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**UNDERSTANDING MEMBRANE FOULING OF OIL IN
WATER EMULSION-BASED SEPARATIONS**

HENRY JONATHAN TANUDJAJA

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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**UNDERSTANDING MEMBRANE FOULING OF OIL IN WATER
EMULSION-BASED SEPARATIONS**

HENRY JONATHAN TANUDJAJA

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 plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

10 January 2019

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SUPERVISOR DECLARATION STATEMENT

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

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.....
Date

.....
Assoc. Prof. Chew Jia Wei

AUTHORSHIP ATTRIBUTION STATEMENT

This thesis contains material from 7 paper(s) published in the following peer-reviewed journal(s) where I was the first author.

Chapter 1 is published as **H.J. Tanudjaja**, C.A. Hejase, V.V. Tarabara, A.G. Fane, J.W. Chew, *Membrane-based separation for oily wastewater: A practical perspective*, Water Research, 156 (2019) 347-365.

The contributions of the co-authors are as follows:

- All authors provided the initial project direction and edited the manuscript drafts.
- I and Charifa prepared the manuscript drafts, and I finalized the draft.
- The manuscript was reviewed by Prof Chew, Prof Tarabara and Prof Fane.

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The contributions of the co-authors are as follows:

- Prof Chew Jia Wei provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was reviewed also by Prof Tarabara and Prof Fane.
- I performed all the laboratory work at the School of Chemical and Biomedical Engineering, NTU and I also analyzed the data.
- All characterization of the feed solution, was conducted by me.

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The contributions of the co-authors are as follows:

- Prof Chew Jia Wei provided suggestions for the study and edited the manuscript drafts.
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- All characterization of the feed solution, was conducted by me.

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- Prof Chew Jia Wei provided the initial project direction and edited the manuscript drafts.
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- Prof Chew Jia Wei provided suggestions for the study and edited the manuscript drafts.
- I initiated the idea, wrote the drafts of the manuscript and performed all the laboratory work at the School of Chemical and Biomedical Engineering, NTU and I also analyzed the data.

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- Prof Chew Jia Wei provided suggestions for the study and edited the manuscript drafts.
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- All characterization of the feed solution, was conducted by me.

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The contributions of the co-authors are as follows:

- Prof Chew Jia Wei and Prof Fane provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- Pee Wen Xi did the early data collection for the project and I followed up the result
- I performed the rest of laboratory work at the School of Chemical and Biomedical Engineering, NTU and I also analyzed the data.

12 April 2019

.....
Date

.....
Henry Jonathan Tanudjaja

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“If you want to go fast, go alone.

If you want to go far, go together.”

-African Proverb-

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UNDERSTANDING MEMBRANE FOULING OF OIL IN WATER EMULSION-BASED SEPARATIONS

ABSTRACT

Oil in water emulsion could be present in many industries, in terms of product or waste and the separation of the oil emulsion from the water is always a challenge due to its small size which could not efficiently handle by conventional separation technologies. Membrane technology has been increasingly employed for this separation process due to its selective and efficient performance, but still has a drawback which is the fouling. Studies regarding the membrane fouling due to oil in water emulsions are done by Direct Observation through Membrane (DOTM) in the microfiltration system to explore more understanding about the fouling. It is observed that different operation parameter could play a role in the membrane fouling. Higher crossflow velocity and lower oil feed concentration decrease the fouling propensity regardless the type of oil used, meanwhile higher viscosity slows down oil emulsion movement on the membrane surface, and bidispersity of the oil emulsion also affects the fouling mechanism. Shear-induced diffusion model helps to predict the critical flux of the oil emulsion separation. From the DOTM images, it is understood that oil emulsion fouling evolves from individual deposit into moving stripes or became a moving oil cake layer, which is a different characteristic in comparison to the unmoved latex particle cake layer. Interaction energy model reveals the physical understanding of the interaction between oil emulsion with the membrane surface during the fouling phenomenon.

Keywords: Direct Observation through the Membrane (DOTM), Membrane fouling, Oil in water emulsion, Cross-flow velocity (CFV), Shear-Induced Diffusion, Interaction Energy (DLVO).

CHAPTER 1: A PRACTICAL PERSPECTIVE OF MEMBRANE-BASED SEPARATION FOR OILY WASTEWATER

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Abstract

The large volumes of oily wastewater generated by various industries, such as oil and gas, food and beverage, and metal processing, need to be de-oiled prior to being discharged into the environment. Compared to conventional technologies such as dissolved air flotation (DAF), coagulation or solvent extraction, membrane filtration can treat oily wastewater of a much broader compositional range and still ensure high oil removals. In the present review, various aspects related to the practical implementation of membranes for the treatment of oily wastewater are summarized. First, sources and composition of oily wastewater, regulations that stipulate the extent of treatment needed before discharge, and the conventional technologies that enable such treatment are appraised. Second, commercially available membranes, membrane modules, operation modes and hybrids are overviewed, and their economics are discussed. Third, challenges associated with membrane filtration are examined, along with means to quantify and mitigate membrane fouling. Finally, perspectives on state-of-the-art techniques to facilitate better monitoring and control of such systems are briefly discussed.

Keywords : Membrane fouling; oil-water separation; oil emulsion; fouling mitigation; on-line monitoring; membrane modification

1.1.Introduction

Oil-water mixtures are found in many industrial processes, and can take the form of a product, a by-product or a waste stream. Whether the goal is for recovering the oil for economic gains or removing the oil phase for environmentally friendly disposal, the separation of the oil and other immiscible components is necessary. Environmental regulations governing the discharge of oily wastewater have become increasingly stricter, with country-specific regulatory limits on the maximum oil concentration of generally within the 5 to 40 mg/L range [1]. The oil phase in wastewater can exist in three forms, classified based on the size of the oil droplets [2], namely, free oil ($> 150\ \mu\text{m}$), dispersed oil (20 to $150\ \mu\text{m}$), and emulsified oil ($< 20\ \mu\text{m}$). The choice and performance of oil-water separation techniques depend not only on oil droplet size, but also on other considerations, such as oil concentration and chemical composition. Membrane filtration is a promising technology for separating oil droplets smaller than $\sim 10\ \mu\text{m}$ [3]. Notably, the increasing interest in the employment of membrane filtration for the treatment of oily wastewater is evident in the significant increase in the number of publications over the last three decades (1988-2018), vis-à-vis more conventional methods, as depicted in Fig 1.1. Correspondingly, a review of the advances to date on this topic is warranted.

Figure 1. 1. Number of publication for each technology from 1988 to 2018. The data was extracted from Web of Science on December 7, 2018, with the keywords of “oil AND wastewater AND (technology)”.

Unfortunately, membrane fouling is a major drawback that reduces productivity and increases operational costs of membrane filtration. Many efforts have been dedicated to understanding the mechanisms of membrane fouling, and to develop methods to effectively monitor and mitigate membrane fouling. The focus of the review is on the practical aspects of applying pressure-driven membranes to the treatment of oily wastewaters, highlighting the requirements, recent development, drawbacks and corresponding mitigation strategies.

In the first section of this paper, we review the common sources and properties of oily wastewater, the discharge regulations, as well as technologies that have been used to treat oily wastewater. In the subsequent section, the advantages of using membranes for the treatment of oily wastewater commercially will be reviewed along with the

related challenges and counter-measures. In the final section, we review the state-of-the-art technologies of monitoring and mitigating membrane fouling, and discuss the potential of membranes for the treatment of oily wastewater.

1.1.1. Oily Wastewater: Sources, Quantities and Composition

Oily wastewater is a by-product generated by many industries including oil and gas, food and beverage, shipping and maritime, tanning, textile, and metal and machining [2, 4]. Oily wastewater not only adversely affects the environment if not adequately treated, but also represents a substantial economic loss if the oil is not recovered.

Oil-water separation has received renewed interest with the recent developments in the fossil fuel sector, particularly for the treatment of produced water, which is oily wastewater stream from the oil and gas extraction operations [1, 2]. Produced water is generated from onshore as well as offshore wells. The global produced water generated is approximated at 250 million barrels/day for every 80 million barrels/day of oil produced, with 800 million m³ of produced water were discharged from offshore facilities throughout the world in 2003 alone [5, 6]. The treatment of the enormous volume of produced water is important from both an environmental perspective to reduce water consumption and minimize waste disposal, and also from an economic perspective as expenses on water management can account for 5% - 15% of drilling costs [5, 6]. Other than oil, complex constituents in produced water include many type of chemicals, such as linear chain hydrocarbons, aromatic hydrocarbons (benzene, toluene, and xylene), metals, naturally occurring radioactive material (NORM), and additive chemicals such as corrosion inhibitors and emulsion destabilizers [2, 4, 5]. The composition of produced water as well as its physical and chemical properties are generally site-specific [5].

In the food, drink and milk industry, water is a significant component in most products [7], and also is involved in many steps and processes, such as washing, rinsing, mixing, pasteurizing, etc. [8]. Because the amount of oily wastewater produced is also large, the implementation of means for reuse is cost-effective due the economies of scale [9]. Most of the oil waste comes from meat, poultry, seafood and dairy, thus the wastewater typically has a very high content of organic carbon.

Another major producer of oily wastewater is the metal processing industry where cutting oil is used as a coolant and flushing fluid [2, 10]. Cutting oils are emulsions consisting of oil, water and additives such as fatty acids, surfactants, heavy metals and biocides [11]. The oil content in such waste streams is too low for it to be incinerated, yet they are too toxic to be treated biologically.

In summary, oily wastewater from various industries tends to be of very complex and varied compositions, which complicates the selection of an appropriate treatment technology and calls for context-specific treatment solutions.

1.1.2. Regulations for Discharging Oily Wastewater

The direct discharge of oily wastewater into the environment without proper treatment can have grave consequences, including the disruption of the aqueous ecosystem, pollution of the groundwater or drinking water resources, and endangering human health [12]. Region-specific regulations have been introduced to enforce the treatment of oily wastewater prior to its discharge to the environment. In the North Sea region, Oslo-Paris (OSPAR) convention regulates that the upper limit for the discharge of oil content in the wastewater is 30 mg/L [13]. According to the Paris convention, the upper limit of oil content to be discharged to the sea is 40 mg/L for the offshore fields and 5 mg/L for the on-land fields [14]. In the U.S., the Environmental Protection Agency

(EPA) stipulates a maximum oil content of 72 mg/L for any 24 hour period and 45 mg/L over a 30 days period [15].

Other studies reported on regulations with similar limits of oil concentration that can be released into the open water, e.g., maximum oil content of 40 mg/L, typical range around 10-15 mg/L [4, 16]. In Norway, the limit on the oil concentration allowed to be discharged into the sea from an offshore installation to the Norwegian Continental Shelf was reduced from 40 to 30 mg/L as of 2007, which implies the increased stringency in the quality of the discharge. In China, the upper limit for oil concentration in the discharged wastewater is 10 mg/L [12]. These regulations compel an urgent need for developing technologies that can reach these treatment goals cost-efficiently. The common technologies for treating oily waste water are discussed in the next section.

1.1.3. Oily Wastewater Treatment: Conventional Technologies

An overview of the common technologies used in treating oily wastewater is provided in Table 1.1, along with the oil concentration ranges in the feed and the removal effectiveness [1, 6, 17]. Each method has its own challenges in treating oily wastewater.

Table 1. 1. Common Technologies for treating Oily Wastewater

No.	Method	Brief Description	Feed Oil Concentration	Extent of Oil Removal in Effluent Concentration	Ref.
1	Dissolved Air Flootation (DAF)	Removal of oil by attachment to micron-size bubbles and floatation	500 ppm	95% removal	[18]
2	Fentone Process	Poly-ferric sulfate used as a coagulant	12,000 ppm	65.8% removal	[19]
3	Coagulation	Adding Coagulant to create oil-contained flocs that sink	7,000-15,000 ppm	90% removal	[20]
4	Solvent Extraction	Removal of free oil or dissolved oil in lighter hydrocarbon solvent	5,410 ppm	93% removal	[21]
5	Froth Flootation	Separation of oil by mixing with surfactant, and aerated in a stirrer to float oil-saturated bubbles	25,000-50,000 ppm	55% removal	[22]
6	Biodegradation	Degradation of oil by microorganisms	10,000 ppm	98% degradation	[23]
7	Adsorption	Usage of porous material to adsorb oil	1,040-1,710 ppm	67% removal	[24]

1.2. Membrane Technology for Oil-Water Separation

Membrane-based separation is the most cost-effective solution for removing oil droplets smaller than $\sim 10\ \mu\text{m}$ [25]. The amount of oil in the emulsified fraction can be significant, making the removal of these droplets a prerequisite for meeting environmental regulations. Separation methods based on the oil/water density differential (e.g., settling, flotation, hydrocyclone) require an exceedingly long retention time for the removal of emulsified oil, while chemical treatment (e.g., fenton process, coagulation) may not effectively de-stabilize oil-in-water emulsions particularly when the emulsified oil is finely dispersed [26]. Compared to the conventional methods, membrane filtration offers several advantages that include higher quality permeate, lower space footprint, more straightforward automation, no need for extraneous chemicals and therefore reduced waste, and lower energy input [4, 27-29]. These advantages, coupled with the ability of membranes to reject other pollutants present in the feed, make membranes competitive with the more traditional technologies.

