component energies and total energies was calculated using Equations 4.1, 4.2 and 4.6-4.12.

4.2.4. Ions in the Surfactant Solutions

Ambient CO₂ can dissolve in water to form CO₂-equilibrated water mainly containing H⁺ and HCO₃⁻ [62]. The CO₂-equilibrated water has a pH of approximately 5.65 [62,63].

In the ionic CTAB and SDS solutions, the measured pH values (Table 4.2) were close to the reported value because no additional H⁺ was generated, so the total number concentration of ions generated from the dissolution of either CTAB or SDS was simply double the number concentration of each of the surfactants.

As for Tween 20, the measured pH value was slightly lower than that of CO₂-equilibrated water and of the CTAB and SDS solutions (Table 4.2), indicating the deprotonation of the hydroxyl groups of Tween 20 that added H⁺ to the solution. Therefore, the total H⁺ concentration (pH = 5.14, Table 4.2) was

the sum of the H^+ concentration from dissolution of ambient CO_2 ($pH = 5.65$) and the H^+ concentration from the deprotonation of Tween 20. A Tween 20 molecule has three hydroxyl groups, which means deprotonation would generate three H^+ ions per Tween 20 molecule. Therefore, each of the deprotonated-Tween 20 ion had valence 3, and the total number concentration of the deprotonated-Tween 20 ion was one-third of the number concentration of the H^+ generated by the deprotonation.

4.2.5. OCT Image Analysis

The operating principle of the Fourier-domain OCT (GANYMEDE-SP5, Thorlabs, USA) used is illustrated in Figure 4.1. The OCT is an optical imaging technique based on low-coherence interference. Low-coherence light beam, with a central wavelength of 905 nm and bandwidth of approximately 200 nm, is emitted from a broadband light source and split at the interference mirror into two beams, namely, reference and sample. The reference beam is reflected by a mirror, while the sample beam is backscattered by the sample (in this case, the membrane). The reflected and backscattered beams are recombined and collected at a spectrometer. The spectrometer generates the intensity versus depth profile, from which 3D images of the sample can be visualized. In the current study, the depth resolution in water was approximately 2 μm (dependent on the light source) and the lateral resolution 4 μm (dependent on the scanning lens).

The analysis of the OCT images was conducted with MATLAB. The identification of the feed-membrane interface in the current study was based on that elucidated earlier [43]. Specifically, the intensity gradient across the depth of the membrane module was compared with a pre-determined threshold value, and the coordinates where the gradient exceeded the threshold value were designated to be the coordinates of the feed-membrane interface [43] (Figure 4.2b). The interface was uneven, because the identification was done voxel by voxel in both horizontal and vertical directions. Note that it was not possible to track the feed-membrane interface as filtration ensued because of the progressive fouling; to minimize spatial shifts of the interface during filtration, a stainless-steel plate was placed below the membrane (i.e., on the permeate side) to provide mechanical support. As per earlier studies [41,50,64], the coordinates of the feed-

membrane interface were indexed as layer 0, and the subsequent parallel layers $2\text{ }\mu\text{m}$ apart in the images (i.e., approximately equal to the height of a voxel) were indexed as layers 1, 2 and so on (Figure 4.2a). Since the distance in the OCT images was the optical path length measured by the refractive index of vacuum, the real physical distance between the layers in the aqueous medium was approximately $1.5\text{ }\mu\text{m}$ (Figure 4.2a).

Figure 4.2. (a) Illustration of the coordinate layers in the image analysis, with the bottom layer (in blue) representing the hydrophilic PVDF membrane structure, the gaps between the blue rectangles representing the membrane pores, and the orange circles representing the deposited oil droplets; (b) representative OCT image of the membrane, with the feed-membrane interface denoted by the red line; and (c) representative snapshots showing the evolution of the fouling voxels (marked as red dots) at various filtration volumes (V) at layer 1.

To deal with the non-linear response of the OCT intensity to the variation of the sample composition, the concept of ‘fouling voxel’, i.e., a statistical single-value threshold technique to identify fouling which was successfully applied in

the previous studies, was employed [41,43,50]. Specifically, the mean and standard deviation of the intensity profile of the clean membrane, i.e., at filtration volume $V = 0$, in each layer were calculated. The voxels in each layer at subsequent filtration volumes having intensities greater than the mean plus twice the standard deviation (i.e., 95% confidence level) [65,66] were defined as the fouling voxels (Figure 4.2c). The evolution of the membrane fouling was investigated using the evolution of the number fraction of the fouling voxels at the layer of interest.

4.3. Results and Discussion

4.3.1. Flux Trends

Figure 4.3 presents the evolution of the normalized fluxes when filtering the feeds containing 50 ppm oil emulsions stabilized by 50 ppm of a surfactant (i.e., either Tween 20, CTAB or SDS). Since the same oil was used, the differences in the trends were due to the surfactant type. Three key observations are worth highlighting. Firstly, surprisingly, the flux in the presence of CTAB increased beyond that of the DI water feed, which implies flux enhancement rather than membrane fouling by CTAB. This is likely due to membrane swelling [67], but the resultant change in pore size distributions cannot be accurately quantified by porometry means. Secondly, the relative trends were similar for the three surfactants at $t = 6 - 10$ min, regardless of whether oil was present or absent (Figure 4.10, Appendix), indicating that the behaviors were closely tied to the effect of the surfactant type rather than the oil. Thirdly, at $t > 10$ min, the feeds containing Tween 20 and CTAB exhibited slight flux declines with time, which contrasts with the respective fluxes in the absence of oil (Figure 4.10, Appendix) and hence indicates membrane fouling caused by the oil emulsion stabilized by Tween 20 and CTAB. Notably, for SDS, the flux remained relatively constant in both the presence and absence of oil, indicating lesser membrane fouling.

Figure 4.3. Evolution of normalized fluxes (i.e., normalized with respect to initial fluxes of feeds containing only DI water) during dead-end filtration of feeds containing 50 ppm of surfactant and 50 ppm of oil. The membrane was hydrophilic PVDF with a nominal pore diameter of 0.22 μm and the TMP was 0.2 bar. The error bars represent the standard deviations of the repeated experiments. The relative trends were similar for the three surfactants at $t = 6 - 10$ min, regardless of whether oil was present or absent (Figure 4.10, Appendix), indicating that the behaviors were closely tied to the effect of the surfactant alone.

To preliminarily explore the interactions due to the different charges of the surfactants, the zeta potential values are presented in Table 4.1 and Figure 4.4. Two interesting observations are noted. Firstly, regardless of surfactant type, the surfactant-stabilized oil emulsion and surfactant-soaked membrane had the same positive or negative charges. This indicates that the surfactants had the same influence on both the oil emulsion and the membrane in terms of conferring the same charge signs on both. Secondly, although Tween 20 is a non-ionic surfactant, the zeta potential of the oil emulsion was negative (Table 4.1 and Figure 4.4). As discussed earlier, this was due to the deprotonation of the hydroxyl groups of Tween 20, as evident in the slightly lower pH compared to

that of CTAB and SDS (Table 4.2). Neither observation can explain the flux trends in Figure 4.3.

Figure 4.4. Zeta potential values of the surfactant-stabilized oil emulsions and of the membrane submerged in the respective surfactant solutions. The surfactant concentration was 50 ppm. The error bars represent the standard deviations of the repeated measurements.

DLVO and XDLVO models were thus adopted to provide more insights on the effect of surfactant type on the interfacial interaction energies between the oil droplets and the membrane, and between the oil droplets and the deposited fouling layer.

4.3.2. Interaction between Oil Droplet and Membrane

Figure 4.5 presents the interaction energy profiles between an oil droplet of diameter of 20 μm stabilized by Tween 20, CTAB or SDS and the membrane as a function of separation distance. Corresponding profiles for a smaller droplet of 4 μm are presented in Figure 4.11 in the Appendix, which reflect the effect of droplet size on interaction energies. Figures 4.5a, b and c respectively present the LW, EL and AB component energies, and Figures 4.5d and e respectively present

the total energies according to the DLVO and XDLVO models. The LW, EL and AB energies were respectively calculated using Equations 4.10, 4.11 and 4.12; and the total energies according to the DLVO and XDLVO models were respectively calculated from the components using Equations 4.1) and 4.2). The separation distances (i.e., x -axes) range from 0.158 nm (i.e., the minimum cut-off distance [56]) to 10,000 nm on a logarithm scale of base 10.

Figure 4.5. Profiles of the (a) LW, (b) EL, (c) AB components, and of the total energies according to (d) DLVO and (e) XDLVO theories as functions of separation distance between an oil droplet of diameter of 20 μ m and the membrane.

Comparing the LW, EL and AB components (Figures 4.5a, b and c), three important points are worth highlighting. Firstly, each energy component had a different range of influence. All three interaction energy components decayed to

zero as the separation distance increased, although the affected ranges (i.e., separation distances) were different. Specifically, the AB component had the shortest range of influence, with magnitudes decayed to 0 at $d \approx 4$ nm, while the EL component had the longest range, with magnitudes diminished to 0 at $d \geq 100$ nm. Comparatively, the ranges of the LW component were intermediate between 1 to 40 nm depending on the surfactant type. The comparison of the range of influence of the EL, LW and AB components reveals that, as an oil droplet approached the membrane surface, it was initially affected by the EL interaction alone, and it was only when the distance between the droplet and the membrane narrowed to ~ 40 nm and below that the LW and AB components contributed to the interaction. Secondly, in terms of energy magnitude within the range of influence, the LW interaction energy was orders-of-magnitude smaller than that of AB and EL, and the EL interaction energy was orders-of-magnitude smaller than the AB component. Thirdly, the various energy components exhibited different types of interaction, i.e., attractive or repulsive. It is clear that the AB component was always attractive (i.e., negative values) within its range of influence (Figure 4.5c), while the EL component was repulsive (i.e., positive value) and then attractive (i.e., negative value) (Figure 4.5b) as the separation distance decreased.

Collectively, the total interaction energy trend predicted by the DLVO model mimicked that of the EL component alone throughout the whole range of the separation distance (Figure 4.5d). The dominance of the EL component over the LW component in the DLVO model is consistent with past studies [28-30]. As for the XDLVO model that has the additional AB component, the total energy reflected the AB component at $d < 4$ nm and the EL component at $d > 4$ nm (Figure 4.5e). Therefore, both models predict similarly that, as an oil droplet approached the membrane, the oil droplet had to overcome the repulsive energy barrier conferred by the repulsive EL interaction energy, before getting to the attractive interaction region conferred by EL attraction (DLVO model) or both EL and AB attraction (XDLVO model). Two important observations related to this are described as follows.

Firstly, the magnitudes of the DLVO interaction energies at shorter separation distances (< 5 nm) correlate well with the flux trends in Figure 4.3.

Figure 4.5d shows that the feed containing CTAB had the most attractive interaction energy, followed by Tween 20 with a slight attractive interaction energy, and then by SDS with a repulsive interaction energy. This is correlated with the greatest flux for CTAB, followed by Tween 20 and then SDS. In particular, since the flux trends were similar for both surfactant-stabilized oil emulsion (Figure 4.3) and surfactants alone (Figure 4.10, Appendix), this indicates that the flux enhancement stemmed from the strong attractive interactions between CTAB and the membrane, whereas the flux decline stemmed from repulsive interaction between SDS and the membrane.