As with all membrane filtration processes, the key drawback that limits the broader implementation of membrane-based oil-water separations is membrane fouling [2], which is the cumulative deposition of the feed constituents like oil on the surface of the membrane and inside the pores that results in a decline in the permeate flux and quality. Other limitations of membrane technology include lower throughput (e.g., much lower than that of hydrocyclones) and relatively higher capital costs.

Given that membrane-based separation is most effective for the oil droplet size range of 1 - $10\ \mu\text{m}$, ultrafiltration (UF) and tighter microfiltration (MF) are the more relevant choices [30]. However, if the wastewater is saline and desalination is an accompanying treatment goal, employing reverse osmosis (RO) and nanofiltration (NF)

can allow for a single-step processing of such waste streams [2]. Membrane distillation (MD) also shows promise [31-34]. In this section, commercially-available membranes are discussed, followed by membrane modules, then batch and continuous modes. The last two sub-sections focus on hybrid or integrated membrane processes and the economics of the membrane process.

1.2.1. Commercially-available membranes for oily industrial wastewater

The membrane-based processing of oily wastewaters, sometimes combined with conventional methods, has been successfully implemented in more than 3000 polymeric UF/MF installations and over 75 inorganic/ceramic ones worldwide since 20 years ago [2]. According to a report by Grand View Research Inc., the global market for the treatment of produced water, which is the major wastewater in the oil and gas industry, reached \$5.81 billion in 2015, of which 46.8% was for secondary separation technologies including membrane-based techniques [35]. Several companies such as Osmonics, Koch, Alcoa, Veolia and Filtration Solution Inc. offer commercial membranes for oil-water separation. Table 1.2 presents a list of some of the membranes available on the market currently.

Table 1. 2. Commercial membranes designed and marketed for oil-water separation applications

Manufacturer	Filtration type	Pore size / MWCO	Configuration	Membrane material	Membrane area per element, m ²	Specific water flux, L/(m ² ·h·bar)	Ref.
Osmonics	UF	0.01 µm	Spiral Wound	Chemically modified PAN	24	-	[36]
Filtration Solution Inc.	UF	0.01 µm	Spiral Wound	Chemically modified PAN	26	-	[37]
Clean Water Tech PTE, Ltd	UF	0.01 to 0.1 µm	Hollow Fiber	Hydrophilic PAN	30	13-20	[38]
Veolia Water Technologies	UF	0.1 µm	Tubular	TiO ₂	10.7	-	[39]
Koch	UF	50 kDa	Hollow Fiber	Polysulfone	25	-	[40]
Hydranautics	RO	-	Spiral Wound	Composite Polyamide	37	0.54	[38]

Osmonics and Filtration Solutions Inc. offer spiral wound ultrafiltration membrane modules to concentrate oily wastewater streams: M-Series UltraFiloc and SHP series membranes, respectively [36, 37]. Both membranes are made from a chemically modified polyacrylonitrile (PAN) and designed to protect the membrane from fouling by “free” oil and from degradation by solvents. To minimize fouling, these membranes have been engineered to be extremely hydrophilic (i.e., water contact angle of 4°) relative to the conventional polyvinylidene difluoride (PVDF) and polysulfone (PS) membranes that are hydrophobic [36]. In addition, both membranes can operate at temperatures of up to 50 °C, and can withstand pH values in the range from 2 to 10 for continuous operation and from 3 to 9 for when Cleaning-In-Place (CIP) is incorporated into the process. Typical permeate fluxes are 8 to 34 L/(m²·h) for the M-Series Ultrafiloc membranes and 17 to 43 L/(m²·h) for the SHP series membranes [36, 37].

Numerous membrane companies offer integrated treatment systems to process oily industrial wastewater. Akvola Technologies established a flotation-filtration system (akvoFloat) that can lower both energy consumption and footprint [41] of treatment. The system consists of two stages that are integrated in the same tank. The first stage is flotation whereby the suspended oil is carried to the surface by bubbles with the aid of the Akvola MicroBubble Generator, which induces fine gas bubbles using low pressure air, nitrogen, ozone or carbon dioxide (CO₂). The role of the microbubbles is to attach to the oil droplets and particles, which are carried to the surface and then continuously skimmed off. The second stage entails membrane-filtration with submerged ceramic membranes ($d_{pore} = 0.2 \mu\text{m}$) positioned below the float layer [41].

CDM Smith is currently marketing a hybrid system to treat produced water containing up to 20,000 mg/L of total dissolved solids. This system combines several commercially available technologies, namely, microfiltration (MF), ion exchange, UV

disinfection and reverse osmosis (RO). The pretreatment consists of filtering the feed solution through prefiltration (cartridge filter with a nominal pore size of 1 to 3 μm) to remove particulates, followed by ion exchange to remove polycations, and then UV disinfection to reduce bacterial activity. Finally, the water undergoes a multi-stage RO process, employing a combination of low-pressure RO (capable of achieving 85% recovery) and seawater RO membranes (80% water recovery) [42].

Veolia Water Technologies offers a produced water system OPUS[®] (Optimized Pretreatment and Unique Separation) technology, which consists of multiple treatment processes, namely, chemical softening via Multiflo[®] with filtration, followed by ion exchange, then RO. The pretreatment processes before the RO step are designed to reduce the hardness and suspended solids in the feed solution, eliminating the potential for precipitative and colloidal fouling of the RO membranes [39].

Clean Water Tech Pte Ltd provided a UF hollow fiber membrane with pore size ranged from 0.01 to 0.1 μm , which was made from hydrophilized polyacrylonitrile (Ultra-Flo U630C). The pH range that this membrane could tolerate was 2 - 12, and the maximum feed pressure and temperature possible were respectively 3.5 bar and 50 °C. In addition, a RO composite polyamide spiral wound membrane (SWC3+) from Hydraunatics could handle feeds with pH ranged from 3 – 10, and maximum operating pressure and temperature of 83 bar and 45 °C, respectively [38].

These examples of commercially available membranes indicate the practical feasibility of such processes. In the last two decades, the focus on the treatment of oily wastewater has made available membranes that can withstand reasonable ranges of temperature, pressure and pH to cater to the complexities of such feeds.

1.2.2. Membrane modules

Different kinds of membrane types and modules and system have been employed in oil-water separation processes (Table 1.3). The common module designs are flat sheet, spiral wound, tubular, capillary, and hollow fiber, with flat sheet and tubular being more popular.

Flat sheet modules are commonly employed in research laboratories for bench-scale experimentation. The advantages include relative simplicity of module design and operation, and availability of wide range of pore sizes (spanning RO, NF, UF and MF). However, one of the key advantages is that the membrane area per unit module volume is low and thereby less feasible for commercial implementation because of the larger footprint necessary. Nonetheless, flat sheet membranes form the basis for the dominant RO module, namely, the spiral wound membrane (SWM) module, which is a stack of flat-sheet membranes, with spacers between the sheets, rolled and placed inside a cylindrical case. Such a packing method significantly enhances the availability of membrane area per unit module volume for filtration. Tubular membranes, capillary and hollow fiber membranes differ by the lumen size (inner lumen diameters greater than 0.635 cm, between 0.1 to 0.635 cm, and between 0.025 to 0.1 cm, respectively). Most of the ceramic membranes, which have greater mechanical strength as well as chemical and thermal stability, are tubular. The drawback is the limited availability of such membranes to only UF and MF. One of the chief advantages of hollow fiber membranes is the greatest membrane area per unit volume vis-à-vis tubular and flat sheet ones, which is giving this membrane type more attention in the membrane community.

Table 1. 3. Membrane type and module for oil-water separation

No.	Module	Type	Material	Reference
1	Tubular	MF	Carbon	[43]
2	Tubular	MF	Ceramic	[14]
3	Tubular	MF	Alumina	[44]
4	Flat Sheet	MF	PVDF ¹	[45]
5	Flat Sheet	MF	PTFE ² / PVDF	[46]
6	Tubular	MF	α -Alumina	[4]
7	Tubular	MF	Alumina	[47]
8	Tubular	MF	PVDF / PS	[48]
9	Tubular	MF	GO ³ - Alumina	[49]
10	Flat Sheet	MF	Nylon	[50]
11	Disk Shaped	MF	Ceramic	[16]
12	Hollow Fiber	UF	S-PPSU ⁴	[51]
13	Tubular	UF	Ceramic	[52]
14	Flat Sheet	UF	Cellulose / PS ⁵	[53]
15	Flat Sheet	UF	Polysulfone	[54]
16	Flat Sheet	FO ⁶	Cellulose Triacetate	[55]
17	Flat Sheet	FO	Polysulfone	[56]
18	SWM	RO	Polymer type	[57]
19	Flat Sheet	RO	Polyamide / Polydopamine	[58]
20	Flat Sheet	NF	PVDF / PDMS ⁷	[59]
21	Flat Sheet	NF	Polyamide	[60]
22	Flat Sheet	UF	Polysulfone	[60]
23	Flat Sheet	NF-RO	Polyester-Polysulfone	[29]

¹PVDF = Polyvinylidene fluoride

²PTFE = Polytetrafluoroethylene

³GO = Graphene oxide

⁴S-PPSU = Sulfonated polyphenylenesulfone

⁵PS = Polysulfone

⁶FO = Forward osmosis

⁷PDMS = Polydimethylsiloxane

1.2.3. Membrane-filtration in batch or continuous operation modes

Membranes can be operated either in batch or continuous mode. Most of the separation processes in the industry are performed in the continuous mode, whereby the feed stream is continuously flowed through the unit, thus the feed concentration remains relatively constant. In contrast, in batch processing, the feed stream becomes increasingly concentrated with time, due to the permeation of water to the permeate side and thus increasing the fouling tendency. Batch processing is useful if the concentrated retentate is one of the desired product also along with the permeate. In the following sub-sections, the reports on batch and continuous membrane-based processes for oily wastewater are summarized.

1.2.3.1. Batch processing

Most of the reports on the use of membrane in de-oiling application in the batch mode are on treating the oily wastewater from the olive oil milling process. Stoller and Chianese optimized the UF and NF batch process for the purification of the olive-washing wastewater by using the critical flux concept [61]. Specifically, the critical flux was determined for various concentrations, then employed as the basis for choosing the permeate flux value near and below the critical flux in order to delay the fouling and extend the membrane lifetime particularly as the feed got more concentrated in the batch process. The reason for using the batch mode was its operability with a smaller active membrane area at a smaller scale relative to the continuous mode; membrane fouling, however, was worse for the batch system with time. The system consisted of a continuous aerobic biological reactor, followed by a SWM UF batch system, and then the NF batch process, after which the purified water was discharged to the municipal

sewage system. The results show that, by implementing a permeate flux based on the critical flux help extend membrane lifetime and decrease fouling. Another study on deoiling olive mill wastewater used an integrated MF/NF system followed by either osmotic distillation (OD) or vacuum membrane distillation (VMD) [62]. The MF system was employed in a batch concentration mode at 0.72 bar and 22 °C, while the NF batch system was operated at 20 °C and 8 bar. This integrated system was used to recover and concentrate the polyphenols from the olive mill wastewater, with 78% of polyphenols recovered in the MF system, and the rest recovered by the NF. The VMD had a higher flux, but required a higher power consumption in comparison to the OD system due to the need for a vacuum pump or a refrigeration step for condensing the permeate. Paraskeva et al. studied a batch process for treating olive mill wastewater by integrating UF, NF and RO at various values of temperature and transmembrane pressure (TMP) [63]. At the pretreatment step, a ceramic ultrafilter with a nominal pore size of 0.1 µm was operated at 15 - 35°C and 1 - 2.5 bar. The NF/RO hybrid system used polymeric membranes (MWCOs of 200 Da and 100 Da for NF and RO, respectively) operated at TMP values of 10-30 bar and 30-40 bar for NF and RO, respectively.

Batch processing is employed mainly to recover or retain certain desired product from the oily wastewater, which means the retentate rather than the permeate is the valuable component. In such cases, the batch mode is preferred, since the lower feed volume vis-à-vis continuous processing allows for better control of the retentate quality and the capital costs are lower. The drawback is the lifetime of the membrane, since the progressive concentration of the product in the retentate inevitably leads to extensive membrane fouling, which necessitates more frequent membrane cleaning or replacement.

1.2.3.2. Continuous flow processing

The continuous flow mode is more suitable for treating large amounts of oily wastewater as is the case, for example, in the oil and gas industry. Ebrahimi et al. used continuous processing for treating produced water using an integration system that included MF, dissolved air floatation (DAF), as well as crossflow UF (CFUF) and NF systems [64]. The MF membrane was made of aluminum oxide (Al_2O_3) and had a pore size in the 0.1 - 0.2 μm range, while the UF and NF membranes were made of titanium dioxide (TiO_2) and had MWCOs of 20,000 (UF), 1000 and 750 Da (NF), respectively. The process was carried out by directing the produced water continuously through the MF unit, followed by a batch DAF unit, and finally by the continuous CFUF or NF system. All the units were operated at TMP values ranging from 0.5 to 2 bar, crossflow velocities of 0.6 to 1.3 m/s, and feed concentrations ranging from 32 to 5420 mg/L of oil. Most of the oil (93%) was removed by MF, with rest of the process train ensuring 99.5% total removal of oil.

Polymeric membranes such as PVDF have also been employed for the continuous processing of oily wastewater [65]. Specifically, the surface morphology was modified by hydrophilic microspheres on the PVDF membrane surface, turning the membrane from naturally hydrophobic to super hydrophilic. The permeate flux when treating the oil emulsion was $\sim 2,700 \text{ L}/(\text{m}^2 \text{ h})$, which was significantly higher in comparison to the pristine hydrophobic PVDF membrane, and the oil rejection was up to 99%.

Continuous processing is mostly used to treat oily wastewater from various industries prior to discharge into the environment to comply to the regulations. The main focus in such cases is to purify the water as much as possible to allow for safe release

into the environment with negligible impact to the ecosystem and reuse in the plant. Although the main target is the volume of the treated water, the retained oil also has economic value. The other advantage of the continuous mode is the feed flow that provides a tangential shear at the membrane surface to mitigate membrane fouling, thereby prolonging the lifetime of the membrane.

1.2.4. Hybrid membrane processes

Oily wastewater can have a very complex composition and contain suspended and dissolved species that differ in concentration, size, charge and density. In order to achieve a sustainable membrane-based separation of oily wastewater, it is often necessary to integrate the membrane unit with other membranes, whether in batch or continuous processes as described previously, or other conventional unit processes. Such integration may ease the foulant load on the membrane thereby mitigating membrane fouling and prolonging the membrane lifetime.

Membrane fouling can be mitigated using adequate pretreatment. Different physical, biological, and chemical methods have been used for the pretreatment of oily wastewater; these include gas sparging [66, 67], coagulation [68], flocculation [69], centrifugation [68], electrocoagulation [70], acidification [71], cartridge pre-filtration [68], dissolved air flotation (DAF) [18], activated carbon adsorption [72] as well as separation by larger pore size membranes such as UF [73-75] and MF [76].

Karakulski and Morawski employed an integrated membrane system based on UF and NF to treat waste oil-water emulsion from a cable factory [68] (Fig. 1.2) UF with 100 kDa MWCO membranes resulted in 99% rejection of suspended solids, and retention of oil and lubricants. The resulting UF permeate was further purified by NF to reject the remaining pollutants and reduce the content of copper ions (i.e., dominant

constituent in the oily wastewater from the cable factory). Another study proposed a hybrid system that used flocculation as a pretreatment [69]. By coupling this pretreatment with the downstream MF with a 0.2 μm pore size zirconia membrane, the permeate flux was increased and permeate quality improved in comparison with MF alone.

Figure 1. 2. Example of hybrid membrane system (UF-NF) used to treat oily wastewater [68].

One study utilized adsorption with membrane-filtration for treating oily wastewater and demonstrated that the integration increased the permeate quality and reduced membrane fouling [77]. Powdered activated carbon (PAC) and natural zeolite were compared in terms of the effectiveness as adsorbents at the MF pretreatment stage. Total organic carbon (TOC) removal was up to 99.5% and 99.9% respectively for PAC and zeolite, with the latter performing better due to the higher oil adsorption rate and thereby lower fouling of the MF membrane. In another study on treating industrial oily wastewater with 550 mg(oil)/L of oil and 6500 mg(COD)/L, coagulation coupled with MF was used as a pretreatment step for UF [78]. Polyaluminum chloride was the coagulant used in combination with a ceramic 0.2 μm pore size MF membrane, followed by a PVDF UF membrane unit. The results demonstrated that the UF permeate flux increased 2.5 times compared to the process without pretreatment. The entire integrated system achieved up to 95.2% of COD reduction and 98.5% oil removal, which was much better than what could be accomplished with the standalone units or with any

other couplings. Other types of coagulation have also been integrated with membrane units, an example of which is electrocoagulation (EC) with RO [79]. In this study with feeds containing 1000 mg(oil)/L, EC functioned as a pretreatment step using either AC or DC current, after which the effluent was left in a sedimentation tank for 5 minutes before going through the RO unit. While EC gave 92% reduction of COD, which was sufficient alone to meet the current regulations for discharge to the sea, the subsequent RO unit achieved 100% removal of COD. The EC unit was also used in another study with MF to treat the oily wastewater from a drilling site [80], as shown by Fig. 1.3.

Membrane technology complements rather than replaces the conventional methods for treating oily wastewater to achieve a higher quality product sustainably. The integration of membrane-based and other methods harnesses the advantages and also circumvents the shortcomings of each.

Figure 1. 3. Schematic of hybrid membrane-electrocoagulation system [80].

1.2.5. Economics of membrane-based treatment of oily wastewater

As mentioned earlier, membrane technology is economically advantageous for oily wastewater treatment compared to the other conventional technologies. Based on the numbers available in literature, the cost of membrane-based treatment was estimated to be $\sim \$1\text{-}3/\text{m}^3$ [2, 81], which compares favorably with that for is $\$3.65/\text{m}^3$ cost of treatment by Dissolved Air Flootation (DAF). The cost inevitably depends on the source of the oily wastewater, since each industry has unique blends of oil and grease as well as other foulants specific to the process. For example, the total cost (including costs of membranes, labor, electricity, cleaning and maintenance) of treating oily wastewater from the fatty acid industry was $\$2.65/\text{m}^3$ [82], that from the railroad industry was $\$1.03\text{-}1.48/\text{m}^3$, while that for the metalworking wastewater using UF was $\$2.8/\text{m}^3$ [81]. In another study using MF, Nandi and coworkers estimated that the annual cost of the membrane-based treatment for oily wastewater with an oil concentration of 50 mg/L could be as little as $\$0.098/\text{m}^3$ for treating feeds at $100 \text{ m}^3/\text{day}$ [83]. Clearly, the cost of membrane-based treatment of oily wastewater is quite varied, but is nevertheless lower than that for conventional technologies. Moreover, more recently, the cost of membrane-based treatment has been slashed due to improvements in membrane fabrication and operation. As a benchmark, the total water treatment cost by RO desalination was around $\$0.5/\text{m}^3$, whereas that by the conventional thermal process was in the range of $\$0.8\text{-}1.1/\text{m}^3$ [84]. As another benchmark, the total cost for treating a secondary agriculture-based effluent stream was around $\$0.15\text{-}0.42/\text{m}^3$ [85].

1.3. The challenges of membrane operation

1.3.1. Mechanisms of membrane fouling by oil

The key obstacle that hinders the widespread implementation of membrane technology for oil-water separation is membrane fouling. Notably, the underlying mechanisms of membrane fouling by emulsified oil remains poorly understood, for example, the conditions under which the accumulated oil forms compressible cakes or contiguous films are unclear. Several studies have analyzed permeate flux decline during the filtration of oil-in-water emulsions and used blocking filtration laws (one of the first reports was by Hermia [86]) to explain the mechanisms of membrane fouling by oil [48, 87-91]. Two studies [83, 87] showed that membrane fouling by oil is due to cake formation whereby multiple layers of oil form a secondary membrane on the membrane surface. Other researchers linked membrane fouling by oil to intermediate pore blocking whereby the membrane is fouled by early stages of cake filtration and complete pore blocking [83, 87, 91]. Six out of the seven aforementioned studies applied the blocking filtration laws to crossflow filtration, although the Hermia blocking laws [86] do not take into account the back-transport of particles away from the membrane surface and only account for spherical, non-deformable particles. Oil droplets, which can both deform and coalesce, are unique foulants that challenge the available knowhow on fouling.

Another study investigated the fouling of NF and UF membranes using hexadecane-in-water emulsions stabilized by different surfactants, namely, a non-ionic surfactant (Triton X-100), anionic surfactant (sodium dodecylbenzenesulfonate; DDBS) and cationic surfactant (cetyltrimethylammonium bromide; CTAB) [60]. Experiments with surfactant-stabilized emulsions and pure surfactant solutions indicate that emulsified oil

rather than free surfactants is responsible for the increase in the TMP. UF crossflow filtration tests revealed that emulsions stabilized by CTAB quickly fouled the negatively charged polysulfone UF membrane due to electrostatic attraction between surfactant-stabilized oil droplets and the membrane. In contrast, membrane fouling was less severe in experiments with DDBS- and Triton-stabilized emulsions. In NF filtration tests, fouling increased exponentially regardless of the type of surfactant used to stabilize the emulsion [60]. For both UF and NF processes, fouling experiments and theoretical calculations indicated that cake layer formation underlies the initial membrane fouling by emulsified oil. However, depending on the type of emulsion and membrane, once the pressure drop across the cake layer reached a critical value, oil droplets can wet the membrane surface and lead to irreversible membrane fouling.

In a different study, He et al. conducted a set of constant permeate flux fouling experiments with PVDF MF membranes using multiple feed solutions, namely, latex bead suspension soybean, motor and crude oil-in-water emulsions [92]. The fouling tests were performed under the same hydrodynamic conditions and with the same membrane where the fouling propensity only depended on membrane-foulant and foulant-foulant interactions. The TMP profiles for motor and crude oil-in-water emulsions, which fouled more severely, exhibited slow TMP increase in the early stage, followed by an abrupt increase due to inhomogeneous fouling, and then the TMP eventually reached a pseudo steady-state with cake filtration as the operative fouling mechanism. The results also revealed that foulants with higher zeta potential have lower fouling propensity. Subsequently, the same group investigated the impact of permeate flux on membrane fouling [93]. Constant permeate flux tests with soybean and crude oil-in-water emulsions and PVDF MF membranes showed that above the threshold flux, TMP profile develops over three distinct stages: initial gradual TMP increase, followed by a TMP

jump, and then a pseudo-steady state TMP, which corresponds to the critical pressure of the oil layer [92].

Membrane fouling is inherently a complex phenomenon, and the fouling by oil droplets further augments the complexity due to unique phenomena such as coalescence [94], moving cake layer (Chapter 2), thinner but denser cake (Chapter 6), viscous effects (Chapter 5), better predictability by the DLVO (Derjaguin-Lewis-Verwey-Overbeek) rather than XDLVO (i.e., extended DLVO) model [95] (Chapter 3), effect of different surfactants [96], and internal membrane pore fouling despite the oil droplets being larger than the membrane pore [97]. While membrane fouling studies are abundant in the literature, the understanding on oil foulants remain comparatively limited. More studies on mechanistically understanding membrane fouling by oil is needed, particularly in view of the recent studies that have collectively shown oil to be distinctive from other particulate foulants.

1.3.2. Mitigating membrane fouling by oil: An overview of methods

This section introduces three main approaches to membrane fouling control and describes case studies to illustrate how each approach is applied in the context of oil-water separation.

1.3.2.1. Materials science approach: Making membranes resistant to fouling

An effective approach to reduce membrane fouling by oil is to increase the hydrophilicity of the membrane surface [71, 98, 99]. Water adsorption onto a hydrophilic surface restricts its interactions with oil and limits fouling with the hydration layer serving as an entropic barrier for oil attachment [71, 98]. Numerous techniques

have been used to increase the hydrophilicity of membranes by either blending common membrane polymers with hydrophilic additives (e.g. hydrophilic polymers, amphiphilic copolymers, and inorganic nanoparticles) or altering the membrane surface properties via chemical or physical post-modification (e.g. surface coating and surface graft polymerization) [71].

The incorporation of polyethylene glycol polymer chains alone or among copolymer blends is a common method for increasing surface hydrophilicity. Chakrabarty et al investigated the performance of four types of polysulfone (PS) UF membranes in the process of separating synthetic emulsions of crude oil in water under crossflow conditions [54, 100]. PS membranes were fabricated using different casting mixtures of N-methyl pyrrolidone (NMP), polyvinylpyrrolidone (PVP) and poly(ethylene glycol), which led to different membrane morphologies. The four membranes successfully rejected ~ 90% of the oil and the oil concentration in the permeate was below 10 mg/L, which met discharge requirements. In another study, Chen et al. modified the hydrophilicity of an ultrafiltration membrane by blending amphiphilic copolymers (Pluronic F127) with poly(ether sulfone) (PES) to separate oil-water emulsions. PES/Pluronic F127 membranes exhibited higher permeate flux and better antifouling property compared to the bare PES membrane [101]. While addition of hydrophilic polymers improves the fouling resistance of membranes, the introduction of hydrophilic polymers can lead to defects in the membrane, resulting in a breakdown of the membrane under high TMP [102]. The modification of commercial membranes to become more hydrophilic for anti-fouling characteristics to enhance oily wastewater treatment has been enabled by Osmonic, Filtration Solution Inc., and Clean Water Pte. Ltd., which offer hydrophilized polyacrylonitrile (PAN) as the membrane material, under different brand names (Section 1.2.1).