Secondly, the magnitude of the energy barrier formed by the repulsive EL interaction played an important role in determining the tendency for oil droplets to adhere to the membrane surface, i.e., membrane fouling. Figures 4.5d and e show that the feeds containing CTAB and SDS had similar and greater repulsive energy peak values than that with Tween 20, which implies the relative ease of deposition for the Tween 20-stabilized oil emulsion. This is confirmed by OCT image analysis in Figure 4.6, which presents the evolution of the fractions of fouling voxels at three different layers (namely, layers 1, 3 and 5, which correspond to physical distances above the feed-membrane interface of respectively 1.5, 4.5 and 7.5 μm) with respect to filtration volume. Despite the similarity in the refractive indices of hexadecane and PVDF, the ability of OCT to monitor fouling by the oil droplets has been proven in our earlier study [50]. Specifically, although the OCT intensity reflected at the boundaries between the membrane surface and the oil droplets was relatively weak compared to the significant background intensity of the PVDF network, this did not obstruct the assessment of external fouling, which was based on the increase in intensity at each layer due to the deposition of the foulants. It should be noted that, although layer 5 represented 7.5 μm from the feed-membrane interface, which was less than half that of the mean droplet diameter (Figure 4.9, Appendix), the number fractions were very low and thereby higher layers were not presented. The thinner fouling layers were because (i) as opposed to rigid particulate foulants, oil droplets can deform upon deposition [21]; and (ii) the smaller droplets (Figures 4.9 and 4.11, Appendix) were more prone to deposit [31]. Figure 4.6 shows that, regardless of surfactant type, the fractions of fouling voxels increased with

filtration volume, with the increase expectedly relatively greater for the layers closer to the membrane. Regarding the effect of surfactant type, Layer 1 of the Tween 20-stabilized oil emulsions exhibited the highest number fraction of fouling voxels (Figure 4.6a), which agree with the lowest repulsive peak of the DLVO interaction energy (Figure 4.5d).

Figure 4.6. Evolution of the fractions of fouling voxels at layers 1, 3 and 5 (i.e., approximately ~ 1.5 , 4.5 and $7.5 \mu\text{m}$ above the feed-membrane interface, respectively) during the filtration of oil emulsions stabilized by (a) Tween 20, (b) CTAB and (c) SDS. The feed contained 50 ppm of the targeted surfactant and 50 ppm of oil. The membrane was PVDF membrane with a nominal pore diameter of $0.22 \mu\text{m}$ and the TMP was constant at 0.2 bar. The error bars represent the standard deviations of the repeated experiments.

4.3.3. Interaction between Oil Droplet and the Deposited Oil Layer

To understand the progressive growth of the fouling layer, Figure 4.7 presents the interaction energy profiles between a surfactant-stabilized oil droplet of diameter $20 \mu\text{m}$ and the deposited oil layer as a function of separation distance. Similar to the interaction energy between the oil droplet and the membrane (Figure 4.5), the DLVO model (Figure 4.7(d)) gave trends similar to that of the EL component (Figure 4.7b), while the XDLVO interaction energy was dominated by the EL component at separation distances of 3 nm and greater and by the AB component at smaller distances (Figure 4.7e). Notably, between the oil droplet and the deposited oil layer, the DLVO model predicted only repulsive interaction, whereas the XDLVO model predicted attractive interaction at smaller separation distances. Compared to the interaction between the oil droplet and the membrane (Figures 4.5d and e), the magnitudes of the peak positive (i.e., repulsive) values between the oil droplet and the deposited fouling layer were greater (Figures 4.7d and e), indicating the lower tendency of oil droplets to deposit onto the deposited fouling layer relative to that onto the membrane.

Figure 4.7. Profiles of the (a) LW, (b) EL, (c) AB components, and of the total energies according to (d) DLVO and (e) XDLVO theories as functions of separation distance between an oil droplet of diameter of 20 μm and the deposited oil layer.

Figures 4.7d and e show that the least repulsive energy was by the feed containing Tween 20, followed by SDS then CTAB. This thus explains the highest fouling layer growth rate exhibited by the feed containing Tween 20 in Figure 4.6. Note that the non-overlapping trendlines of each layer suggests uniform fouling layers [41]. The difference in the evolution of the fouling layer thickness with filtration volume for the oil emulsions stabilized by the three surfactants was further assessed in Figure 4.8, which presents the OCT intensity of the fouled membrane subtracted by that of the clean membrane (i.e., at $V = 0$) at three filtration volumes of 100, 300 and 600 mL. As filtration progressed, the layer index versus OCT intensity profiles evolved to become more contoured,

indicating the increased extents of fouling at the lower layers and the presence of fouling at the higher layers, i.e., increased fouling layer thickness. Comparing the three surfactants, it is clear that the feed containing Tween 20-stabilized oil emulsion consistently had the most extensive fouling, as evident in the greatest OCT intensity and thickest fouling layer. This is consistent with the fouling voxel trends in Figure 4.6 that also shows worst fouling for Tween 20, and also the least repulsive energy predicted by the DLVO and XDLVO models (Figures 4.7d and e).

Figure 4.8. OCT intensity of the fouled membrane (subtracted by that of the clean membrane) at filtration volumes of (a) 100 mL, (b) 300 mL and (c) 600 mL. The feed contained 50 ppm of the targeted surfactant and 50 ppm of oil. The membrane was PVDF membrane with a nominal pore diameter of 0.22 μm and the TMP was constant at 0.2 bar. The error bars represent the standard deviations of repeated experiments.

4.4. Conclusions

He et al. [29] indicated that, for oil emulsions stabilized by the same surfactant, the interaction energies predicted by the DLVO model correlated well with the extents of fouling at different concentrations of salt. Tanudjaja et al. [20] subsequently explained that the reason the DLVO model, rather than the XDLVO model, was better for predicting fouling by oil emulsions was because the dominant magnitude of AB in the XDLVO model drowned out the other interactions like that of EL, which resulted in the inability to predict the different tendencies of the different oils investigated. This study further extended the understanding to fouling by oil emulsions stabilized by different surfactants (namely, nonionic Tween 20, positively charged CTAB and negatively charged SDS).

The surprising flux trends in Figure 4.3, particularly with regards to the flux enhancement conferred by CTAB-stabilized oil emulsion, were correlated with interaction energies predicted by DLVO and XDLVO models (Figures 4.5 and 4.7), which also served to substantiate the fouling phenomena monitored using OCT (Figures 4.6 and 4.8). The profiles of interaction energy versus separation distance are able to explain the flux and fouling trends if properly interpreted. For the interaction between the surfactant-stabilized oil emulsion and the membrane (Figure 4.5), (i) the flux enhancement conferred by CTAB was linked to the greatest attraction between CTAB and the membrane at shorter separation distances (< 3 nm) predicted by the DLVO model, although it should be noted that this attraction was unexpectedly not tied to the worst fouling by the oil emulsion observed via OCT; and (ii) the more extensive fouling of Layer 1 (i.e., the first fouling layer on the membrane) by the Tween 20-stabilized oil emulsion was tied to the least peak (repulsive) energy value given by both DLVO and XDLVO models. As for the interaction between the surfactant-stabilized oil emulsion and the deposited oil layer (Figure 4.7), the extent of fouling was similarly determined by the magnitudes of repulsive energy. The thickest fouling layer for the feed containing Tween 20 was tied to the least repulsive energy at separation distances of less than 10 nm predicted by the DLVO model (Figure 4.7d) and the least peak (repulsive) energy magnitude at a separation distance of about 3 nm predicted by the XDLVO model (Figure 4.7e).

Taking the results here, along with two earlier ones on correlating DLVO and XDLVO predictions with membrane fouling by surfactant-stabilized oil emulsion [20,29], into account, the key conclusions are (1) extensive attractive interaction between the surfactant and membrane, as predicted by the DLVO model but not the XDLVO model, led to flux enhancement vis-à-vis a DI water feed; and (2) the repulsive energy, but not the attractive energy, predicted either by the DLVO or XDLVO model correlated well with the extent of fouling.

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Appendix

Figure 4.9. Droplet size distribution of oil droplets stabilized by three surfactants (50 ppm oil, 50 ppm surfactant) of different charges, namely, (a) non-ionic Tween 20, (b) positively charged CTAB, and (c) negatively charged SDS. The means and standard deviations of the emulsions are shown in Table

Figure 4.10. Evolution of normalized fluxes (i.e., normalized with respect to initial fluxes for feed containing only DI water) during dead-end filtration of feeds containing 50 ppm of surfactant and without oil. The membrane was hydrophilic PVDF with a nominal pore diameter of 0.22 μm and the TMP was 0.2 bar. The error bars represent the standard deviations of the repeated experiments. The fluxes of filtration without oil had similar patterns to the fluxes of filtration with oil emulsions (Figure 4.3) at $t = 6 - 10$ min, suggesting that the behaviors of the fluxes during this period were tied to the effect of the surfactant alone.

Figure 4.11. Comparison of the DLVO (left column) and XDLVO (right column) total energy profiles versus the separation distance for oil droplets of different diameters and (a, b) the membrane, (c, d) the deposited oil layer.

Table 4.5. Means and standard deviations of the oil droplet size distributions of oil emulsions stabilized by Tween 20, CTAB and SDS (50 ppm oil, 50 ppm surfactant).

	Mean (μm)	Standard Deviation (μm)
Tween 20-stabilized oil emulsion	19.03	11.90
CTAB-stabilized oil emulsion	22.10	13.96
SDS-stabilized oil emulsion	18.42	10.64

List of symbols

a	radius of oil droplet, m
d	separation distance between the oil droplet and the membrane, m
d_0	minimum equilibrium cut-off distance, m
e	electron charge, 1.60217×10^{-19} C
ΔG^{AB}	Lewis acid-base (AB) interaction energy, J
ΔG^{EL}	electrostatic double layer (EL) interaction energy, J
ΔG^{LW}	Lifshitz van der Waals (LW) interaction energy, J
ΔG_{mlo}	interaction energy between oil droplet and membrane in surfactant solution, J
ΔG_{DLVO}^{total}	total interaction energy based on DLVO theory, J
ΔG_{XDLVO}^{total}	total interaction energy based on XDLVO theory, J
k	Boltzmann's constant, 1.3806×10^{-23} m ² kgs ⁻² K ⁻¹
n_i	number concentration of ion i , m ⁻³
T	temperature, K
z_i	valence of ion i
γ	total surface tension, N/m
γ^{AB}	polar component of total surface tension, N/m
γ^{LW}	dispersive component of total surface tension, N/m
γ^+	electron acceptor component of polar surface tension, N/m
γ^-	electron donor component of polar surface tension, N/m
γ_l	surface tension of liquid, N/m
γ_s	surface tension of solid, N/m
ϵ_0	permittivity of vacuum

ε_r	permittivity of water
ξ	zeta potential, V
θ	contact angle, °
κ	reciprocal Debye length, m ⁻¹
λ	characteristic decay length of the AB interaction, m

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Chapter 5. MICROFILTRATION OF MONODISPERSE SUSPENSION OF SOLID FOULANTS: EFFECTS OF SURFACE CHARGES ON INTERNAL FOULING

The content of this chapter has been accepted by Journal of Membrane Science under the title of *Internal fouling during microfiltration with foulants of different surface charges*.