The usage of nanomaterials to improve membrane performance has also emerged in recent years. Zhan et al. used a halloysite nanotubes (HNTs) intercalated graphene oxide (GO) coating on a porous poly(arylene ether nitrile) nanofibrous support layer, which was further enhanced with another layer of mussel-inspired polydopamine (PDA) coating [103]. This combination gave superior performance of more than 99% oil rejection and high permeate flux of 1130.56 l/m²h for the gravity-driven filtration of a feed containing oil emulsion, because the nanotubes provided more water channels for permeation, and the hydrophilic PDA increased water flux and also rejected oil more effectively. Nano-sized polydopamine (nanocluster) coating was also employed by Wang et al. on a electrospun nanofibrous (ENF) membrane constructed from the cross-linking of polyacrylonitrile and hyperbranched polyethyleneimine (PAN/HPEI) [104]. The resulting membrane gave a high permeate flux of 1600 l/m²h and oil rejection of 98.5% also for gravity-driven filtration. Li et al. surface-modified a commercial PTFE membrane by using a polydopamine layer infused with nano-microsphere and hydrophilic carboxyl groups in a tetrahydrofuran (THF)-Tris buffer mixture [105]. The membrane exhibited rejection of up to 99% and permeate flux of around 2000 l/m²h for feeds containing various oils and surfactants. Another new trend for oil-water separation is the surface modification of an inorganic mesh, rather than polymer or ceramic membrane. Hou et al. had nano-sized nickel particle coating on a stainless steel mesh, which was made by using electrodeposition in deep eutectic solvent (DES) composed by choline chloride (ChCl) – ethylene glycol (EG) to separate oil and water [106]. Such modified meshes expressed superhydrophilicity and underwater superoleophobicity characteristics, which made the oil-water separation excellent for various oils (such as silicon oil, corn oil and crude oil). For feeds containing oil emulsion, the modified mesh was altered further by more electrodeposition to reduce the pore size of the mesh from

14 μm to 4 μm improve the rejection of the micron-sized oil droplets. The permeate flux of this gravity driven process was around 300 $\text{l/m}^2\text{h}$, but rejection was poor. Another study had a stainless steel mesh coated with copper via electrodeposition to make a hydrophilic membrane, which was modified further by applying dodecanethiol to make the membrane became superhydrophobic [107]. Both membranes were used concurrently in the filtration setup, such that water permeated through the superhydrophilic membrane and oil permeated through the superhydrophobic membrane, giving high permeate flux and separation efficiency greater than 99.8%.

Though the reported performances are excellent for such modified membranes, the practicality for commercial implementation has to be critically assessed. Firstly, the longer-term durability of such coatings particularly in the presence of cross-flow in practical operations. Most of these membranes and meshes were tested using gravity-driven filtration, which is not congruent with the presence of a continuous tangential shear on the membrane surface that may wash away the coatings with time. The hydrodynamic stability, on top of thermal and chemical stability, of such membranes needs to be addressed. Secondly, quite a number of such studies focused on treating feeds with free oil (i.e., droplets larger than 150 μm), which is more effectively separated by other means like hydrocyclones [2]. Thirdly, the uniformity of such modification across larger membranes has to be assessed, particularly because membrane fouling is a self-accelerating process.

1.3.2.2. Hydrodynamics-based approach: Controlling mass transfer of oil to the membrane surface in membrane modules

The hydrodynamics in the membrane filtration system is one of the most important factors that can be controlled to reduce membrane fouling. The velocity field

in the membrane module can be described by the Reynolds number (Re), an aggregate characteristic of the flow domain. At higher Re , the higher shear near the membrane surfaces compresses the mass transfer boundary layer and helps minimize deposition of foulants. Promoting turbulence in membrane flow channels has been accomplished by a number of means including vibration [108], bubbling [109], ultrasound [110] and spacers [111].

Inserting a static mixer into the flow channel of the tubular membrane [112] is one approach that can be effective in minimizing fouling by emulsified oil. The effect of different designs of static mixers was studied by computational fluid dynamics (CFD) simulations and experiments. A ZrO_2 ceramic membrane with an inner diameter of 6.8 mm and a nominal pore size of 50 nm was challenged by the oily wastewater feed consisted of 5 wt% of a cutting lubricant oil additive. The CFD results showed that the “spiral-ribbon” design for the static mixer was the optimal design for the membrane process, since the velocity increase caused by the static mixer caused the least increase of pressure drop inside the membrane channel, which agree with experimental results that indicated the positive impact on the permeate flux, higher retention of oil and also decreased fouling. Another study with a static mixer was carried out involved crossflow UF of cutting oil emulsion (5% w/w) at a constant temperature of 50 °C [113]. The zirconia membrane had a pore size of 20 nm, and the results showed that the presence of the static mixer as a turbulence promoter inside the membrane increased the permeate flux by up to 6 times at the highest TMP. A schematic of the static mixer and its coupling with the membrane cell is shown in Fig. 1.4. The static mixer increased the shear rate at the membrane surface, along with turbulence, secondary flow and instability effects, which led to significant flux enhancement. The static mixer was also used in another study for treating produced water from the Daqing oilfield, China, with 12.52 - 84.42

mg/L of oil [114]. Four different kinds of static mixer positioned inside an UF (100 kDa) PVDF tubular membrane, which gave an increase of flux in the range of 83-164%, as well as a decrease of dissipated power per unit volume of permeate of around 31-42%. The flux enhancement also increased with the increase of TMP and crossflow velocity.

Figure 1. 4. The schematics of the KenicsTM static mixer as a turbulence promoter in the tubular membrane [113]. (1) feed tank, (2) circulation pump, (3) pressure gauge, (4) membrane cell, (5) flow meter.

Turbulence promoters can also be in the form of a high-shear rotary device used in a UF unit, like the one studied by Viadero and coworkers to treat a synthetic oily wastewater of metal working fluids [115]. This system was operated by placing a static membrane in the membrane channel that was connected to a rotating shaft, which enhanced the hydraulic turbulence on the membrane surface and thereby minimized the buildup of concentration polarization (CP) and membrane fouling. The feed solution entered via the opening near the static membrane and the permeate was drawn out in the direction of the rotating shaft. In another study [116], a self-cleaning piezo electric membrane, made by modifying the porous lead zirconia titanate (PZT) membrane, enabled the promotion of turbulence on the membrane surface by the generation of an ultrasound wave using an alternating voltage. This membrane was hydrophilic and

oleophobic, which further enhanced the removal of the oil fouling layer. The system was challenged with a soybean oil emulsion with 200-500 mg/L of oil, and the results showed that higher permeate flux was achieved, but the effectiveness of the ultrasound wave decreased as the operating TMP increased.

The turbulence promoters mitigate membrane fouling and reduce the mass transfer resistance at the boundary layer, thereby increasing the permeate flux. Some limitations need to be resolved. For the static mixer, usage is limited to tubular ceramic membranes, which in turn limits the application to UF and MF, since such membranes are not available in the pore size ranges corresponding to NF and RO. The size of the static mixer could be shrunk to a smaller size amenable for use with hollow fiber membranes, which are more common and have more versatile applications. Nanoimprinting of patterned membranes are novel embodiments of static mixers [117, 118]. Regarding the high-shear rotary device, the current drawback is similarly the limitation to flat-disk membranes, but innovative designs for amenability to other membrane types are possible particularly with 3D printing [119]. Trade-offs are inevitable in the optimization of membrane processes. Increasing the shear stress gives better membrane fouling mitigation on one hand, but may affect the membrane integrity on the other hand and thereby reduce rejection.

1.3.2.3. “Damage-control” approach: Devising effective methods of membrane cleaning

Different cleaning procedures have been proposed and employed in practice to remove foulants from the membrane surface and/or from within membrane pores. Based on the nature of the cleaning methods, they can be classified as hydraulic, chemical and mechanical.

Hydraulic cleaning methods rely on water flushes, water back-flushes, and periodic TMP relaxation [120]. One of the studies employed hydraulic cleaning methods (back-flushing and cross-flushing) to clean UF and NF membranes fouled by hexadecane-in-water emulsions stabilized by Triton X-100, CTAB and DDBS [60]. The results showed that hydraulic cleaning can be used to recover membrane flux when operating below a critical pressure drop across the cake layer. However, once the membrane is wetted by oil, hydraulic cleaning is not effective at restoring the permeate flux.

Hydraulically irreversible fouling calls for the application of a more aggressive cleaning strategy such as chemical cleaning. The chemicals include aqueous solutions at extreme pH (alkaline or acidic, depending on the predominant foulant) and oxidizing compounds (e.g., hypochlorite) [121, 122]. Aggressive chemical cleaning gradually degrades membrane materials, accelerates membrane aging and shortens membrane's lifespan [122]. Another study employed two chemical cleaning techniques to remove oil adsorbed onto a PVDF UF membrane [123], namely, (i) washing with a micellar solution consisting of a surfactant (SDS) and an alcohol in water (pentan-1-ol); and (ii) immersion of the fouled membrane in a HCl-NaCl-gasoline aqueous solution. Both could restore the properties of the membranes to 97% of the initial permeability. Zhang et al. evaluated cleaning strategies for removing crude oil from a polyamide NF membrane using flux measurements, salt rejection experiments, atomic force microscopy (AFM), contact angle measurements and ATR-FTIR. The results indicated that optimal cleaning consisted of two stages: cleaning with an alkaline (pH 11) solution of 0.05% EDTA, 0.2% sodium pyrophosphate and 0.2% SDS for 0.5 h, followed by an HCl solution (pH of 2) for 0.5 h. The cleaning approach recovered permeate flux without damaging the membrane [124].

Mechanical cleaning methods include air flushing, ultrasound, vibrational cleaning and sponge ball cleaning [4]. Juang and Lin used a horn ultrasonicator to recover permeate flux of a UF membrane used to filter water-in-oil emulsions [125]. Experiments explored the effects of sonicator tip position, ultrasonic power, and solution properties such as percentage of emulsification and volumetric ratio of emulsions to the external aqueous phase. The results demonstrated that the membrane lifespan could be prolonged with careful control of the ultrasonic intensity, such as below about 80 W/cm², due to the trade-off between the higher fouling mitigation efficiency and the higher degradation of organics associated with a higher power. One of the commercial membrane modules which include both chemical and hydraulic cleaning via the cleaning-in-place (CIP) method is CeraMem® from Veolia Water Tech [39]. Chemical cleaning is done using a combination of caustic soda, citric acid and sodium hypochlorite, while hydraulic cleaning by backwash. Another chemical cleaning bench-scale study was done at the Qatari LNG Plant by Suez Water Technologies & Solutions, USA. A sequence of cleaning by hypochlorite and then followed by citric acid was found to be adequate to recover the flux in membrane bioreactors [126].

Due to the deformability of oil droplets and the propensity to form a contiguous film, cleaning the membrane fouled with oil is more difficult than that fouled with rigid particulates. Hydraulic cleaning is effective for external fouling (i.e., fouling on the membrane surface) but not irreversible fouling. On the other hand, chemical cleaning is more effective due to its capability to remove irreversible fouling as well. Past studies indicate that cleaning, whether physical or chemical, cannot recover the membrane performance totally, so effective membrane fouling mitigation is essential to prolong filtration and delay cleaning as much as possible.

1.3.3. Quantifying the extent of membrane fouling

1.3.3.1. Permeate flux

Membrane separation is characterized in terms of permeate flux and selectivity. When the feed is ultrapure water, the hydraulic resistance of the membrane, R_m (m^{-1}), can be obtained using Darcy's equation [120]:

$$J_0 = \frac{TMP}{\mu R_m} \quad (1.1)$$

where J_0 is volumetric permeate flux membrane ($\text{m}^3/\text{m}^2 \cdot \text{s}$), TMP is the transmembrane pressure differential (Pa), and μ is the dynamic viscosity of the permeating solution ($\text{Pa} \cdot \text{s}$). When the feed contains components other than water, Eq. (1.1) needs to be modified to include the osmotic pressure differential across the membrane, $\Delta\pi$ (Pa) and added resistance to the permeate flux due to fouling, R_f (m^{-1}):

$$J = \frac{TMP - \sigma \Delta\pi}{\mu(R_m + R_f)} \quad (1.2)$$

where σ is the reflection coefficient.

For the permeate flux to occur in the direction from the feed to the permeate side of the membrane, the pressure exerted across the membrane needs to be larger than the osmotic pressure. The osmotic pressure can be calculated using van't Hoff's equation (1.3):

$$\Delta\pi = i \cdot R \cdot T \cdot (C_m - C_p) \quad (1.3)$$

where i is the van't Hoff's factor (unitless), R is the ideal gas constant ($\text{J}/\text{mol} \cdot \text{K}$), T is the temperature of the solution (K), C_m (mol/L) is the concentration of solute in the immediate vicinity of the membrane surface and C_p (mol/L) is the solute concentration in the permeate. Rejected solutes form a mass transfer boundary layer adjacent to the feed face of the membrane. This effect, known as concentration polarization, describes

how C_m relates to the concentration of the bulk feed, C_f . Thin film theory can be used to predict C_m in terms of C_f , permeate flux J and mass transfer coefficient k (m/s):

$$\frac{C_m - C_p}{C_f - C_p} = e^{\left(\frac{J}{k}\right)} \quad (1.4)$$

The mass transfer coefficient k is given by a ratio of the diffusion coefficient of the solute (m^2/s) to the thickness of the boundary layer (m). The latter can be predicted based on the Sherwood correlations available for membrane channels of several geometries (e.g. flat slit, tubular, hollow fibers) commonly employed in membrane systems [127].

Eq. (1.2) can be recast as the energy balance equation (e.g., [128]) to illustrate the individual contributions of osmotic pressure and hydraulic resistance of the deposited oil layer to the permeate flux decline:

$$\frac{\Delta P_m(t)}{TMP} + \frac{\Delta P_d(t)}{TMP} + \frac{\Delta \pi_m(t)}{TMP} = 1 \quad (1.5)$$

1.3.3.2. Selectivity

The selectivity of the membrane is important in conferring the rejection needed to ensure the purity of the retentate and/or permeate. In the membrane-filtration of oily water, the selectivity of the membrane can be represented by the percentage rejection (R), which is quantified by factoring the difference of oil concentrations at the feed (C_f) and the permeate (C_p) sides [16, 51]:

$$R (\%) = \left(\frac{C_f - C_p}{C_f} \right) \times 100\% \quad (1.6)$$

A trade-off inevitably exists between permeability and selectivity. On the one hand, larger pore sizes give higher permeability but lower selectivity. On the other hand, smaller pore sizes give lower permeability but higher selectivity. To this end,

researchers have continuously striven to push the limits of both permeability and selectivity simultaneously.