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Abstract

In view of the inevitability of membrane fouling, it is critically important to understand the underlying mechanisms to alleviate fouling and thereby improve the feasibility of membrane-filtration for more applications. This study was targeted at understanding the internal membrane fouling mechanisms by three types of polystyrene (PS) particles (sized at $\sim 0.45\ \mu\text{m}$) with different surface charges during microfiltration with the same polycarbonate track-etched (PCTE) membrane (nominal pore size of $2\ \mu\text{m}$). Optical coherence tomography (OCT) technique, which was employed to monitor membrane fouling, indicated greater extents of particle deposition in the case of the positive and less negative PS particles, which is consistent with the more severe flux declines relative to the more negative PS particles. The new fouling model developed that additionally accounts for internal cake filtration, on top of the well-reported pore constriction and pore blockage, revealed the fouling mechanisms at play. For the positive PS particles, the attractive particle-membrane interaction led to a more homogeneous layer-by-layer cake growth, which resulted in denser packing in the pore and higher internal cake resistance, and thereby the worst flux decline. In contrast, for the negative PS particles, the repulsive particle-particle and particle-membrane interactions resulted in more random deposition of the particles inside the pores, resulting in more extensive pore constriction and blockage, as well as lower resistance of the internal cake. This study underscored the importance of surface charge in internal fouling and provided insights on the lesser reported internal fouling mechanisms.

Keywords: Membrane Fouling; Optical Coherence Tomography; Internal Fouling Model; Surface Charge; Colloidal Foulant

5.1. Introduction

In recent decades, membrane filtration has rose to prominence as an efficient method for treating water in various applications ranging from metal processing, petroleum refining and food industry [1,2], attributed to significant benefits with respect to low cost, no additional chemicals required and ease of scalability [3-6]. Despite the advantages, membrane fouling – the progressive deposition of the feed constituents onto the membrane and thereby reduces the filtration throughput – remains the Achilles' heel for all liquid membrane-filtration processes that limits wider implementation of membrane-based separations [7-9]. Consequently, more understanding of membrane fouling is needed to enhance the efficiency of the separation process.

Although membrane fouling has been widely researched, a complete mechanistic understanding of membrane fouling is still far from perfect, mainly due to the complexity of various factors that can affect membrane fouling. Among them, the surface charge of the foulants in the feed is well-acknowledged as important in influencing the extent of fouling and the underlying fouling mechanisms. McDonogh *et al.* [10,11] reported that the zeta potential of the colloidal foulants affect the specific cake resistance of the cake. Moreover, in our recent studies regarding the impact of foulant charge on membrane fouling by colloidal particles [12,13] and oil emulsions [14], the foulant-foulant and foulant-membrane interactions were found to significantly affect membrane fouling with respect to permeate flux and cake characteristics. Such results have been explained via modeling [12] or DLVO and extended-DLVO theories [13,14]. Delavari *et al.* [15] demonstrated that the membranes with net zero charge were more prone to fouling than those with strong negative charges, and Fu *et al.* [16] agreed that the zeta potential of the membrane governed membrane fouling. On the other hand, Liu *et al.* [17] found that zeta potential is poorly correlated with membrane fouling. Notably, most of the studies on the effect of surface charge have focused on external fouling (i.e., the foulants deposit on the membrane surface), while that on internal fouling (i.e., the foulants deposit within the membrane matrix) remains poorly understood, in part due to the challenges associated with monitoring the latter.

Recent studies demonstrated the capability of optical coherence tomography (OCT) to monitor internal fouling by proteins [18] and oil emulsions [19] in real-time and non-invasively. In particular, OCT has been employed to monitor external membrane fouling during filtration with various foulants (such as bentonite [20,21], glass [22], latex [12,23], biofilm [24-27], protein [18] and oil emulsion [14,19]) based on near-infrared light (wavelength $\sim 900 - 1300$

nm) and low coherence interference to generate three-dimensional (3D) images from the depth profile intensity of the scanned sample. Algorithms have been developed to analyze the images to extract information on the development of membrane fouling [20,22,28,29]. For internal fouling, it was indicated that OCT could qualitatively reveal the evolution of internal fouling, but because of the different reflectance of the different membranes, quantitative comparison was not possible [18]. Here, OCT was used to monitor the internal fouling of the same membrane by the same colloidal foulants with different surface charges.

Regarding fouling models, the four key fouling mechanisms that are well-accounted for mathematically are pore constriction, intermediate pore blockage, complete pore blockage and cake filtration [30], whereby the first corresponds to internal fouling whereas the latter three represent external fouling. While earlier studies focused on each fouling mechanism individually [31-33], later studies have employed methods that combined a few fouling mechanisms to more accurately describe membrane fouling. Ho and Zydney [34] were among the first to combine the cake filtration and pore blockage mechanisms to model external fouling, and subsequently Duclos-Orsello *et al.* [35] additionally incorporated pore constriction to also account for the concurrently occurring internal fouling. These combined fouling models have been valuable in understanding the membrane fouling mechanisms, though external fouling has always been presumed to be present. For cases wherein internal fouling is dominant, not only would the presence of the external fouling parameters cause over-fitting to the combined model, but the availability of only one internal fouling parameter may not be adequate to represent the internal fouling mechanisms at play. Therefore, a fouling model that focuses on internal fouling and also account for mechanisms other than pore constriction is necessary.

The key objective of the current study was to better understand internal membrane fouling, specifically with respect to the effect of foulant charge. Three types of polystyrene (PS) particles ($\sim 0.45 \mu\text{m}$) with different zeta potentials were investigated with the same polycarbonate track-etched (PCTE) membrane (nominal pore size $\sim 2 \mu\text{m}$). Flux decline trends were obtained. OCT analysis was employed to monitor both external and internal fouling. A new combined internal fouling model that additionally accounts for internal cake filtration was developed.

5.2. Modeling of Membrane Internal Fouling

5.2.1. Pore Constriction Model

Pore constriction refers to the narrowing of the membrane pores due to the deposition of foulants whose characteristic sizes are smaller than that of the pores. The pore constriction model is one of the popular classical fouling models used to describe such internal fouling of the membrane [36]:

$$\frac{Q}{Q_0} = \left(1 + \frac{\gamma Q_0 C t}{\pi r_0^2 \delta}\right)^{-2} \quad (5.1)$$

where Q is permeate flowrate at time t , Q_0 is initial permeate flowrate at time $t = 0$, γ reflects the volume occupied per unit mass of the particles deposited, C is particle concentration, r_0 is radius of the membrane pores, and δ is membrane thickness. For the same membrane, γ , r_0 and δ are constants and hence Equation 5.1 can be rewritten as:

$$\frac{Q}{Q_0} = (1 + \beta Q_0 C t)^{-2} \quad (5.2)$$

where

$$\beta = \frac{\gamma}{\pi r_0^2 \delta} \quad (5.3)$$

Equation 5.2 can thus be readily used for regression analysis of the experimental data to find the best-fitted value of β , which reflects the extent of pore constriction.

5.3. Development of Combined Model Accounting for Pore Constriction, Pore Blockage and Internal Cake Filtration

The classical pore constriction model attributes flux decline to the narrowing of the pore diameter due to foulant deposition and only considers the flow through the unblocked regions. In practice, even if foulants fill up the entire pore, the flow still can permeate through the voids between deposited foulants, as per the classical cake filtration model in the case of external fouling. Such forms of deposits within the pore can be regarded as the internal cake layer, which differs from the classical cake filtration in that (i) the former refers to internal fouling (i.e., within the membrane matrix), while the latter to external fouling (i.e., atop the membrane surface); and (ii) the former is such that the cake grows perpendicular to permeate flow due to restriction by the pore walls (Figure 5.1), while the latter is such that the growth of the cake is parallel to the permeate flow. In essence, on top of accounting for the permeate flow through

the unblocked region of the pore (i.e., the pore constriction model; Figure 5.1a), the comprehensive description of internal fouling must also consider the permeate flow through the blocked region of the pore (i.e., the internal cake; Figure 5.1b).

The total flowrate through the unblocked region of the pore and the rate of increase of the blocked region of the pore can be modeled based on the approach developed earlier [35], as described as follows. Note that in this approach, the membrane pores were assumed to be cylindrically straight through with no interconnection between the pores, so that the deposition of the particles was solely due to the particles from the bulk and not by the transfer from the other pores. At time t , the unblocked area of the pore A_u can be calculated using the combination of the complete blockage model and the pore constriction model:

$$\frac{A_u}{A_0} = \exp\left(-\frac{\alpha C J_0 t}{1 + \beta Q_0 C t}\right) \quad (5.4)$$

where A_0 is pore area at time $t = 0$, J_0 is permeate flux at time $t = 0$ and α is pore blockage parameter corresponding to the blocked area per unit mass of the depositing particles. The permeate flux through the unblocked pores J_u can be described with the pore constriction model:

$$\frac{J_u}{J_0} = (1 + \beta Q_0 C t)^{-2} \quad (5.5)$$

Combining Equations 5.4 and 5.5 gives the total flowrate through the unblocked regions of the pores Q_u :

$$\frac{Q_u}{Q_0} = \frac{1}{(1 + \beta Q_0 C t)^2} \exp\left(-\frac{\alpha C J_0 t}{1 + \beta Q_0 C t}\right) \quad (5.6)$$

The rate of increase of the blocked region of the pore A_b can be given by:

$$\frac{1}{A_0} \frac{dA_b}{dt} = -\frac{1}{A_0} \frac{dA_u}{dt} = \frac{\alpha C J_0}{(1 + \beta Q_0 C t)^2} \exp\left(-\frac{\alpha C J_0 t}{1 + \beta Q_0 C t}\right) \quad (5.7)$$

To model the flowrate through the blocked region of the pore Q_b , Darcy's law can be applied:

$$Q_b = \int \frac{P}{\mu R_c} dA_b \quad (5.8)$$

where P is trans-membrane pressure (TMP), μ is viscosity of the solution and R_c is resistance of the internal cake layer. Note that, as the cake grows perpendicularly to the flow of the permeate for internal fouling, R_c is constant. Combining Equations 5.7 and 5.8 gives:

$$\frac{Q_b}{Q_0} = \int_0^t \frac{\frac{\alpha C J_0}{(1 + \beta Q_0 C t_p)^2} \exp\left(-\frac{\alpha C J_0 t_p}{1 + \beta Q_0 C t_p}\right)}{\frac{R_c}{R_m}} dt_p \quad (5.9)$$

where t_p is the time at which the fouling transitions from pore-constriction to internal cake filtration and R_m is the membrane resistance. Therefore, the total flowrate through the membrane at time t is:

$$\frac{Q}{Q_o} = \frac{1}{(1 + \beta Q_o C t)^2} \exp\left(-\frac{\alpha C J_o t}{1 + \beta Q_o C t}\right) + \int_0^t \frac{\frac{\alpha C J_o}{(1 + \beta Q_o C t_p)^2} \exp\left(-\frac{\alpha C J_o t_p}{1 + \beta Q_o C t_p}\right)}{\frac{R_c}{R_m}} dt_p \quad (5.10)$$

Figure 5.1. Schematic of the progression of internal fouling: (a) at the earlier stage (i.e., time t_1), internal fouling occurs per the pore constriction model; and (b) at the later stage (i.e., time t_2), after the build-up fills up the whole pore cross-section, permeation persists through internal cake filtration.

5.4. Materials and Method

5.4.1. Experimental setup

The experimental setup employed in this study is schematically shown in Figure 5.2; details have been described earlier [14]. The filtration experiments were operated in the constant TMP, dead-end mode, as per previous fouling models [34,35,37]. The TMP was constantly 0.15 bar, which was generated via the height difference between the feed and the permeate (i.e., gravity-driven). At the start of each experiment, before the foulants were

introduced, only DI water was used as the feed for 30 minutes to condition the membrane. The permeate flux was recorded every 30 seconds throughout the experiments. The OCT (GANYMEDE-SP5, Thorlabs) A-scan rate was 30 kHz.

Figure 5.2. Principle of the optical coherence tomography (OCT) method applied for dead-end filtration.

5.4.2. Materials

The membrane in this study was the polycarbonate track-etched (PCTE) membrane (nominal pore size = 2 μm ; Whatman, WH-111111), and the effective filtration area was 9.6 cm^2 .

Polystyrene (PS) particles with three different surface charges were used, namely, aminated (Magsphere, AM500NM), non-modified (Magsphere, PS500NM) and carboxylated (Magsphere, CA500NM). Note that the PS particles were purchased and used as is; neutral charged PS particles are not available due to severe agglomeration. The particle concentration in each initial feed was consistently 0.001 g/L. As listed in Table 5.1, the zeta potentials (Malvern, Zetasizer Nano) of the three feeds were 31.83, -33.34 and -40.43 mV respectively for the aminated, un-modified and carboxylated PS particles, and the zeta potential of the PCTE membrane was -35.3 mV [12]. The particles had similar size distributions with similar mean diameters of $\sim 0.45 \mu\text{m}$ (Appendix, Figure 5.11), which are less than a quarter that of the nominal membrane pore diameter (2 μm).

Table 5.1. Means and standard deviations of the zeta potentials of the solutions containing 0.001 g/L aminated, un-modified or carboxylated PS particles, and the polycarbonate track-etched (PCTE) membrane.

	Mean (mV)	Standard Deviation (mV)	Medium
Aminated PS particles	31.83	1.74	DI water
Un-modified PS particles	-33.34	6.72	DI water
Carboxylated PS particles	-40.43	3.23	DI water
PCTE Membrane [12]	-35.3	0.75	1 mM KCl

5.4.3. OCT Image Analysis

Figure 5.2 overviews the working principle of the OCT used; details can be found in earlier reports [14,19]. The obtained images had a depth resolution in water of $\sim 2 \mu\text{m}$ and lateral resolution of $\sim 4 \mu\text{m}$, which were determined respectively by the light source and scanning lens.

The image analysis method is illustrated in Figure 5.3; details can be found elsewhere [12,14,19,22] so only given in brief here. Firstly, Layer 0, corresponding to the feed-membrane interface (Figures 5.3a and b), was determined [22]. Subsequently, the adjacent parallel layers $2 \mu\text{m}$ apart from one another below and above Layer 0 were indexed as Layers with negative and positive integers, respectively (Figure 5.3a). In the OCT images, the distance is the path length of the light calculated by the refractive index in vacuum; thus, in water, the real physical distance between the layers was $\sim 1.5 \mu\text{m}$. Then, the “fouling voxels” in each layer [12,14,19,22,23], defined as voxels with intensities greater than the 95% confidence interval of the intensity profiles at the same layer at the start of filtration [38,39], was determined to assess the evolution of membrane fouling.

Figure 5.3. (a) Overview of the layer-by-layer analysis, with the PS particles represented by the circles, the pore walls represented by the rectangles and the pore represented by the gap between the pore walls; (b) OCT image of the PCTE membrane; the red line denotes the feed-membrane interface identified; and (c) representative 2D images showing the fouling voxels (red dots) at Layer -6 (i.e., 9 μm below the feed-membrane interface) at different filtration volumes (V).

5.5. Results and Discussion

5.5.1. Flux Trends

Figure 5.4 displays the variation of normalized flux with respect to filtration time for feeds with 0.001 g/L of PS particles of different charges (Table 5.1) and sizes (Figure 5.11) smaller than the membrane pores. Specifically, the aminated PS particles were positively charged, whereas the carboxylated PS particles were more negatively charged than the un-

modified ones. The largest error bars (i.e., standard deviations) of the carboxylated particles are likely tied to the largest normalized flux values and correspondingly the greatest convective flow through the pores increasing the dynamism of the fouling behavior. Two observations are noteworthy. Firstly, among the three types of PS particles, the positive aminated ones gave the greatest flux decline, followed by the un-modified then the more negatively charged carboxylated ones. In particular, the flux declined drastically to less than 10% and approximately 20% of the initial fluxes for the aminated and un-modified particles, respectively, at $t = 26$ min. Secondly, the aminated and un-modified PS particles went through similar rates of decline initially before the former exhibited more severe flux decline, while the carboxylated PS gave comparatively more gradual flux decline throughout the filtration. The different flux decline trends for the similar-sized PS particles (Figure 5.11) suggest the significant impact of particle charge on membrane fouling.

Figure 5.4. Variation of normalized fluxes with respect to time during the dead-end filtration with feeds containing 0.001 g/L of PS particles, TMP at 0.15 bar, and PCTE membrane (pore size of 2 μm). The error bars represent standard deviations.

5.5.2. Evolution of Fouling

To explore further the fouling phenomena during the filtration, the 3D OCT scanning technique was employed. Although the OCT images as is do not show clearly the extent of

fouling (Figure 5.3b) [19], statistical analysis of the images gave Figures 5.5 and 5.6, which respectively quantify the evolution of external and internal membrane fouling through the fouling voxel profiles. The data points are the mean values and the error bars are the standard deviations of the repeated experiments. Note that the error bars in Figure 5.6 appear larger, because the quantitative values of the average intensities are influenced by variations between repeats (e.g., membrane, positioning of the filtration cell), particularly for internal fouling whereby the contrast between the foulant and the membrane matrix was lesser. Despite the larger error bars, the fouling extent on each layer within the membrane was distinct, which is otherwise not readily trackable non-invasively and in real time by other means.

It is clear in Figure 5.5 that the fouling voxels increased negligibly on and above the membrane for all three PS particle types, indicating minimal external fouling due to the smaller sizes of the foulant particles relative to the membrane pores. This affirms that the flux declines (Figure 5.4) were not attributable to external fouling. On the other hand, Figure 5.6 shows that the fouling voxels well beneath the feed-membrane interface (i.e., as deep as Layer 8, which is 12 μm below) increased with time, verifying the progressive worsening of internal fouling during the filtration. Two observations are noteworthy. Firstly, despite the aminated and unmodified PS particles having opposite charges, they display more similar trends, which agrees with the flux decline trends (Figure 5.4) and thereby ascertains the consistency between the two measurements. More specifically, among the three PS types, the aminated and carboxylated PS particles had respectively the greatest and least increase in the fraction of fouling voxels, which indicates the most and least extensive internal fouling. Secondly, for all three PS particle types, the highest fractions of fouling voxels were consistently on Layer 6 (i.e., 9 μm below the feed-membrane interface), which indicates that the internal fouling was such that the foulant particles preferentially penetrated some distance into the membrane matrix before depositing.

Figure 5.5. Fraction of fouling voxels at and above the feed-membrane interface (i.e., external fouling) versus filtration volume during the dead-end filtration (TMP = 0.15 bar) with 0.001 g/L of (a) aminated, (b) un-modified and (c) carboxylated PS particles and PCTE membrane (pore diameter = 2 μm). Error bars represent standard deviations.

Figure 5.6. Fraction of fouling voxels below the feed-membrane interface (i.e., internal fouling) versus filtration volume during the dead-end filtration (TMP = 0.15 bar) with 0.001 g/L of (a) aminated, (b) un-modified and (c) carboxylated PS particles and PCTE membrane (pore diameter = 2 μm). Error bars represent standard deviations.

5.5.3. Modeling Results

To further explore the influence of particle charges on internal fouling, the fouling models were employed to shed additional insights on top of the flux and OCT results. In this study, the pore constriction model (i.e., one-mechanism model; Equation 5.2), the combined pore constriction and pore blockage model (i.e., two-mechanism model; Equation 5.6) and the combined pore constriction, pore blockage and internal cake filtration model (i.e., three-mechanism model; Equation 5.10) were adopted.

5.5.3.1. Model-fitting

Figure 5.7 shows the regression analysis of the mean experimental flux decline data (Figure 5.4, which has error bars displayed) using the three models. The coefficients of determination (R^2) for the best-fitted lines in both Figures 5.7 and 5.8 are presented in Figures 5.12, 5.13 and 5.14 for the aminated, un-modified and carboxylated PS particles, respectively. Furthermore, in line with the classical fouling models, Figures 5.15, 5.16 and 5.17 plot $\log (d^2t/dV^2)$ versus $\log (dt/dV)$ for the aminated, un-modified and carboxylated PS particles, respectively. Although the experimental data had too much scatter and thus low R^2 values, the slopes of the best-fitted lines are consistently 1.5, indicating pore constriction.

Clearly, among the three models, the three-mechanism model consistently gave the best fit for all three PS particle types. While the two-mechanism model gave good fits for aminated and carboxylated PS particles (Figures 5.7a and c), the one-mechanism model only fitted well for the carboxylated PS particles (Figure 5.7c). This indicates that the three-mechanism was the best suited to describe the fouling phenomena, while the one-mechanism the worst.

Analogous to Figure 5.7, Figure 5.8 presents the total resistance (i.e., cake and membrane) calculated based on the obtained flux results. Similarly, (i) the three-mechanism model gave the best fit, affirming that this model captures the fouling phenomena most adequately; and (ii) the carboxylated PS particles were the most insensitive to the variations in the models. For the aminated PS particles (Figure 5.8a), the fitting was good initially for the one-mechanism and two-mechanism models for the first 10 and 20 mins, respectively, but deviated significantly towards the end, suggesting that the pore blockage and cake filtration mechanisms became increasingly important as the filtration progressed.

Collectively, Figures 5.7 and 5.8 indicate that (1) for the aminated and un-modified PS particles, the fouling mechanisms at play involved pore constriction, pore blockage and cake filtration (Equation 5.10), verifying that the consideration of internal cake filtration is crucial;

(2) for the carboxylated PS particles, pore constriction alone was sufficient to describe the fouling underlying the flux decline, which suggests that pore blockage and internal cake filtration were relatively insignificant, and agrees with the least flux decline (Figure 5.4) and least increase in fouling voxels (Figures 5.5). While the least fouling by the carboxylated PS particles (Figures 5.4 and 5.5) can be expected in view of the electrostatically repulsive interaction between negatively charged membrane and the most negatively charged foulant (Table 5.1), the starkly different behaviors between the un-modified and carboxylated PS particles are surprising considering that both are negatively charged (Table 5.1).

(a)

(b)

(c)

Figure 5.7. Best-fitted normalized fluxes for the three PS particle types: (a) aminated, (b) un-modified and (c) carboxylated for the three fouling models (namely, one mechanism, two mechanisms and three mechanisms).

(a)

(b)

(c)

Figure 5.8. Total resistance calculated based on the best-fitted fluxes for the three PS particle types: (a) aminated, (b) un-modified and (c) carboxylated PS particles using the one-, two- and three-mechanism models.