As fouling progresses, oil rejection or selectivity deteriorates [3]. Oil, unlike other rigid colloidal foulants, can deform and penetrate through the membrane pores and thereby reduces the permeate quality [129]. Penetration of the oil occurs only if the TMP is high enough to overcome the critical pressure, which is based on the Young-Laplace equation and developed to describe the penetration of the oil droplet or oil film into the pores [130]. In the presence of the typical cross flow implemented to mitigate fouling, the permeation of the oil is not only dependent on TMP alone, but also on the force balance between permeation and drag force from the cross-flow shear. Darvishzadeh et al. subsequently extended the simulation study to incorporate this shear effect for an oil droplet pinned on the pore entrance [129], and considered many parameters that can affect the permeation of the oil droplet, such as droplet to pore size ratio, surface tension and viscosity ratio. Experimentally, one study found that, increasing the cross-flow velocity (CFV) decreased then increased oil rejection [131]. This is because the cross flow has the twin effects of enhancing permeation due to the higher pressure and also enhancing coalescence to form a secondary membrane that resists permeation. In another experimental study, as the TMP increased, the flux increase accelerated pore blockage and thereby decreased oil rejection [132]. Clearly, the trade-off between permeability and selectivity has to be considered, with particular consideration of the deformation and coalescence of the oil droplets.

1.3.4. Evaluating the fouling potential of the feed solution

Several indices have been devised to quantify the fouling propensity of the membrane feed. The indices can be obtained in simple tests by following standard testing procedures and can help with the choice of the suitable membrane type.

1.3.4.1. Silt Density Index (SDI)

The Silt Density Index (SDI) is a common method used to quantify the fouling propensity of feed water. The test procedure involves measuring the time needed for 500 ml of the feed solution to pass through a 0.45 μm microfiltration membrane at 30 psi (~ 207 kPa) [133]. After 15 minutes of filtration, the time required to filter the same volume is recorded. Conventionally, the measurement is taken over a period of 15 min, but when the solution has high fouling properties, the 15-min time interval can be shortened to 10, 5 or 3 min. SDI can be calculated using the following equation:

$$\text{SDI} = \frac{100}{t} \cdot \left(1 - \frac{t_i}{t_f}\right) \quad (1.7)$$

where t is the total filtration duration, t_i is the time at the start of the filtration, and t_f is the final time to filter 500 ml of sample after 15 minutes. SDI is not a sensitive fouling index since it is a static measurement of resistance at preset time intervals (i.e., only based on initial and final measurements) and does not measure the rate of change of resistance during the filtration test. In addition, it only measures the fouling rate associated with particles larger than 0.45 μm , although RO fouling can be caused by particles much smaller than 0.45 μm [134]. The standard blocking method of fouling was found to be the more dominant fouling mechanism during the SDI measurement, but was not in a good agreement with the base assumption of the SDI measurement of total rejection of the colloidal particles. The question regarding of the applicability of

SDI also revolved around the fact that fouling is affected by many factors, which include both membrane and colloidal characteristics. Ghaffour et al. [135] found that the variability of the SDI values between two MF membrane with similar mean pore sizes of 0.45 μm was due to differences in membrane thickness and pore size distribution. The thinner membrane gave a higher permeate flux, which brought more particles to the membrane and increased the fouling extent, and thus the SDI value. A similar result was reported by Alhadidi et al regarding the effect of membrane properties on the SDI value [136]. In their study, eight different membranes with similar mean pore sizes were employed to study the variance of the SDI values. They proved that the SDI value was affected by factors that affect membrane resistance like pore size and shape, bulk and surface porosity, thickness, morphology, surface roughness and also zeta potential. These results suggest that SDI is not the best parameter for characterizing the potential of fouling from the feed water, but it is still one of the most popular means due to its simplicity. Other fouling indices such as Modified Fouling Index (MFI) and Combined Fouling Index (CFI) have been proposed as more accurate fouling metrics than SDI.

1.3.4.2. Modified Fouling Index (MFI) and Combined Fouling Index (CFI)

The Modified Fouling Index (MFI) is a dynamic index that takes into account the evolution of the cake resistance during the filtration test. MFI is determined using the same equipment (0.45 μm microfiltration membrane) as the SDI, but the volume is recorded every 30 seconds over a 15 minutes filtration period [137]. This fouling index is based on the concept of cake filtration where the thickness of the cake layer formed at the membrane surface is directly proportional to the filtered volume. The MFI value can be determined from the gradient of the general cake filtration equation for constant pressure in a t/V versus V plot [120]:

$$\frac{t}{V} = \frac{\mu R_m}{\Delta P A} + \frac{\mu \alpha C_f}{2 \Delta P A^2} V \quad (1.8)$$

Equation 1.8 can be rewritten as:

$$\frac{1}{Q} = \alpha + MFI \cdot V \quad (1.9)$$

where V is the filtrate volume, t is the filtration time and α is the specific resistance of the deposited cake.

The assumption implicit in the MFI approach is that cake filtration is the only fouling mechanism [120]. However, other mechanisms often contribute to permeate flux decline (e.g., pore blocking by smaller particles). Thus, both SDI and MFI are deficient in that they do not account for fouling mechanisms occurring when smaller particles are present in the feed. Therefore, SDI and MFI underestimate the extent of fouling that would be observed in practice with UF, NF and RO membranes.

Unlike SDI and MFI, the Combined Fouling Index (CFI) estimates the potential RO/NF fouling due to various fouling mechanisms by combining MFI values obtained from individual MFI tests. Choi et al. used three different membranes (hydrophilic MF, hydrophobic MF and hydrophilic UF) to measure MFI [138] and calculated CFI by assuming a linear combination of the three MFI values:

$$CFI = \omega_1 M_1 + \omega_2 M_2 + \omega_3 M_3 \quad (1.10)$$

where M_1 , M_2 and M_3 are the MFI values of the three membranes. The weighing factors ω_1 , ω_2 and ω_3 are calculated based on the flux decline rate (φ) of each membrane, which is defined as [138]:

$$\varphi = \frac{1}{J_o^2} \cdot \frac{dJ}{dt} \Big|_{t=0} \quad (1.11)$$

where J_o is the initial permeate flux and t is the filtration time.

1.3.4.3. Applicability of SDI, MFI, and CFI to quantifying membrane fouling by oil-water emulsions

The fouling indices (SDI, MFI, and CFI) described above are measured using dead-end filtration, but most practical oil-water membrane separations are performed in a crossflow mode. Thus, these fouling indices do not account for the possibility of back-transport due to crossflow. Yet, hydrodynamic conditions can have a profound impact on membrane fouling. For example, membrane fouling by emulsified oil can be mitigated by oil coalescence [94] wherein oil droplets coalesce to reach a critical size and then are swept off the membrane surface by the crossflow shear.

Another concern is the applicability of the same fouling indicator to a variety of oil/water emulsion feed solutions. As described in Section 1.1.1.1, oily industrial wastewater can vary in composition depending on its source. For instance, produced water may have much higher salinity than oily wastewater produced by food industries. In addition, oil content and droplet size can impact permeate flux decline as increasing oil concentration in the feed can lead to a greater decline in flux. The other limitation is that MFI and SFI tests use a microfiltration membrane and it is questionable to what extent this membrane can predict the performance of different membranes.

1.4. Understanding membrane fouling by oily wastewater: Measurement approaches and techniques

Significant research efforts have been directed at understanding membrane fouling and development of effective fouling mitigation strategies. The suite of technologies reviewed in this section includes non-invasive and in-situ approaches to assess membrane fouling. These will be categorized as online and offline measurements.

1.4.1. Online measurements

Real-time and non-invasive fouling measurement is needed to monitor practical membrane processes, in order to provide for early warning on membrane fouling.

1.4.1.1. Electrical Impedance Spectroscopy (EIS)

EIS was initially used to estimate the thickness of membrane cell [139] and the application of the method was subsequently extended to membrane filtration processes [17, 140-152]. EIS uses alternate current at a range of frequencies. The measured values of current, voltage and frequency are translated to capacitance and conductance values and plotted versus frequency in a Nyquist plot. In this plot, the y-axis is the inverse of capacitance which is known as negative imaginary impedance axis ($-Z_{\text{img}}$) and the x-axis is the inverse of conductance which is known as real impedance (Z_{real}). The number of effective layers and the electrical properties of the system can thereby be interpreted. The schematic of the EIS cell is shown in Fig. 1.5. EIS has been used to study membrane fouling mostly in RO and FO tests, where different types of fouling have been observed, such as colloidal fouling, biofouling and scaling. In most of these studies, EIS was more sensitive to changes in the filtration process (e.g. rising TMP or declining salt rejection) compared to the conventional methods. Sim et al. [152] studied the effect of silica, BSA, and the mixture of both on fouling. Whereas feeds containing silica shifted the Nyquist plot leftwards due to the build-up of the silica layer and due to cake-enhanced osmotic pressure (CEOP), feeds containing BSA shifted the Nyquist plot rightwards due to the build-up of a dense but thin fouling layer. For the feed containing both silica and BSA, the shift of the Nyquist plot depended on the ratio of the foulants.

EIS is a versatile technology with applications not only limited to the study of membrane fouling. Two studies [140, 141] used EIS to assess the stability of oil-in-

water (O/W) emulsion, while Roldan-Cruz et al. used EIS to monitor the complexation between biopolymers in the bulk solution [145]. This indicates that EIS can potentially be applied to the study of membrane fouling by oil emulsions.

Figure 1. 5. Schematic of a cross-flow EIS membrane cell, connected to the Inphaze™ Impedance Spectrometer [152].

1.4.1.2. Ultrasonic Time-Domain Reflectometry (UTDR)

First used in the construction and materials engineering application, and in weld inspection to locate and size hidden cracks, the UTDR method has been used also in the study of membrane fouling. The UTDR is a non-invasive and non-destructive measurement technique which uses ultrasonic waves to measure and locate interfaces (moving or stationary), therefore useful for the detection of the membrane fouling, specifically the thickness of the foulant layer. In the UTDR, a transducer emits

ultrasonic waves through the top of the membrane module/cell, and the waves are reflected when in contact with an interface; the time taken (t) for the waves to return to the detector can be used to distinguish different layers in the membrane module. This time (t) is plotted against amplitude, which provides a means of monitoring the evolution of membrane fouling. The UTDR is a versatile technique that can be used to study different types of membrane filtration (including microfiltration [50, 153-155], nanofiltration (NF) [156, 157], reverse osmosis (RO) [154, 158-161]) and also different membrane types (including both flat-sheet and hollow fiber (HF) membranes [153]). The schematic of a UTDR system is shown in Fig. 1.6. UTDR was employed to study the formation of scaling or inorganic fouling by calcium sulfate at different axial velocities in a RO desalination process [161]. UTDR showed significantly greater sensitivity to fouling detection in comparison to traditional fouling monitoring methods, such as those that rely on measuring flux decline or transmembrane pressure (TMP). For membrane-based oil-water separation, the UTDR has also been used to investigate fouling by feed mimicking produced water in crossflow microfiltration with both flat sheet [50] and hollow fiber [162] membranes, whereby 2D and 3D visualization for the fouling was enabled. Both studies consistently found that the fouling progression by the oil was oil adsorption on the membrane surface before the oil layer compaction due to permeate drag force.

Figure 1. 6. Schematic of UTDR system [162].

1.4.2. Offline Measurement

Offline measurements have also been used for studying the membrane fouling phenomena. Either a scaled-down version of the process is studied or the membrane is taken offline for measurement of pore size or membrane autopsy after the operation is shut down.

1.4.2.1. Direct Observation through Membrane (DOTM) and other microscopy-based techniques

The direct observation through the membrane (DOTM) technique [94, 96, 163-176] and other microscopic techniques, such as Direct Microscopic Observation (DMO) [177] or Direct Visual Observation (DVO) [178, 179], are based on the usage of light microscopy to directly observe the membrane surface. Firstly introduced by Li et al. [173] as a novel way to study particle deposition on the membrane, the DOTM uses

transparent membranes to enable the visualization of the feed-membrane interface (Fig. 1.7). In the other microscopic techniques, non-transparent membranes can be studied of different types (e.g. hollow fiber) [178, 180], materials (e.g. cellulose acetate) [179], and pore sizes (e.g. NF membranes) [177]. The DOTM studies were largely correlated with critical flux [181], which is the permeate flux value below which fouling is negligible. Regarding oil emulsions, DOTM was used by Tummons et al. [94, 176] to study the behavior of deposited oil droplets on the membrane surface. DOTM tests with hexadecane-in-water emulsion stabilized by sodium dodecyl sulfate (SDS) revealed three characteristic stages of membrane fouling by emulsified oil: (1) droplet attachment and clustering, (2) droplet deformation, and (3) droplet coalescence. Visualization by DOTM was complemented with a force balance analysis on an oil droplet pinned on a single pore at the membrane surface. Another study used molecular dynamics simulations and DOTM to explain the coalescence behavior by some oils [96].