5.5.3.2. Fouling parameters from the fitting of the new three-mechanism model

As the flux of the carboxylated PS particles fitted well with the one-mechanism (i.e., pore constriction) model, using the two-mechanism (namely, pore constriction and pore blockage) or three-mechanism (namely, pore constriction, pore blockage and internal cake filtration) models would result in over-fitting with additional parameters. Also, the β parameter for the carboxylated particles obtained via the one-mechanism model is orders-of-magnitude greater than that for the other two particle types obtained via the three-mechanism model, affirming that the parameters obtained from different models cannot be directly compared. As a result, the following analysis using the three-mechanism model omitted carboxylated PS particles.

Figure 5.9 shows the membrane fouling parameters acquired from best-fitting the normalized flux-decline data using the three-mechanism model. Specifically, Figures 5.9a, b and c display α , β and R_c/R_m , which correspond to pore blockage, pore constriction and cake filtration, respectively, for the aminated and un-modified PS particles.

Comparing the aminated and un-modified PS particles (Figure 5.9a and b), the α and β values were greater for the latter, indicating that the un-modified PS particles exhibited higher tendencies to cause pore constriction and pore blockage. On the other hand, the R_c/R_m ratio (Figure 5.9c) shows that the cake formed by aminated PS particles had the higher resistance. These results imply that, while the membrane pores for the case of the aminated particles were

more densely packed (Figure 5.9c), as also reflected in the higher fractions of fouling voxels in Figure 5.6, that of the un-modified PS particles were more extensively blocked (Figures 5.9a and b). The denser packing of the aminated particles in the membrane pores can be ascribed to the electrostatically attractive interactions with the membrane, as well as the relatively lesser inter-particle repulsion due to the smallest zeta potential magnitude, which caused the most severe flux decline (Figure 5.4). Analogously, the least flux decline exhibited by the carboxylated PS particles can be tied to the most repulsive inter-particle and particle-membrane interactions that led to the least internal fouling.

Figure 5.10 illustrates the fouling mechanisms for the aminated versus un-modified PS particles. For the aminated PS particles (Figure 5.10a), because of the electrostatically attractive interactions with the membrane, the particles tended to fully cover the membrane pore wall first before forming subsequent layers on top of the deposits, which resulted in denser packing and thereby internal cakes with higher resistance. As for the un-modified PS particles (Figure 5.10b), because the incoming negatively charged PS particles were as likely to deposit either on the negatively charged pore wall or on deposited particles, the deposition was more random, causing higher rates of pore constriction and pore blockage, along with lower packing density of the internal cake. The results here agree with our earlier study on investigating the effect of surface charge of PS particles on external fouling [12], in which the external cake formed by aminated PS particles was more homogeneous due to more sequential deposition, while that by the un-modified and carboxylated PS particles was less homogeneous.

(a)

(b)

(c)

Figure 5.9. Best-fitted membrane fouling parameters via regression analysis of the normalized flux declines using the three-mechanism model: (a) pore blockage parameter α , (b) pore constriction parameter β , and (c) ratio of cake to pristine membrane resistances R_c/R_m .

Figure 5.10. Schematic of membrane internal fouling by the (a) aminated and (b) unmodified PS particles. The rectangles represent membrane pore walls, the gaps between the rectangles represent pores, the circles represent PS particles, and the arrows denote directions of permeate flow. The left and right columns represent earlier and later stages of fouling.

5.6. Conclusions

The current study was targeted at understanding the internal membrane fouling mechanism by colloidal foulants (namely, polystyrene; size was less than a quarter of the membrane pore size) with different zeta potentials using the 3D OCT imaging technique and a newly developed internal fouling model that additionally accounts for internal cake filtration. The OCT analysis indicated greater extents of particle deposition in the case of the positively charged aminated and less negatively charged un-modified PS particles, which is consistent with the more severe flux declines relative to the carboxylated PS particles. Furthermore, the internal fouling model that factors in pore constriction, pore blockage and internal cake filtration further revealed the differences in the deposition mechanisms due to the different foulant surface charges. For the positively charged aminated PS particles, the attractive particle-membrane interaction led to a more homogeneous layer-by-layer cake growth, which resulted in denser packing in the pore and higher internal cake resistance. In contrast, for the less negatively charged un-modified PS particles, the repulsive particle-particle and particle-membrane interaction resulted in more random deposition of the particles inside the pores, resulting in more extensive pore constriction and blockage, as well as lower resistance of the internal cake. With respect to the most negatively charged carboxylated PS particles, because of the greatest repulsive interaction with the membrane and with other PS particles, the internal pore fouling was the least extensive, thereby giving the least flux decline.

This study indicates the significance of the surface charge of colloidal foulants in internal fouling and provide valuable insights on the less understood internal fouling mechanisms. The findings in this study are based on ideal spherical, rigid particles, but serves as a good baseline from which less ideal foulants can be further investigated. For example, for elastic or deformable foulants, or foulants that tend to form gels or bridges, the particle shape and characteristic size change due to factors like operating pressure, particle-membrane interaction and particle-particle interaction, which are expected to affect the fouling parameters (e.g., denser cake and hence higher R_c). As another example, for membranes with more complex matrices (e.g., inter-connected pores in polymeric membranes), internal fouling is expected to be quite different too. On one hand, regardless of depositing particle characteristics, the mathematical basis and physical meanings of the three fouling parameters β , α and R_c still hold to reflect the extent of pore constriction, pore blockage and internal cake filtration. On the other hand, the mathematical model may need to be modified to account for the effect of the interconnection of the pores on the internal fouling.

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Appendix

Figure 5.11. Size distribution of solution of 0.2 g/L aminated, un-modified and carboxylated PS particles. The 0.001 g/L solutions were not used to measure the size distributions because the concentration was too low for representative results.

Figure 5.12. Best-fitted normalized fluxes (left column) and total resistance (right column) for aminated PS particle type. (a) and (b): three-mechanisms model, (c) and (d): two-mechanisms model, (e) and (f): one-mechanism model.

Figure 5.13. Best-fitted normalized fluxes (left column) and total resistance (right column) for un-modified PS particle type. (a) and (b): three-mechanisms model, (c) and (d): two-mechanisms model, (e) and (f): one-mechanism model.

Figure 5.14. Best-fitted normalized fluxes (left column) and total resistance (right column) for carboxylated PS particle type. (a) and (b): three-mechanisms model, (c) and (d): two-mechanisms model, (e) and (f): one-mechanism model.

Figure 5.15. Plot of $\log (d^2t/dV^2)$ vs. $\log (dt/dV)$ for aminated PS particles.

Figure 5.16. Plot of $\log(d^2t/dV^2)$ vs. $\log(dt/dV)$ for un-modified PS particles.

Figure 5.17. Plot of $\log(d^2t/dV^2)$ vs. $\log(dt/dV)$ for carboxylated PS particles.

Table 5.2. Values of best-fitted membrane fouling parameters via regression analysis of the normalized flux declines using the three-mechanism model.

	Aminated PS	Un-modified PS
Pore blockage, α (m^2/kg)	1989.73	3058.66
Pore constriction, β (kg^{-1})	3285.38	5706.14
Resistance ratio R_c/R_m	24.39	4.4

List of symbols

A_b	membrane area blocked by the particles, i.e., blocked region, m^2
A_0	initial membrane area, m^2
A_u	membrane area not blocked by the particles, i.e., unblocked region, m^2
C	particle concentration, kg/m^3
J	permeate flux, $m^3/(s.m^2)$
J_b	permeate flux through the blocked region, $m^3/(s.m^2)$
J_0	initial permeate flux, $m^3/(s.m^2)$
J_u	permeate flux through the unblocked region, $m^3/(s.m^2)$
P	trans-membrane pressure, Pa
Q	permeate flow, m^3/s
Q_b	permeate flow through blocked region, m^3/s
Q_0	initial permeate flow, m^3/s
Q_u	permeate flow through unblocked region, m^3/s
r_0	pore radius, m
R_c	cake resistance, m^{-1}
R_m	membrane resistance, m^{-1}
t	filtration time, s
t_p	transition time between pore constriction and cake filtration, s
α	pore blockage parameter, m^2/kg
β	pore constriction parameter, kg^{-1}
γ	volume of the pore occupied per unit mass of particles, m^3/kg
δ	membrane thickness, m

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Chapter 6. CONCLUSIONS AND OUTLOOK

6.1. Conclusions

In Chapter 3, the OCT 3D imaging was applied to the investigation of membrane fouling by oil emulsions, both external fouling and internal fouling. The insights obtained here are useful for ascertaining the fouling tendencies of oil emulsions and thereby formulating mitigation means accordingly. The current study confirms that comparing the OCT results from the fouling by oil droplets with those by glass beads is an effective way to identify the optical artifacts and retrieving useful information from the OCT datasets.

The application OCT imaging to study membrane fouling by oil-in-water emulsions was extended to a more complicated cases in Chapter 4, where stabilizing surfactants were taken into accounts (namely, nonionic Tween 20, positively charged CTAB and negatively charged SDS). The thermodynamic models DLVO and XDLVO were applied to correlate the fouling with the interaction energies. (i) The flux enhancement conferred by CTAB was linked to the greatest attraction between CTAB and the membrane at shorter separation distances (< 3 nm) predicted by the DLVO model, although it should be noted that this attraction was unexpectedly not tied to the worst fouling by the oil emulsion observed via OCT; and (ii) the more extensive fouling by the Tween 20-stabilized oil emulsion was tied to the least peak (repulsive) energy value given by both DLVO and XDLVO models. The thickest fouling layer for the feed containing Tween 20 was tied to the least repulsive energy at separation distances of less than 10 nm predicted by the DLVO model and the least peak (repulsive) energy magnitude at a separation distance of about 3 nm predicted by the XDLVO model.

The study in Chapter 5 aimed at understanding the internal membrane fouling mechanism by colloidal foulants (namely, polystyrene; size was less than a quarter of the membrane pore size) with different zeta potentials using the 3D OCT imaging technique and a newly developed internal fouling model that additionally accounts for internal cake filtration. The OCT analysis indicated greater extents of particle deposition in the case of the aminated and un-modified PS particles, which is consistent with the more severe flux declines relative to the

carboxylated PS particles. Furthermore, the internal fouling model that factors in pore constriction, pore blockage and internal cake filtration further revealed the differences in the deposition mechanisms due to the different surface charges. For the positively charged aminated PS particles, the attractive particle-membrane interaction led to a more homogeneous layer-by-layer cake growth, which resulted in denser packing in the pore and higher internal cake resistance. In contrast, for the less negatively charged un-modified PS particles, the repulsive particle-particle and particle-membrane interaction resulted in more random deposition of the particles inside the pores, resulting in more extensive pore constriction and blockage, as well as lower resistance of the internal cake. As for the most negatively charged carboxylated PS particles, due to the greatest repulsive interaction with the membrane and with other PS particles, the internal pore fouling was the least extensive, thereby giving the least flux decline.

6.2. Outlook

This series of studies provided more detailed mechanistic understandings of external by solid particles and liquid oil droplets. In Chapter 3, the ability to monitor internal fouling in real time and non-invasively paves the way for more in-depth understanding of membrane filtration. The study in the chapter revealed that various optical artifacts could be involved in the OCT results, which reduced the spatial resolution of OCT and increased the difficulty in interpreting the fouling process. Also, the OCT analysis carried out his limited to low concentrations of foulants (since the refractive index was assumed to be that of water) and cases whereby the oil coalescence is not too severe (since the intensity at the lower layers may decrease too significantly). Therefore, further studies shall be carried out to develop more effective algorithms to improve the accuracy of the quantitative analysis. Based on the findings in Chapters 3 and 4, further studies of membrane fouling by oil droplets could focuses on the investigation of internal fouling phenomena. In that case, as said, further development of more effective analysis method could be conducted, as internal fouling is usually the more complicated when dealing with the deformable, wettable oil droplets. In Chapter 5, the internal fouling studies was extended to the case of solid foulant.

The model developed in this chapter could be modified further to account for more complicated membrane fouling phenomena such as those when the membrane pores are interconnecting or when the foulants are deformable or clustering.

As mentioned at the beginning of this thesis, although many studies have been conducted, the understanding of the membrane fouling is still far from perfect due to its very inherent complication. There are lots of work need to be done until the full picture of membrane fouling mechanism is revealed.

Chapter 7. LIST OF PUBLICATIONS

1. T.A. Trinh, Q. Han, Y. Ma, J.W. Chew, Microfiltration of oil emulsions stabilized by different surfactants, *Journal of Membrane Science*, 579 (2019) 199-209.
2. T.A. Trinh, W. Li, Q. Han, X. Liu, A.G. Fane, J.W. Chew, Analyzing external and internal membrane fouling by oil emulsions via 3D optical coherence tomography, *Journal of Membrane Science*, 548 (2018) 632-640.
3. Internal fouling during microfiltration with foulants of different surface charges. Accepted by *Journal of Membrane Science*. Authors: T.A. Trinh, W. Li, J.W. Chew
4. Q. Han, T.A. Trinh, J.W. Chew, Cake formation of bidisperse suspensions in dead-end microfiltration, *Journal of Membrane Science*, 577 (2019) 31-40.
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6. Q. Han, W. Li, T.A. Trinh, X. Liu, J.W. Chew, A network-based approach to interpreting pore blockage and cake filtration during membrane fouling, *Journal of Membrane Science*, 528 (2017) 112-125.
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Chapter 8. APPENDIX

8.1. MICROFILTRATION OF MONODISPERSE SUSPENSION OF SOLID FOULANTS: EFFECTS OF SURFACE CHARGES ON EXTERNAL FOULING

The content of this section has been published under the title of *Effect of the surface charge of monodisperse particulate foulants on cake formation* in Journal of Membrane Science, Volume 548, 15 February 2018, Pages 108-116 (<https://doi.org/10.1016/j.memsci.2017.11.017>).

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

Abstract

In membrane filtration process, membrane fouling is inevitable whereby the particulate foulants deposit on membrane surface and reduce the filtration throughput and selectivity. This study investigated the impact of membrane external fouling by three types of latex particulate foulants of similar size but with different surface charges. Interesting results were found that the negatively charged latex particles gave the worst performance in comparison with the positively charged latex, which was counter-intuitive in terms of particle-membrane charge interactions. Three-dimensional (3D) optical coherence tomography (OCT) image analysis [1] were employed to reveal the underlying mechanisms for the different fouling behaviors: (i) negatively charged particles tended to deposit on the pore region of the negatively charged membrane due to the repulsive particle-membrane electrostatic interactions, rather than deposit on the non-pore region (i.e., the dead zone), leading to complete pore blockage and greater initial cake resistance; (ii) the negatively charged particles, due to the

similar repulsive particle-membrane and particle-particle interactions, also tended to cluster more and deposited on other deposited particles, leading to a more inhomogeneous cake and thereby greater specific cake resistance.

Keywords: Membrane fouling; Surface charge; External Fouling; Optical coherence tomography; Microfiltration

8.1.1. Introduction

Membrane fouling is a major problem of membrane filtration, which requires in-depth understanding of the fouling phenomena to mitigate the fouling. Experimentally, various techniques have been used to study the fouling [2-4] to figure out the fouling mechanisms. Many observations and understandings have been obtained via different monitoring techniques such as electrical impedance spectroscopy (EIS) [5], direct observation through the membrane (DOTM) [6], confocal laser scanning microscopy (CLSM) [7] and optical coherence tomography (OCT) [1]. Together with the experimental efforts, mathematical modeling has also been applied to provide more understandings of the fouling mechanisms [8]. Although many studies have been done investigating various kinds of foulants in membrane filtration, the effect of colloidal surface charge on membrane fouling is not yet completely answered. In natural waters, colloidal particles are ubiquitous, having a wide size range from nanometers to micrometers and negative surface charges [9,10]. Their zeta potential can become positively charged when pH changes [11] or in the presence of a coagulant [12,13]. Research efforts have been made to reveal the impact of the surface charges of particulate foulants. McDonogh et al. [14,15] found that when 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 classical DLVO theory was used to explain the decreasing specific cake resistance trend. Similar trends, with colloidal particles of higher surface charge tending to give more porous cakes, were reported in other studies [16-18]. However, in contrast, Huisman et al. [19] found that neither the charge of the membrane nor the charge of the particles had any effect on the critical flux. Recently [20], two types of negatively

charged particulate foulants were investigated 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 [21]. In this work, however, the electrostatic component of the total energy was found to be minor in comparison to the Lewis acid-base and Lifshitz-van der Waals components in the XDLVO theory, which agrees with previous reports [22,23]. In summary, various reports have revealed differences in the observed effects of particle surface charge on membrane fouling; however, the zeta potential values reported was mostly negative and therefore, the understanding remains incomplete. As a result, this study extended the investigation of the particle surface charges to both positive and negative zeta potentials using non-invasive observation via OCT.

The objective of this work is to investigate the effect of surface charges of particulate foulants on membrane fouling mechanisms via OCT image analysis [1], with the assistant of network modeling [24]. Polystyrene particles of similar size but different surface charges (namely, positively charged aminated particles and negatively charged un-modified and carboxylated particles) were investigated. The OCT technique was applied to provide 3D imaging of the fouling process, via which the underlying mechanism of the membrane external fouling progress was revealed.

8.1.2. Experimental Procedure

8.1.2.1. Membrane Fouling Experiments

Dead-end filtration was in this study. Polycarbonate track-etched (PCTE) membrane (WH-111111, Whatman) was used, with pore diameter of 2 μm and porosity of 0.05. The zeta potential (Malvern Zetasizer nano-zs) of the membrane was -35.3 mV. Three types of latex particles with similar particle diameters of 3 μm were used: non-modified (catalog number 79166, Sigma, Aldrich), aminated (catalog number AM003UM, Magsphere) and carboxylated (CA003UM, Magsphere) particles. The zeta potentials (Malvern Zetasizer nano-zs) of the three particles was listed in Table 2.1, showing that the aminated particles had positive charge and the other two were negatively charged. It should be noted that since uncharged particles would naturally aggregate, the neutrally charged

latex particles were unavailable to use as a control. The concentration of the latex particles was 0.005 g/L.

The dead-end filtration cell was made of acrylic, consisting of an upper feed chamber (70mm × 70mm × 24mm) and a lower permeate chamber (70mm × 70mm × 24mm). The two chambers were separated by the membrane, with an effective filtration area of 962 mm². Constant trans-membrane pressure (TMP) was applied and generated by the gravity difference between the feed and permeate. The feed stream entered the upper chamber via four inlets (each with a diameter of 6 mm) uniformly distributed on the chamber walls to minimize the lateral flow of the feed in the chamber. To provide mechanical support to the membrane, a porous stainless-steel plate was positioned right under the membrane. The permeate flow was recorded every 30 s. To minimize any difference in the hydrodynamic conditions among the three particle types, particularly in view of the deviation from purely normal flow associated with track-etched membranes [25,26], the TMP was fixed at different values of around 6 kPa in order to maintain the initial permeation flow rate of DI water at a value of 80 mL/min. Each test for each condition was repeated at least three times.

Table 8.1. Zeta potential values of the PCTE membrane (pore diameter of 2 μm and membrane porosity of 0.05) and the three latex particles with similar diameters of 3 μm.

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

8.1.2.2. Membrane Fouling Characterization via Optical Coherence Tomography

The optical coherence tomography (OCT; GANYMEDE-SP5, Thorlabs) technique was used to carry out three-dimensional (3D) scans of the membrane

filtration cell during fouling. The light beam had a central wavelength of 905 nm and a bandwidth of 200 nm, giving a depth resolution of 2 μm in water. The working principles of OCT can be found in Section 2.1 and other reports [1,27]. In every experiment, the 3D OCT scan was initially performed for 5 min with DI water and another 35 mins with the feed solution of 0.005 g/L of latex particles. The A-scan to provide a depth profile [28] was performed at 30 kHz every 1.5 s.

To analyze the OCT image, a method was proposed by Li et al. [1], where the coordinate of the feed-membrane interface was determined by comparing the intensity gradients across the z -direction of the image with a pre-determined threshold value; the positions where the OCT intensity gradients were greater than the threshold value were designated as the feed-membrane interface and as layer 0. Based on the determined feed-membrane interface, a series of layers parallel to the feed-membrane interface was defined which were evenly spaced 2 μm apart in vacuum, which was approximately equal to the depth resolution of the OCT system. In pure water, the real physical distance approximately equaled 1.5 μm . (Figure 8.2a).

After the layers were identified, the concept of fouling voxels was adopted to monitor the evolution of the cake layer. Specifically, the means and standard deviations of the OCT intensities were calculated for each layer at $t = 0$, after which a voxel in that layer was determined as a fouling voxel if its intensity was greater than the mean plus twice the standard deviation (i.e., 95% confidence interval [29,30]) (Figure 8.2b). To quantify the evolution of fouling, the number fraction of fouling voxels with respect to the total number of voxels in each layer were quantified with respect to the filtration volume V .

Figure 8.1. (a) Schematic depicting the principle of the 3D scan of dead-end membrane cell using the low-coherence Fourier-domain OCT; (b) representative OCT image of a clean membrane (the red line indicates the feed-membrane interface); and (c) representative OCT image of the fouled membrane ($t = 35$ min, TMP = ~ 6 kPa, foulant concentration = 0.005 g/L).

Figure 8.2. (a) Schematic indicating the layers identified from the analysis method for interpreting the OCT data; and (b) snapshots showing the evolution of fouling voxels during membrane filtration.

8.1.3. Results and Discussion

8.1.3.1. Evolution of Permeate Flux for Latex Particles of Three Different Surface Charges

According to the surface charges of the membrane and the foulants (Table 8.1), the positively charged aminated latex was expected to have the worst fouling due to attractive foulant-membrane interactions. However, Figure 8.3 indicates that it was the more negatively charged carboxylated latex that gave the worst membrane fouling, whereas the fouling was the least in the case of the positively charged aminated latex. This counter-intuitive observation of the flux results was further investigated by OCT imaging.

Figure 8.3. Normalized permeate flowrate in membrane filtration with feeds containing each of the three different surface charges of latex particles. The TMP was constant at ~ 6 kPa. The foulant concentration was 0.005 g/L.