Figure 1. 7. Direct Observation through the Membrane (DOTM) Setup

1.4.2.2. Evaporoporometry (EP)

The evaporoporometry (EP) is a novel technique initially proposed to measure the pore size distribution of membranes with key advantages of allowing measurement at ambient conditions [182, 183], which thereby allows for membrane autopsy [184] to understand the extent of internal fouling. EP is based on the measurement of the evaporation rate of the volatile wetting liquid from the pores, then applying the Kelvin equation to quantify the pore size distribution, as schematically depicted in Fig. 1.8. Recent enhancements to the EP technique include the extension of the measurable pore size range by a judicious choice of the surface tension and vapor pressure of the wetting volatile liquid [185], and extending the applicability to hollow fiber membranes whose active layers are on the lumen side [186].

Figure 1. 8. Schematic of the EP system [183]: (a) test cell, and (b) setup that consists of the balance and incubator.

1.4.2.3. Optical Coherence Tomography (OCT)

Optical Coherence Tomography (OCT) was used initially in the medical field and now commonly in membrane-based filtration processes. OCT is based on light

interference generated by a near-infrared light beam, which is split into two channels, with one going to the reference mirror and the other to the membrane cell. In the membrane cell, the light is back-scattered from different media and recombined again with the light from reference mirror, which results in an interference spectrum detected by the spectrometer. The schematic of the OCT is presented in Fig. 1.9. By using Fourier Transform Interferogram, the depth information can be known (A-scan), and the collection of these A-scans is known as B-scan, which gives the plane-view of the membrane. Gao and coworkers used OCT to characterize the velocity profile normal to the membrane surface when different orientations of spacers (i.e., 0°, 45°, and 90° to the crossflow) were used [187]. Another study utilized OCT to image biofilms in NF and RO systems, and found that the biofilm was more compact when the permeate flux increased [188]. This indicates that membrane performance deterioration was not only related to biofilm thickness but also the internal biofilm structure. The OCT was also used to study colloidal fouling (silica and bentonite) [189], and internal fouling by oil emulsions [97].

Figure 1. 9. (a) The OCT system that gives a 3D tomographic image of the scanned region (b), which can be further analyzed to identify the feed-membrane interface (c) and layers parallel to the feed-membrane interface to detect fouling (d) [97].

1.4.3. Coupling two state-of-the-art techniques to monitor membrane fouling online

The Electrical Impedance Spectroscopy (EIS) and Ultrasonic Time Domain Reflectometry (UTDR) technology can be implemented on-line in practical membrane processes. Both of these techniques were used in a side-stream ‘canary cell’ [190-192] whereby a part of the feed stream is channeled to a designated monitoring cell, which has the same hydrodynamics and material as the main membrane process. For the UTDR system, one study [158] simulated the ‘canary cell’ at the laboratory scale for monitoring

biofouling in a RO system by dosing silica to enhance the signal due to the low acoustic signal given by biofouling which has similar acoustic properties as water. The system was further developed [193], as shown schematically in Fig 1.10. The canary cell had the same hydrodynamics and material as the SWM module, and shown to be representative of the SWM with respect to accuracy and reproducibility in the detection of fouling. The same concept and design of a canary cell was also used in a trial field study in a water treatment plant (NEWater) in Singapore [17], whereby EIS was used for monitoring and giving advance warning of fouling in the canary cell that mimics the SWM operated in parallel. The schematic for the canary cell, which was termed as EISFM (Electrical Impedance Spectroscopy Fouling Monitor) canary cell, is shown in Fig 1.11. The feed used here was secondary treated municipal wastewater after treatment by MF. In the canary cell, the membranes, spacers, hydrodynamics and flux used were the same as that in the RO module. During the eight months of operation, the results showed four peaks in the graph of $Z_{\text{real-DP}}$ versus operation time, which appeared earlier than the scheduled cleaning in place (CIP) protocol. This indicates that the EISFM canary cell can be used to detect fouling earlier than conventional methods. For the EIS and UTDR to be used in detecting fouling by oil emulsions, more understanding on this unique foulant is warranted.

Figure 1. 10. The schematic of a canary cell system monitored by UTDR [193].

Figure 1. 11. The schematic of a canary cell system monitored by EISFM in NEWater plant, Singapore [17].

In view of the possibility for practical implementation of the UTDR and EIS using the canary cell system, it is potentially feasible to incorporate other advanced monitoring techniques such as DOTM and OCT, particularly since both DOTM and OCT have been

proven to be capable of monitoring membrane fouling by oil [94, 96, 97, 164, 174-176, 194]. To use the same canary cell, some limitations of DOTM and OCT have to be overcome, namely, the need for transparent membranes for DOTM and the cumbersome data-analysis for OCT. Transparent membranes are not realistic for the conventional polymeric ones, but possibly instead of focusing through the membranes, the focal plane could be on the membrane surface. The precision would be lower than that necessary for the mechanistic understanding sought in lab experiments, but acceptable for the goal of detecting the onset of fouling in commercial applications. As for the large volumes of data generated by OCT, advancement in computing prowess mitigates this issue and also the analyses can possibly be much simplified with the development of correlations based on mechanistic understandings from lab experiments. Furthermore, in view of the limited optical area monitored by DOTM and OCT, the collection of data from multiple optical spots can be implemented.

1.5. Conclusion and Study Objectives

The abundant oily wastewater would harm the environment if discharged without proper treatment. In view of the urgent need to treat the vast volumes of oily wastewater and the promises of membrane technology playing an important role, a comprehensive review on the practical aspects of membrane-based filtration for oil-water separation was carried out. The present review focuses on practical aspects of applying membrane technology to treatment of oily wastewater. The sources and composition of oily wastewater are appraised. Depending on the source, the composition of oily wastewater can vary broadly complicating the selection of an appropriate treatment technology. Yet, environmental regulations mandate a certain degree of treatment before the water can be discharging into the environment. Commercially available membrane technologies

used to separate oil and water has been used increasingly in the last few years, with ceramic tubular membranes and flat sheet polymeric membranes being most popular. Membrane technology complements rather than replaces the conventional methods for treating oily wastewater to achieve a higher quality product sustainably. The integration of membrane-based and other methods harnesses the advantages and also circumvents the shortcomings of each. The cost of membrane-based treatment of oily wastewater is quite varied, but is generally lower than conventional technologies.

Approaches to mitigating membrane fouling include fouling-resistant membranes, turbulence promoters and membrane cleaning. For the novel membranes, on top on proving superiority in performance, practical issues such as longer-term durability of the coats in the presence of cross-flow, treatment of realistic feeds, and uniformity of modification across large membrane areas have to be addressed too. With respect to turbulence promoters, increasing the shear stress gives better membrane fouling mitigation on one hand, but may affect the membrane integrity on the other hand and thereby reduce rejection. As for membrane cleaning, the deformability of oil droplets and the propensity to form a contiguous film makes total recovery more difficult, so effective membrane fouling mitigation is essential to prolong filtration and delay cleaning as much as possible.

Online and offline methods to study membrane fouling have been gaining more attention lately. Online means allow for real-time monitoring of practical membrane processes in order to provide for early warning of membrane fouling. In contrast, offline methods allow for a more in-depth mechanistic understanding of membrane fouling. The discussion of the monitoring methods is concluded by a perspective on the potential of coupling state-of-the-art techniques to facilitate better monitoring and control of membrane fouling by oil.

1.6. Objectives

The challenges associated with membrane filtration of oily wastewater are centered on membrane fouling – a key obstacle that hinders broader implementation of membrane technology for oil-water separation. Oil droplets, which can both deform and coalesce, are unique foulants that challenge the available knowhow on fouling. More studies on mechanistically understanding membrane fouling by oil is needed, particularly in view of the recent studies that have collectively shown oil to be distinctive from other particulate foulants. Direct Observation through the Membrane (DOTM) system is chosen for the further studies of oil fouling in the membrane separation system. This method offers a real-time, in-situ observation of the filtration process and also the fouling evolution of various foulants which has mentioned above and also has been proven successfully to study oil fouling by Tummons et al [94], thus it has promising potentials to explore more understanding that underlies the fouling mechanism and evolution of oil emulsion on the membrane surface. Since fouling is affected by many factors, this study will dig deeper the effect of different operation parameters and feed characteristic to the membrane performance and also the fouling mechanism on the membrane surface in a real time situation provided by the DOTM system, which represents similarly what happens in the process of oil filtration in practice, and a novel method in this oil fouling study. Comparison of the behavior of oil fouling in the flat sheet and hollow fiber membrane will be explored as well to comprehensively understand the membrane fouling by oil-in-water emulsion.

1.7. References

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CHAPTER 2: EFFECT OF CROSS-FLOW VELOCITY, OIL CONCENTRATION AND SALINITY ON THE CRITICAL FLUX OF AN OIL-IN-WATER EMULSION IN MICROFILTRATION

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Abstract

Microfiltration is an attractive means for treating oily wastewater, especially when the size of the oil droplets are micrometer-sized since the conventional techniques become deficient. A systematic study on the critical flux of oil-in-water emulsion, which behaves differently from other colloidal foulants with regards to deformation, coalescence and splitting, has not been carried out to date. This was the goal of the current study, which employed the Direct Observation Through the Membrane (DOTM) technique to characterize the critical flux of oil-in-water emulsions of various concentrations, at various cross-flow velocities (CFV) and salt concentrations. Five observations can be highlighted here. Firstly, the oil droplets with a mean droplet diameter of approximately 5 μm exhibited critical fluxes equal to or greater than latex particles of 10 μm . This is likely due to the twin effects of membrane oleophobicity effecting drop capture and the presence of a droplet size distribution with larger drops

that can enhance the shear-induced diffusion of the average drops. Secondly, the critical flux values did not agree with the model that is valid for the size range the mean droplet diameter falls in, but instead agreed with the model adapted for smaller particulate foulants. Thirdly, the increase in the critical flux with CFV was more significant for the lower oil concentration. Fourthly, a striping phenomenon was observed at higher oil concentrations and lower CFV values. Striping was not observed for latex particles. Fifthly, the critical flux decreased with salt concentration. These findings highlight the unique fouling behavior of oil-in-water emulsions in microfiltration.

Keywords : Microfiltration; Direct Observation Through the Membrane (DOTM); Critical Flux; Oil-in-Water Emulsion; Fouling

2.1. Introduction

Oil-water separations have widespread, economically significant applications, with industries spanning Wastewater, Oil and Gas, Food and Beverage (F&B), Shipping and Maritime, and Metal and Machining. Notably, produced water, which is the largest waste stream generated by oil and gas industries, represents the largest source of oily wastewater [1, 2]. The oil-in-water emulsions treated have a wide range of concentrations that depend on the industry, such as low concentrations in the range of 50 - 1000 mg/l in produced water in the oil and gas industry, and high concentrations in the range of 3,000 - 200,000 mg/l in the food and metal processing industries [3]. Conventional techniques employed, like gravity separation (which is the most common primary treatment of oily wastewater) and the hydrocyclone (which is a staple technology for oil companies to de-oil produced water), are unable to remove smaller micrometer-sized droplets [4, 5]. However membrane-based oil-water separations are

able to separate such oil droplets [6-9], and additionally confer many benefits relative to other separation methods, for example, small footprint, high oil removal efficiency, low investment and operation cost, operational simplicity, consistent quality of effluent, and amenability to be implemented in-process [4, 5]. Unfortunately, the primary disadvantage of membranes is that fouling leads to ineffective separation and higher energy costs. Hence, a mechanistic understanding of the fouling caused by oil droplets is needed to ensure the technical and economic success of membrane applications in oil-water separations.

Several studies of membrane fouling by oil emulsions during ultrafiltration and microfiltration have been carried out. The permeate flux and rejection is well acknowledged to be correlated with operating parameters like trans-membrane pressure (TMP), feed concentration, temperature and cross-flow velocity [10-15]. Arnot et al. [16] indicated that oil emulsion fouling was unique in terms of significantly lower initial fouling rate for higher cross-flow velocities (≥ 0.8 m/s), although this would be membrane-specific in terms of flux. Furthermore, fouling by oil emulsion was found to best correspond to the cake filtration model, rather than incomplete pore blocking or complete pore blocking [15-20]. A model for calculating the critical pressure required to force the entry of an oil drop into a membrane pore was formulated based on the Young-Laplace equation and found to be a reasonable predictor of the operating pressure at which oil droplets deposit on the membrane [21, 22]. Another study advanced the modeling for cross-flow applications for the behavior of an oil droplet pinned at the entrance of a micrometer-sized pore by solving the Navier-Stokes equation; the shear induced by cross-flow not only increases the critical pressure of permeation but may also cause the oil droplet to break into smaller droplets [23]. More recently, computational fluid dynamics (CFD) was employed to qualitatively study

membrane pore blockage by oil emulsions, and found contact angle and interfacial tension to be dominant parameters [24]. Models, which are necessary for extracting the underlying physics, require complementary experimental data. Our recent fundamental study of microfiltration membrane fouling by emulsified oil was conducted using a combination of real-time visualization via the direct observation through the membrane (DOTM) technique, force balance on a droplet, and permeate flux analysis [25]. The results indicate that membrane fouling by an oil emulsion is mitigated by both cross-flow shear and droplet coalescence, the latter of which is more typical of oil emulsion foulants than solid particles. In the rich database of knowledge accumulated for membrane-based oil-water separations, a gap exists with regards to critical flux [26], which is a function of various parameters and provides important operational and design heuristics [27-29], of the oil emulsion. Correspondingly, the focus of this work was on a systematic analysis of the critical flux of oil emulsions and how it is impacted by practical operating parameters such as oil concentration, cross-flow velocity and salt concentration.

DOTM, which was developed to enable real-time visualization of particulate fouling phenomena at the feed-membrane interface [30], was used in this study to measure the critical flux of the oil-in-water emulsion. The specific objectives were to: (i) assess the effects of cross-flow velocity (CFV), oil concentration and salt concentration on critical flux; (ii) compare the critical flux of oil droplet foulants with latex particles of similar sizes; (iii) verify the agreement or lack thereof between the critical flux of oil droplets and shear-induced diffusion models developed for particulate foulants; and (iv) visualize the fouling phenomena at permeate fluxes just above the critical flux.

2.2. Experimental Method

2.2.1. Oil-in-Water Emulsion

The dispersed phase was hexadecane (Sigma Aldrich), with a density of 773 mg/l (at 25 °C) and molecular weight of 226 g/mol, while the continuous phase was deionized water (Milli-Q, Millipore) and Tween 20 (Sigma Aldrich). Tween 20 was chosen due to its non-ionic charge that would have minor interaction with the membrane thus reduced the effect of surfactant to the membrane. 800 ml of the oil emulsion stock solution was prepared, which consisted of 20 ml hexadecane, 4 ml Tween 20 and 776 ml deionized water, and was sufficient for all the experiments. The three components were mixed using a blender (Warring 8011S) operated at 18,000 rpm for 10 s. Prior to every experiment, the feed solution was prepared by diluting the oil emulsion stock solution to the desired oil concentration, specifically, that typical in produced water of 50 – 500 ppm [31, 32], where the surfactant concentration after dilution were 10, 40, 70 and 100 ppm, respectively. A new feed solution was prepared for each experiment, and the consistency of the feeds was verified by ensuring the oil emulsion droplet size distributions were similar.

The oil emulsion droplet size distribution was measured via the Focused Beam Reflectance Measurement system (FBRM; Lasentech S400, PI-14/206). Fig. 2.1 displays the droplet size distribution of the stock solution with 25,000 ppm of oil in both the absence and presence of salt at various salt concentrations. The effect of increased salt concentration was such that the distributions became wider due to the greater percentage of oil droplets in the lower diameter range of smaller than 4 μm and in the upper range of larger than 7 μm . In both the absence and presence of salt, the number-

based average oil droplet diameter was in the range of 4 - 6 μm , and 90% of the emulsion was in the diameter range of 1 - 20 μm throughout every experiment.

Figure 2. 1. Average oil droplet size distribution of 25,000 ppm of oil (stock solution) in the absence and presence of salt (NaCl concentrations between 5,000 – 35,000 ppm).

2.2.2. Direct Observation Through Membrane (DOTM) Setup

The Direct Observation Through Membrane (DOTM) setup employed was the same as that described in Appendix, which was based on the first report of this technique by Li et al. [30]. The schematic of the DOTM setup is depicted in Fig. 2.2, the key component of which is the light microscope (Zeiss Imager.A2 m) coupled with a camera (Axiocam 105 Color) to enable the observation of the feed-membrane interface during the cross-flow membrane filtration in real-time.

As the name DOTM implies, the membrane (Anopore, Whatman, Germany), which was a circular disk with a diameter of 47 mm and a nominal pore diameter of 200 nm, is transparent when wetted due to its relatively high porosity and straight through

pores. Specifically, the membrane cell was such that the permeate channel was on top, and the focus was adjusted through the permeate channel and the membrane, such that the focal plane was the feed-membrane interface. The membrane was sandwiched using glue (Araldite) between two pieces of paper with dimensions of 55 mm by 135 mm and with a square cut-out in the center with dimensions of 27 mm by 27 mm. The cross-flow acrylic membrane cell had dimensions of 105 mm length by 35 mm width by 3 mm height, with 2 mm being the feed channel height and 1 mm being the permeate channel height.

The beaker containing the feed solution was placed on a magnetic stirrer plate (Heidolph, MR Hei-Mix S) to homogenize the oil emulsion suspension throughout the experiment, and a gear pump (Micropump Inc, GJ-N25.PF/S.A) enabled the circulation of the feed solution between the membrane cell and the feed solution beaker. For the permeate side of the membrane cell, a peristaltic pump (Cole Palmer; Masterflex L/S 7519-20/85) was employed to control the permeate flux during the flux-stepping experiments to determine critical flux (J_{crit}). The permeate was directed to a beaker placed on a balance (Kern; 572) to quantify permeate flux. In addition, three pressure transmitters (Cole Palmer; Transducer 206) were used to characterize the pressures in the membrane cell (namely, feed inlet pressure, feed outlet pressure, and permeate inlet pressure). A computer recorded the images from the camera, the pressure signals from the pressure transmitters and the mass from the balance.

Figure 2. 2. Direct Observation Through the Membrane (DOTM) Experimental Setup

2.2.3. Critical Flux (J_{crit}) Determination

The flux-stepping method was used in this study to determine critical flux (J_{crit}), which is defined as the permeate flux above which fouling becomes observable [26]. For every experiment, the initial permeate flux was set at 5 l/m²h for 10 minutes, after which the flux was increased by 5 l/m²h every 10 minutes. For each 10 minutes of constant flux, two images were captured at the end of the 2nd minute and 10th minute, and analyzed for coverage (C) using ImageJ. The rate of change of coverage between these two images ($\frac{\Delta C}{\Delta t}$) was then calculated using the following equation [33]:

$$\frac{\Delta C}{\Delta t} = \frac{C_{10th\ minute} - C_{2nd\ minute}}{8\ minutes} \quad (2.1)$$

The critical flux (J_{crit}) was determined as the intersection point between the $\frac{\Delta C}{\Delta t}$ versus flux curve and the threshold value of 0.2 %/min, as determined in a previous study (see Appendix) and verified in this study. Fig. 2.3 shows the critical flux (J_{crit}) determination with current method and TMP data, which the critical flux (J_{crit}) were 21 and 25 l/m²h, respectively and by this result, it was shown that our current method is comparable with the flux determined by TMP data.

Figure 2. 3. Critical flux (J_{crit}) of oil emulsion (500 ppm, CFV of 0.1 m/s) with current method and TMP data

2.3. Results and Discussion

2.3.1. Critical Flux (J_{crit}) of Oil-in-water Emulsion

It should be noted that although the critical flux (J_{crit}) of colloids (e.g., latex particles) has been well-characterized [30, 34-38], this represents the first systematic study of the J_{crit} of an oil-in-water emulsion. Notably, such emulsions are distinctly different from other foulants due to the ability to deform and coalesce, as observed in a previous DOTM study [25]. Fig. 2.4 presents the critical flux (J_{crit}) versus cross-flow velocity (CFV) of the oil-in-water emulsions vis-à-vis monodisperse latex particles with particle diameters (d_p) of 3 and 10 μm at the same concentration (namely, 50,000 ppm). The range of CFV values investigated was in the range of 0.1 – 0.4 m/s, whereby the lower limit was such that the DOTM images were still clear enough to be analyzed at the highest oil concentration investigated and the upper limit was because the membrane started to vibrate at higher CFV values. As described in the previous section, J_{crit} was determined as the minimum flux at which the $\frac{\Delta C}{\Delta t}$ value exceeds the threshold value of

0.2 %/min during the flux-stepping experiments. Each data point in Fig. 2.4 represents the average of three repeats and each error bar represents the span of the repeats. At the lowest CFV of 0.1 m/s, the critical flux (J_{crit}) of the oil emulsion was similar to that of the larger latex particles ($d_p = 10 \mu\text{m}$) and greater than that of the smaller ones ($d_p = 3 \mu\text{m}$). On the other hand, at the higher CFV values of greater than 0.1 m/s, the critical flux (J_{crit}) values of the oil emulsion were greater than both of the latex particles. One of the main reasons for the generally higher critical flux (J_{crit}) values for the oil emulsion could be the oleophobicity of the Anopore membrane, as reflected in the contact angle of 151° for hexadecane [25]; the effect of salt on the contact angle was found via Dataphysics Contact Angle System OCA 15EC found to be negligible in this study. It should be noted that the densities of the oil emulsion and latex particles were approximately 770 and 1050 kg/m³, respectively, thereby the greater buoyancy of the oil emulsion should encourage more deposition, since the feed was below the membrane. However, the oleophobicity of the membrane caused the critical flux (J_{crit}) of the oil emulsion to be similar to that of the larger latex particles at a CFV of 0.1 m/s, despite the former being smaller. As the CFV increased, the oil emulsion droplets had greater J_{crit} values than the larger latex particles. This seems to contradict an earlier study [38], which reported that the effect of foulant-membrane interaction became less dominant at higher CFV values. However droplet-membrane interactions through oleophobicity imply subtle differences in the critical flux mechanisms. Thus the original concept behind critical flux is that there is a flux where back transport of ‘particles’ is balanced by convection. The back transport could be hydrodynamic (shear induced diffusion) or electrokinetic and these mechanisms occur in the boundary layer close to but not necessarily on the membrane. The question is how could oleophobicity manifest itself with oil droplets? Our hypothesis is that a droplet can actually reach and settle on

the membrane surface but then does not stay due to surface shear on the surface. At higher CFV the effect of oleophobicity would be more evident due to the increased surface shear. Droplet capture would require the net drag force to exceed a critical value to overcome the tangential slip force. This provides a qualitative explanation for the trends in Figure 2.4.

In the case of oil emulsions there could also be another effect caused by the size distribution. The latex particles previously studied were strictly monodisperse, but the oil emulsion had a size distribution (Fig. 2.1) with about 2-6 number % or 65-77 volume % of the emulsion having diameters greater than twice the number-based mean. In previous work on bidisperse particle suspensions [35] we have demonstrated that the presence of large particles can increase the shear induced diffusion effect in the boundary layer and significantly increase the critical flux (J_{crit}) of the smaller particles. Similar size interactions would be expected for the oil emulsion, thereby increasing the critical flux (J_{crit}) of the average drop size.

Figure 2. 4. Critical flux (J_{crit}) of latex particles (Appendix) and oil emulsion at the same feed concentration of 50,000 ppm.

The critical flux (J_{crit}) values of the oil emulsion were compared against the shear-induced diffusion model predictions by Li et al. [34]:

$$J_{crit} = 0.0595 \gamma_0 \left(\frac{a^4}{L} \right)^{\frac{1}{3}} \ln \left(\frac{\phi_w}{\phi_b} \right) \quad (2.2)$$

where J_{crit} represents critical flux, γ_0 represents shear rate at the membrane surface (s^{-1}), a represents particle radius (m), L represents membrane length (m), ϕ_w represents particle volume fraction at the membrane surface (-), and ϕ_b represents particle volume fraction in the bulk suspension (-). Because Eq. (2.2) was found to incur greater errors for the smaller particulate foulants ($d_p \leq 3 \mu m$), Li et al. [34] further incorporated an empirical constant (C_d) to improve the prediction for the smaller particles ($d_p = 3 \mu m$) investigated:

$$J_{crit} = 0.807 \gamma_0 \left(\frac{C_d^2 \phi_w^2 a^4}{L} \right)^{\frac{1}{3}} \ln \left(\frac{\phi_w}{\phi_b} \right) \quad (2.3)$$

It should be noted that C_d is an empirical constant evaluated from the gradient of a plot of $J/a^{4/3}$ versus γ_0 , and may be either constant or a function of feed concentration, and from our data, it was shown in Fig 2.4 that C_d was a function of feed concentration. The value of C_d was set at 0.31 for the smaller latex particles with $d_p = 3 \mu m$ in Li et al. [34] and 0.29 in our previous study on binary-size mixtures ($d_p = 3$ and $10 \mu m$) [Appendix]. However, for the oil-in-water emulsions with $d_p \approx 5 \mu m$ and feed concentration of 50 ppm in this study, C_d was found to be much higher at 0.54, presumably because the oleophobicity of the membrane enhanced the removal transport mechanism of the oil emulsion foulants.

Fig. 5 plots the experimental results and also model predictions (Eqs. (2.2) and (2.3)) for 50 ppm of oil emulsion at CFV values between 0.1 and 0.4 m/s. The values of 27 mm, 0.2 and 0.00005 were substituted for L , ϕ_w and ϕ_b , respectively, in both Eqs. (2.2) and (2.3); while the L and ϕ_b values were experimental values, ϕ_w was an assumed

value (namely, 0.2) similar to that used in Li et al. [34], since the average value of surface coverage (namely, 0.29) from all experiments would give similar results to the literature assumed value. Fig. 2.5 illustrates the good agreement between Eq. (2.3) and the experimental results on oil emulsion, despite the oil emulsion droplets being much less rigid than the colloids typically investigated (e.g., glass and latex particles) and the oleophobicity of the membrane, both effects of which may be accounted for in the C_d value of 0.54 used. In contrast, Eq. (2.2), which was applicable for particulate foulants with diameters greater than 3 μm [34], under-predicted the J_{crit} values, despite the average oil droplet diameter being about 4 - 6 μm .

Figure 2. 5. Comparison of critical flux (J_{crit}) values of oil-in-water emulsion obtained experimentally and from a shear-induced diffusion model [34].