8.1.3.2. Analyzing Fouling using OCT

Figure 8.4 displays the evolution of the fraction of fouling voxels in four different layers (namely, 1, 3, 5 and 7) with respect to filtration volume. In the figure, the fraction of fouling voxels increased for all three cases of particle types as the filtration progressed, implying the increasing in the extent of fouling with time. Besides, it also showed that the layers closer to the membrane had greater extent of fouling. Hereby, three observations are notable. Firstly, the fractions of fouling voxels were the greatest for the carboxylated latex, corresponding to the most flux decline as shown in Figure 8.3. The fractions of fouling voxels increased less in the case of non-modified latex and least for the aminated latex. Secondly, among the three particles, the increasing in the fouling voxels of the four layers were most distinctive for the positively charged aminated latex (Figure 8.4a), while those of Layers 1 and 3 were closer to each other for the non-modified latex (Figure 8.4b) and carboxylated latex (Figure 8.4c). For the aminated latex (Figure 8.4a), its distinctive rates of fouling in different layers suggests the sequential build-up of the cake layers, in which case the formed cake layer would tend to be more uniform (Figure 8.5c). On the other hand, the less distinctive rates of fouling between Layers 1 and 3 for the other particles imply

a more similar rate of deposition of the particles in both layers, indicating the more inhomogeneous cakes (Figure 8.5d). Lastly, for the carboxylated particles, the significantly greater value in the fractions of fouling voxels in Layers 5 and 7 compared to that of the aminated particles suggests a growth of the clusters (Figure 8.5d) which was absence in the case of the uniform cake (Figure 8.5c). The proposed mechanism of deposition in Figure 8.5 was further affirmed using the network modeling analysis which can be found in the full version of the published paper of this chapter [31].

Via the flux decline, OCT image analysis and the network modeling, it was found that the aminated particles, which was attractive to the membrane due to the opposite charge signs (Table 8.1), tended to deposit on the non-pore region (i.e., the dead-zone) which led to the incomplete blockage (Figure 8.5a) and hence less flux decline. Also because of the same attractive interaction, the aminated particles deposition was sequentially layer-by-layer deposition and more homogeneous cake (Figure 8.5c) which was revealed by the OCT image analysis. On the other hand, the non-modified and the carboxylated particles, which had the same charge sign with the membrane, was repulsed by the membrane and therefore tended to deposit on the pore region, resulting in complete blockage (Figure 8.5b) and inhomogeneous cake with clusters (Figure 8.5d).

Figure 8.4. 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 Figure 8.4(c), but too small to be clearly visible.

Figure 8.5. Schematic of the hypothesized membrane fouling schemes.

8.1.3.3. Topology of the Deposits

Taking the advantage of 3D imaging by OCT, patterns of the fouling voxels in each layer were further analyzed based on the techniques described by Dixmier [32] to explore the topology of the deposition. Specifically, the patterns in each layer were classified into four categories: individual fouling voxels (Category A); groups of 2–5 adjoining fouling voxels (Category B); groups of 6–10 adjoining fouling voxels (Category C); groups of more than 10 adjoining fouling voxels (Category D). Figure 8.6 and Figure 8.7 presents the fraction of fouling voxels of each category at various filtration volumes for Layer 1 and Layer 3, respectively.

In Figure 8.6, at a distance $\sim 1.5 \mu\text{m}$ above the feed-membrane interface (i.e., Layer 1), as the filtration volume increased, the fouling pattern shifted from

individual fouling voxel to clusters of higher number of fouling voxels. At 200 mL (Figure 8.6a), the deposits were more dispersed, thus the largest fractions was of Categories A and B. At this state, the effect of surface charge was insignificant which was revealed that the difference among the three particle types was negligible. At 500 mL (Figure 8.6b), the fraction of Categories A and B reduced and the fraction of Categories C and D increased, and the three particles showed differences between one another. The positively charged aminated particles had the greatest fractions in individual voxels (Category A) and small clusters (Category B), while the negatively charged carboxylated particles had the greatest fraction in Category D which was the largest cluster group. This indicates the tendency of the aminated particles to cluster less compared to the negatively charged particles. For the non-modified particles, their tendency to cluster rather than to form a more dispersed layer of deposits agrees with a previous study, and was explained by the attractive Gibbs free energy of interaction [20]. At filtration volume of 800 mL (Figure 8.6c), it was easily expected and observed that the fractions in Category D increased while those in Categories A and B decreased, as much more particles had deposited. The effect of the different surface charges was consistent with that of filtration volume of 500 mL that the positively charged aminated particles deposition was more dispersed and the negatively charged carboxylated particles deposition was most clustered. The higher dispersity in the deposition of the aminated particles could be explained by the particle-membrane attraction but particle-particle repulsion; whereas for the negatively charged carboxylated particles, the greater tendency to form larger clusters in deposition could be attributed to the more similar particle-membrane and particle-particle affinities. Besides layer 1, at Layer 3 (Figure 8.7), similar trends as Layer 1 (Figure 8.6) were observed. Collectively, the results in Figures 2.6 and 2.7 are consistent with the hypothesized cake morphology resulting from the earlier OCT results (Figure 8.4) and backed by network modeling as in [31]: the aminated particles tended to form a more uniform cake (Figure 8.5c) while the carboxylated particles a more inhomogeneous cake (Figure 8.5d). The effects of particle charge on membrane fouling was clearly observed.

Figure 8.6. 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 fouling voxels, while Categories B, C and D represent groups of fouling voxels consisting of 2–5 adjoining fouling voxels, 6–10 adjoining fouling voxels and greater than 10 adjoining fouling voxels, respectively. Each error bar represents the 95% confidence interval based on a t -test.

Figure 8.7. 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 fouling voxels, while Categories B, C and D represent groups of fouling voxels consisting of 2–5 adjoining fouling voxels, 6–10 adjoining fouling voxels and greater than 10 adjoining fouling voxels, respectively. Each error bar represents the 95% confidence interval based on a *t*-test.

8.1.4. Conclusions

3D OCT image analysis [1] has been employed in this study to reveal the impact of the surface charge of monodisperse solid particulate foulants on

membrane external fouling. Interesting counter-intuitive results were observed in the permeate flux that the positively charged aminated particles showed the least flux decline relative to the two negatively charged particles, despite the expectation that the attractive electrostatic interactions between the positively charged and the negatively charged membrane would lead to the worst flux decline. OCT image analysis was used to provide more understands of the underlying fouling mechanisms.

Three observations were obtained from OCT analysis. Firstly, the fractions of fouling voxels were the greatest for the carboxylated particles, which was consistent with the most severe flux decline, followed by the non-modified particles and lastly the aminated particles. Secondly, the rate of fouling at different layers were most distinctive for the positively charged aminated particles, suggesting the progressive cake growth and the homogeneous cake; on the other hand, fouling rates at layers 1 and 3 were more similar to each other for the non-modified latex and carboxylated latex, suggesting the inhomogeneous cake growth. Last but not least, the significantly greater fraction of fouling voxels in layers 5 and 7 of the carboxylated latex particles compared to that of the aminated further affirmed the proposed cake morphology: more inhomogeneous cake for carboxylated particles and more uniform cake for the aminated particles. the differences in the deposition patterns between the particles was attributed to the membrane-particle interaction: aminated particles with attractive membrane-particle interaction preferred incomplete blockage and carboxylated particles with repulsive membrane-particle interaction tended toward complete blockage. The hypothesis obtained from the OCT characterization results was affirmed by the adoption of the network model method presented in detail in [31], which was not included in this thesis. In summary, the mechanistic understanding of the counter-intuitive filtration performance of the three solid particulate foulants of different surface charges was revealed. From this, further investigations are warranted such as effects of membrane property (e.g., membrane porosity [33]), operating condition (e.g., different initial permeate flux [26]) and foulant property (e.g., polydisperse particulate foulants [34-36]).

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8.2. MICROFILTRATION OF BIDISPERSE SUSPENSIONS OF SOLID FOULANTS: EFFECTS OF BIDISPERSITY ON EXTERNAL FOULING

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Abstract

Membrane external fouling in dead-end microfiltration of feeds of different bidispersity compositions was investigated using three-dimensional (3D) optical coherence tomography (OCT) imaging. Polystyrene particles of two different sizes, namely, 3 and 5 μm was chosen as solid particulate foulants, and polycarbonate track-etched (PCTE) membrane with nominal diameter of 2 μm was used. The OCT imaging and analysis revealed that (i) in terms of cake growth, homogeneous cakes was formed in the case of bidisperse feeds, but heterogeneous cakes was formed with higher concentration of larger particles; (ii) in terms of clustering, clustering was enhanced by the lower concentration of larger particles and reduced by a higher concentration of the same larger particles; and (iii) in terms of dynamic of the deposition, the deposition and detachment of the particles were more dynamic in the case of the monodisperse feed of small particles, while they were negligible in the case of the bidisperse feed with the highest concentration of larger particles.

Keywords: Microfiltration; Membrane fouling; Bidisperse feeds; Cake formation

8.2.1. Introduction

In industry, membrane filtration is widely used to improve the quality of the feed or the permeate streams in the production line [1]. However, membrane fouling is inevitable that both reduces productivity and efficiency [2] and increases operating cost [3]. Mitigation of membrane fouling requires in-depth understandings of the fouling mechanisms, which are usually complex and not yet fully understood. Research efforts have been made to solve the puzzle piece by piece, in which various membrane fouling monitoring and characterization techniques have been applied, such as electrical impedance spectroscopy (EIS) [4-6], ultrasonic time domain reflectometry (UTDR) [7,8], confocal laser scanning microscopy (CLSM) [9,10], direct observation through the membrane (DOTM) [11] and optical coherence tomography (OCT) [12]. With these techniques, many interesting observations and understandings have been acquired. For examples, with UTDR Xu et al. monitored the fouling by kaolin particle on a single hollow fiber membrane, and Sim et al. employed EIS in characterizing the fouling evolution of the reverse osmosis membrane with the silica and protein as the foulants [6]. Besides, in other studies, DOTM was applied to reveal the effect of particle size and crossflow rate on critical flux [13,14] and CLSM was employed to study the 3D structure of monodisperse and bidisperse cakes [10]. With OCT, Gao et al. visualized the velocity field and the growth of fouling layers [15].

In practical microfiltration, the feeds, such as fermentation broth, wastewater, juices, alcoholic beverages, etc. [16], are usually the suspensions of mixture of particles of different sizes which led to membrane fouling. However, the characteristics of the cake formation of polydisperse particles still lack understandings and therefore requires more investigation. In literature, Zhang et al. found that with the presence of larger particles, the critical fluxes of the mixed suspensions increased [14]. Tanudjaja et al. investigated the effect of spacer and crossflow velocity on the critical flux of bidisperse suspensions and figured out the effectiveness of the bidispersity in enhancing critical flux at lower crossflow velocities [13]. Ngene et al. visualized cake formation and found the specific cake resistance to be higher than the theoretical values obtained from the Kozeny-Carman relation, which implied better ordering or compaction of the cake formed

by bidisperse particles [17]. Klaver et al. found that small particles hinder migration of large particles in all the cases of the reviewed study [18]. Prior works have revealed various effects of the bidisperse particles on cake formation in membrane fouling; however, the bidisperse cake characteristics and dynamics are still not yet a complete picture.

This study aimed to provide more understandings of the influence of bidisperse feed on membrane fouling, focusing on the external fouling. Four different cases of filtration feed (namely, one monodisperse and three bidisperse feeds of different compositions for comparison) were investigated. The real-time non-invasive 3D OCT characterization was applied to provide in-depth information of the cake morphology and the evolution of the cake.

8.2.2. Experimental and Analysis Methods

8.2.2.1. Membrane Fouling Experiments

Dead-end filtration was employed in this study. The dead-end filtration was employed with constant TMP generated by gravity. The filtration cell consisted of upper feed chamber and lower permeate chamber separated by the membrane with an effective filtration area of 9.62 cm². The membrane was polycarbonate track-etched (PCTE) membrane (Whatman, USA) with pore diameter of 2 µm and porosity of 0.05. The feed was the suspensions of polystyrene (PS) particles with identical density of 1.05 g/cm³ but different mean diameters of 3 µm and/or 5 µm (Sigma Aldrich). The zeta potentials of particles (Malvern Zetasizer nano-zs) and membrane (Anton Paar, Surpass) were shown in Table 8.2. The fouling test for each condition was repeated at least three times.

Table 8.2. Zeta potentials of PS particles and the PCTE membrane.

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

Four different feeds of PS particles were investigated (Table 8.3) as follows:

- Case I, consisted of 5 mg/L of monodisperse 3 μm particles and served as a benchmark.
- 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 5 mg/L and similar to the total mass in Case I.
- Case III was a bidisperse suspension of 5 mg/L of 3 μm and 2.5 mg/L of 5 μm particles. Case III was Case I added 2.5 mg/L of 5 μm particles.
- Case IV was a bidisperse suspension of 2.5 mg/L of 3 μm and 11.6 mg/L of 5 μm particles. In this case, the numbers of 3 μm particles and 5 μm particles was equal. The number of 3 μm particles was similar to Case II. The total number concentration is similar to the total number concentration in Case I.

The four cases were chosen as listed because: (i) comparing Cases I and II provides understanding of the effect of bidispersity at the same total mass concentrations with mono-dispersity; (2) comparing Cases I and IV provides understanding of the effect of bidispersity at the same total number concentrations with mono-dispersity; (3) comparing Cases I and III reveals the effect of the addition of larger particles to the suspension of smaller particles; and (4) comparing Cases II, III and IV investigates the effect of the component ratio in the bidisperse suspension.

8.2.2.2. OCT Imaging

The Fourier-domain [12] optical coherence tomography (OCT; GANYMEDE-SP5, Thorlabs) was used to monitor and capture the membrane fouling images. The light beam had a central wavelength of 905 nm and a bandwidth of 200 nm, yielding a lateral and a depth resolution of respectively 4 μm and 2 μm in water. The principles of OCT have been detailed in past studies [12,19] and in Chapter 2.

The filtration was started with DI water as the feed for the first 5 mins, followed by the PS particles suspensions (Table 3.2) as the feed for the next 35 mins. The permeation flux was recorded every 30 s and the 3D OCT scans were

performed at an A-scan rate of 30 kHz every 1.5 s. Each experiment was repeated at least three times.

Table 8.3. Summary of the four different feeds investigated in the current study.

Cases A*, B* and C* were from our earlier study [20] and used here for comparison. M_f and N_f represent the mass concentration and number concentration, respectively.

	Total mass concentration of the feed (mg/L)	Total number concentration of the feed ($\times 10^{-8}$ L)	3 μm		5 μm		Mass ratio of 3-5 μm latex	Number ratio of 3-5 μm latex
			M_f (mg/L)	N_f ($\times 10^{-8}$ L)	M_f (mg/L)	N_f ($\times 10^{-8}$ L)		
Case I	5	3.37	5	3.37	-	-	-	-
Case II	5	2.054	2.5	1.69	2.5	0.364	1:1	4.6:1
Case III	7.5	3.734	5	3.37	2.5	0.364	2:1	9.3:1
Case IV	14.1	3.37	2.5	1.69	11.6	1.69	0.22:1	1:1
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	-	-

8.2.2.3. OCT Image Analysis

The identification of the feed-membrane interface were done based on method developed by Li et al. [12]. Specifically, the intensity gradients across the z-direction of the images was compared with a predetermined threshold value, and the positions at which the OCT intensity gradients were greater than the threshold value were designated as the feed-membrane interface and indexed as Layer 0 (Figure 8.8). From Layer 0, the subsequent layers that were evenly 2 μm apart from one another were indexed as Layers 1, 2, 3 and so on. (Figure 8.9a). In water, the actual physical distance between these layers was approximately 1.5 μm , since the distances in the OCT images are the optical path lengths based on the refractive index of vacuum. To monitor the extent of fouling, the concept of fouling voxels [12,20-22] was applied. Specifically, the mean and standard

deviation of the OCT image intensities were first calculated for each layer at $t = 0$; in subsequent images at $t > 0$, the voxels having the intensity greater than the mean plus twice the standard deviation (i.e., 95% confidence interval) [23,24] was defined as the fouling voxel (Figure 8.9b). Furthermore, using the method described by Dixmier [25], the patterns of the fouling voxel on each layer can be analyze to give the information of the pattern of the deposition. Specifically, in this study the pattern of the fouling voxels was categorized as follows: individual fouling voxels (Category A), groups of 2–5 adjoining fouling voxels (Category B), groups of 6–10 adjoining fouling voxels (Category C), groups of more than 10 adjoining fouling voxels (Category D).

Figure 8.8. Representative OCT image of membrane, with the red line indicating the feed-membrane interface: (a) clean membrane and (b) fouled membrane.

Figure 8.9. (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 fouling voxels at three time points (namely, 30 s, 100 s and 1800 s) of membrane filtration.

8.2.3. Results and Discussion

8.2.3.1. Analyzing the Fouling Phenomena using OCT

8.2.3.2. Layer-by-Layer Cake Growth

Figure 8.10 shows the evolution of flux of the four cases (Table 8.3), among which Case IV gave the least flux decline. Case IV was the bidisperse system with the smallest mass ratio ($M_{f,3\mu m}/M_{f,5\mu m} = 0.216$) and number ratio ($N_{f,3\mu m}/N_{f,5\mu m} = 1$), 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 [10]. 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 [13,14].

Figure 8.11 presents the growth of the cake layer for the four bidisperse feeds (Table 8.3). Each sub-figure in Figure 8.11 displays the fractions of fouling voxels at 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.

Figure 8.11 showed that the fraction of fouling voxels in all layers increased with time, indicating the progressive growth of the cake layer as the filtration proceeded, with the layers closer to the membrane generally had more particles deposited. Two interesting observations that highlight differences in the cake characteristics should be noted. Firstly, while in Cases II and III, the growth of the cake of the four layers were distinctive from one another (Figures 8.11b and c), indicating the layer-by-layer growth of the cake; in Case I (Figure 8.11a) and also to some extent in Case IV (Figure 8.11d) the cake growth at Layers 1 and 3 were similar, implying the uneven cake thickness [20]. Therefore, Case I displayed an inhomogeneous cake whereas Cases II and III exhibited uniform cakes. Secondly, Case IV showed to have the fastest rate of particle deposition, followed by Case III, then Cases I and II. This fastest cake growth and the least flux decline trend of Case IV (Figure 8.10) implied the higher cake porosity compared to the other cases.

Figure 8.10. Evolution of the permeate flow rate normalized with respect to the initial permeate flow rate for four different feeds.

Figure 8.11. 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.

8.2.3.3. Topology of the Deposits

Figures 8.12 and 8.13 presents the patterns 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) at different deposited mass D_m .

Regarding both Layers 1 (Figure 8.12) and 3 (Figure 8.13), as the filtration proceeded, the deposit pattern shifted from individual fouling voxels and smaller clusters to the larger clusters. On Layer 1 (Figure 8.12), Cases II and III had the largest clusters throughout the filtration, while for Case I, the highest fractions were always of individual voxels (Category A) or smaller clusters (Category B), meaning that the bidispersity enhanced clustering at the lower concentration of larger particles, while the higher concentration of the larger particles eliminated

that (Case IV) due to the augmented shear-induced diffusivity [13,14]. This is consistent with the uniform cake formation by Cases II and III seen in Figure 8.11. Similar clustering patterns by bidisperse feeds have been observed, whereby the smaller particles tended to deposit around the larger particles [10].

On Layer 3 (Figure 8.13), similar to Layer 1, at the earlier stage of the filtration (Figure 8.13a) Cases II and III had more clusters compared to Cases I and IV. However, for large clusters (Category D) at the deposited mass of 2 mg, their fractions 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 as discussed earlier.

Figure 8.12. 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 fouling voxels, while Categories B, C and D represent groups of fouling voxels consisting of 2–5 adjoining fouling voxels, 6–10 adjoining fouling voxels and greater than 10 adjoining fouling voxels, respectively.

Figure 8.13. 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 fouling voxels, while Categories B, C and D represent groups of fouling voxels consisting of 2–5 adjoining fouling voxels, 6–10 adjoining fouling voxels and greater than 10 adjoining fouling voxels, respectively.

8.2.3.4. Analyzing the Fouling Dynamic

Figures 8.14 and 8.15 respectively present the dynamic of the deposition of the particles (i.e., the dynamic deposition and removal of the particles) in layers 1 and 3, represented by the change in the fraction of fouling voxels with time. Firstly, at each time point it was the difference between the higher value in Figure 8.14a and the lower value in Figure 8.14b, and between the higher value in Figure 8.15a and the lower value in Figure 8.15b that contribute to the net increment of the fraction of fouling voxels as depicted in Figure 8.11. Secondly, in general, the fractions of deposited and removed fouling voxels both increase for between 200–1000 s before decreasing with time, indicating the higher initial dynamic of the particle deposition which became steadier at the later time point. Thirdly, the fractions were greater at layer 3 compared to layer 1, implying that the dynamic was 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) had (i) shorter the initial increasing period, (ii) higher increasing and decreasing slopes, and (iii) higher fractions before the peak fractions and lower fractions after the peak fractions. This indicates the significant influence of the enhanced shear-induced diffusion associated with larger particles in affecting deposition and removal dynamics [10,13,14]. For Case IV that had the greatest concentration of large particles, the fractions peaked the earliest and were the lowest after the peak. For Cases II and III, since the concentration of the larger particles were similar, their trends were more similar to each other too.

Figure 8.14. 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 8.15. 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..

8.2.4. Conclusions

The current study applied the 3D OCT imaging to understand cake formation by feeds containing bidisperse particles. Polystyrene particles of two sizes (3 μm and 5 μm) were used. Four different feeds were investigated: a monodisperse feed of the smaller particles serving as a control and three bidisperse feeds with different component compositions (Table 8.3). The flux decline was observed to be the least for the bidisperse feed with the greatest concentration of large particles despite having the greatest overall concentration.

From the OCT image analysis it was found that, (i) the monodisperse feed and the bidisperse feed with the greatest concentration of large particles gave inhomogeneous cakes, while the bidisperse feeds with lower concentrations of large particles gave homogeneous cakes; (ii) clustering was enhanced by the lower concentration of the larger particles but reduced by a higher concentration of the larger particles; and (3) the bidispersity enhanced the dynamic of the particle deposition.

This study therefore contributed to the mechanistic understanding of cake formation by bidisperse particles, which is valuable in microfiltration in practice. Further studies on different factors such as different membranes and different polydispersities are warranted.

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List of Symbols

D_m	deposit mass (mg)
M_f	mass concentration, mg/L
N_f	number concentration, $\times 10^{-8}$ /L

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