2.3.2. Effect of Oil Concentration and Cross-flow Velocity (CFV)

It is well-acknowledged that foulant concentration and CFV affect critical flux (J_{crit}), but this has not been reported for oil emulsions, which as noted earlier are distinctly

different from other colloids in terms of their amenability for deformation, coalescence and splitting [25]. Generally, while a higher concentration of foulant increases the tendency for the membrane to foul, a higher CFV increases the shear induced diffusion and the shear on the membrane surface countering the permeate drag and mitigates fouling. Fig. 2.6 presents the critical flux (J_{crit}) versus CFV trends for oil emulsions at various concentrations. The range of CFV (i.e., 0.1–0.4 m/s) correspond to a Reynolds number (Re) range of 419–1677, which indicate laminar flow. Two observations are worth highlighting. Firstly, J_{crit} decreased with oil concentration but increased with CFV, which agree with reported trends for fouling in general. Secondly, CFV had a more significant influence on the J_{crit} of the feed with lower oil concentration, as reflected in the steepest gradient of the plot representing the lowest oil concentration of 50 ppm. This may be related to the different fouling mechanisms at play at different concentrations. Specifically, it was reported that, while the key fouling mechanism was pore plugging at lower concentrations, the fouling mechanism was a mixture of bridging between particles and competing for optimal deposition spots on the membrane at the higher concentrations [39]. In this case, the increase in CFV was more effective in mitigating pore plugging at the lowest concentration. Also the droplet removal due to oleophobic slip would tend to be easier for the low concentration coverage and require higher fluxes to achieve droplet capture.

Figure 2. 6. Critical flux (J_{crit}) of oil emulsion at various oil concentrations and cross-flow velocities (CFVs)

Notably, interesting observations were made on the different fouling phenomena for the different oil concentrations. Fig. 2.7 shows DOTM images at the feed-membrane interface at various permeate fluxes and oil concentrations at CFV = 0.1 m/s. Each row represents each of the four concentrations investigated (namely, 50, 200, 350 and 500 ppm), while each of the three columns represents permeate fluxes of 0 l/m²h, 5 l/m²h above the critical flux (J_{crit}) and 10 l/m²h above J_{crit} after 10 minutes at that flux. At the lower oil concentrations of 50 ppm (Fig. 2.7a) and 200 ppm (Fig. 2.7b), the oil emulsion tended to deposit as individual droplets or clusters of oil droplets at both fluxes of 5 and 10 l/m²h above J_{crit} . On the other hand, at the higher oil concentrations of 350 ppm (Fig. 2.7c) and 500 ppm (Fig. 2.7d), stripes of oil droplets, parallel to the flow direction, were observed at both 5 and 10 l/m²h above J_{crit} . It should be noted that stripes were not observed for the latex particles. Such ‘clusters’ or ‘stripes’ have been reported in both the gas-solid flows [40-42] and granular flows [43, 44] community, but less so for

membrane filtration applications. The formation of clusters is generally acknowledged to be due to inelastic collisions leading to decreased kinetic energy, which thereby results in lower local pressure regions that attracts surrounding particles [41]. The decreased of kinetic energy correlates to the drop of the particle velocity and also the granular temperature of the particle (i.e. collisional cooling), which quantifies the kinetic energy of the collision. As the energy dissipation happens, the inter-particle distance drops and the inter-particle forces (van der Waals-VDW interaction and capillary bridges) increase to attract other particle which make the formation of a cluster[41]. The ‘stripes’ observed at higher concentrations are likely due to the more dominant clustering effect. Higher particle concentrations have been reported to lead to higher growth rate coefficients in perturbation waves and lower particle stability, both of which encourage cluster formation [45-47]. A few studies have reported on a similar striping phenomenon during membrane filtration. The first to report the experimental observation of the striping phenomenon in the ultrafiltration of dextran in water was Jonsson [48], where the stripes had widths of 0.1 – 0.15 mm and were similarly parallel to the feed flow. Larsen [49] then attempted to explain the phenomenon by instability modeling. Subsequently, Henriksen et al. [50] indicated that the stripes occurred in the Reynolds number range of 400 - 1000, and at a lower Reynolds number range when the viscosity of the liquid increases. More recently, Li et al [51] observed the striping phenomenon via Optical Coherence Tomography (OCT) during the filtration of 0.1 g/l of bentonite and silica nanoparticles at a CFV of 0.06 m/s. The stripes were observed at low shear rate and high concentration, which agrees with the current study.

Figure 2. 7. Fouling phenomena at various permeate fluxes (J), CFV = 0.1 m/s and oil concentration of: (a) 50 ppm, (b) 200 ppm, (c) 350 ppm and (d) 500 ppm. The photos were taken at the end of the 10th minutes after the targeted flux was set.

Other than higher feed concentration, a higher permeate flux also causes a higher concentration of oil droplets at the membrane surface, which could in turn increase the probability of striping. Fig. 2.8, which displays the evolution of the fouling phenomenon at two minute intervals for two permeate fluxes, verifies this. Both permeate fluxes were higher than the J_{crit} value of 29 l/m²h (Fig. 2.6). Whereas striping was absent at the lower

permeate flux of 35 l/m²h (Fig. 2.8a), the striping phenomenon was obvious throughout the ten minutes at the higher permeate flux of 45 l/m²h (Fig. 2.8b). Regarding the stripes (Fig. 2.8b), the orientation remained the same but the parallel stripes were observed to be moving transversely back and forth across the membrane with time.

Figure 2. 8. Evolution of fouling for 500 ppm of oil at a CFV of 0.1 m/s for permeate fluxes of (a) 35 l/m²h and (b) 45 l/m²h. J_{crit} in this case was determined as is 29 l/m²h.

Also, CFV is expected to affect the occurrence of the striping phenomenon. Fig. 2.9 shows the DOTM images for 500 ppm of oil at various CFV values. The left column depicts the images at 0 l/m²h as a benchmark, while the right column the images at 10 l/m²h above J_{crit} . Each row represents a different CFV, namely, 0.1, 0.2 and 0.4 m/s, where the Re were in laminar region (namely, 419, 838, and 1677). Fig. 2.9 shows that striping only occurred at the lowest CFV of 0.1 m/s (Fig. 2.9a), but was absent at the higher CFVs of 0.2 and 0.4 m/s (Figs. 2.9b and c). This result agrees with previous

studies [48-51], which reported that the increase in shear stress alters the hydrodynamic stability, which in turn causes the stripes to disperse.

Figure 2. 9. DOTM images at two permeate fluxes (namely, 0 l/m²h, and 10 l/m²h above J_{crit}) for 500 ppm of oil at a CFV of (a) 0.1 m/s, (b) 0.2 m/s and (c) 0.4 m/s.

2.3.3. Effect of Salinity

The presence of salt is inevitable in produced water, which represents the largest source of oily wastewater. Salt is known to affect the characteristics (e.g., stability) of oil emulsions [52, 53] and also the membrane surface [39, 54], which would affect the oil-membrane interactions and thereby fouling behavior. Hence this study sought to investigate the effect of salt concentration on the critical flux (J_{crit}) of the oil-in-water

emulsion. It should be noted that the average droplet diameter remained in the same range of 4 – 6 μm in the presence of salt up to a concentration of 35,000 ppm (Fig. 2.1).

Fig. 2.10, which illustrates the relationship between J_{crit} and salt concentration, indicates that J_{crit} decreased as salt concentration increased. This implies that the presence of salt increased the membrane fouling tendency, which can be due both to the changes in the (i) density of the continuous phase and also (ii) emulsion-membrane interfacial interaction energy. Regarding (i), as the salt concentration increased, the density of the continuous phase increased, thereby the density differential between the continuous and dispersed (i.e., oil emulsion) phases increased, which increased the tendency of the oil droplets to rise towards the membrane. Specifically, because the membrane cell (Fig. 2.2) was oriented such that the feed channel was at the bottom, as necessitated by DOTM to allow for the observation of the foulant deposition events at the membrane surface without obstruction by solids on the feed side, the more buoyant oil droplets hence were more likely to be deposited on the membrane. This effect is dependent on the density differential between the continuous and dispersed phases, which underlies the Stokes velocity, was approximately a 10% difference between the lowest and highest salt concentrations; in this case, the density differential was approximately 230 kg/m^3 in the absence of salt and 260 kg/m^3 in the highest concentration of 35,000 ppm of salt. As for (ii), the charges on both the oil droplets and membrane surface are expected to change as the salt concentration increased. Fig. 2.11a shows that the zeta potential (Phase Analysis Light Scattering Zetasizer, Brookhaven Instruments Corporation, New York, USA) of the oil emulsion increased from negative to positive values as the salt concentration increased. This agrees with our previous study, whereby the less negatively charged latex particles gave lower critical flux (J_{crit})

values than the more negatively charged glass particles [38]. Other studies also found that the presence of salt caused the permeate flux to decline due to the reduced charges on the foulant particles, which correspondingly decreased the repulsion between the particles and increased the tendency for deposition as a cake layer [55]. Fig. 2.11b further shows that the surface potential (Malvern Zetasizer Nano ZS) of the membrane became less negative as the salt concentration increased; note that the upper bound of salt concentration used for the characterization of the surface potential was only 10 mM (585 ppm) due to the limitation of the instrument used. The diminished charges on the membrane as salt concentration increased also caused less repulsion with the charged oil emulsion, which also contributed to the reduced critical flux (J_{crit}) values in Fig. 2.10.

Figure 2. 10. Critical flux (J_{crit}) of 500 ppm of oil emulsion at CFV = 0.1 m/s and various salt concentrations

Figure 2. 11. (a) Zeta potential of the 500 ppm of oil emulsion and (b) Surface potential of the membrane at various salt concentrations. Note that the highest salt concentration possible for the instrument (Malvern Zetasizer Nano ZS) used for measuring surface potential was 10 mM (585 ppm).

Fig. 2.12 presents the effect of CFV on the critical flux (J_{crit}) of the oil emulsion in the presence and absence of salt. Agreeing with Fig. 2.10, Fig. 2.12 indicates that the J_{crit} values were consistently lower when salt was present over the entire range of CFV investigated. This contradicts our previous study, which reported that an increase in CFV diminished the surface charge effects, such that the differences in the J_{crit} values between latex and glass particles (which have respectively attractive and repulsive Gibbs free energy of interfacial interaction) became lesser [38]. A plausible explanation for the discrepancy is that, whereas both foulant particles investigated were negatively charged in the previous study, the current study was such that the oil emulsion became less charged at the higher salt concentrations, which implies less repulsion from the negatively charged alumina membrane (which also became less charged with increasing salt concentration). The effect of increased shear associated with the increased CFV may be inadequate in overcoming the stronger foulant-membrane affinity.

Figure 2. 12. Critical flux (J_{crit}) of 500 ppm of oil emulsion in the absence and presence of 35,000 ppm of salt

2.4. Conclusions

In this study, DOTM was used to obtain the critical flux (J_{crit}) values of oil-in-water emulsions (concentrations between 50 – 500 ppm) at various cross-flow velocities (CFVs; between 0.1 and 0.4 m/s), and in the absence and presence of salt (concentrations up to 35,000 ppm). The oil droplets were in the diameter range of 1 - 20 μm , with an average diameter between 4 - 6 μm . Although the critical flux of colloids have been studied using DOTM, this represents the first systematic study of oil-in-water emulsions, which have been observed to behave distinctly differently in terms of coalescence, deformation and splitting [25].

Five interesting observations are highlighted here. Firstly, the oil-in-water emulsion surprisingly exhibited similar critical flux (J_{crit}) values as the larger latex particles ($d_p = 10 \mu\text{m}$) at lower cross-flow velocities (CFVs) and higher J_{crit} values at higher CFV values. This is presumably due to the twin effects of membrane

oleophobicity and the oil-in-water emulsion having droplets with diameters up to 20 μm to enhance the shear-induced diffusion effect of the average sized droplets [35]. Secondly, the J_{crit} results obtained did not agree with the shear-induced diffusion model by Li et al. [34] that applied for particulate foulants with diameter greater than 3 μm , but did agree with the other model proposed for particulate foulants with diameters of 3 μm wherein an empirical constant (C_d) was incorporated. The C_d value in the absence of salt was higher than that reported for latex particles [34], but that in the presence of salt was lower. Thirdly, the J_{crit} values expectedly increased with CFV, and the increase was greater for the lowest oil concentration. Fourthly, a striping phenomenon, where the fouling was such that distinct bands of oil droplets formed on the membrane, was observed for higher oil concentrations and lower CFV values. The stripes, which were not observed with the latex particles, were parallel to the cross-flow and to one another, and moved across the membrane with time. Such a phenomenon is probably due to hydrodynamic instabilities and has not been rigorously studied for membrane filtration applications. Since it directly impacts fouling and anti-fouling means, future efforts to lend more understanding is warranted. Fifthly, the increase in salt concentration decreased the J_{crit} values in the range of CFV values investigated. Two contributing factors are (i) the increased buoyancy of the oil droplets increasing their tendency to deposit on the membrane which is positioned above the feed channel; and (ii) the zeta potential of the oil-in-water emulsion became less negative then positive as the salt concentration increased, which increased the affinity with the negatively-charged membrane.

This study represents the first systematic investigation on the critical flux of oil-in-water emulsions, and the results here indicate that a typical oil-in-water emulsion behaves differently from other typical particulate foulants, hence a more in-depth

understanding is warranted. It should be noted that the behaviors may be unique to the combination of oil and surfactant used in this study.

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CHAPTER 3: ASSESSMENT OF OIL FOULING BY OIL-MEMBRANE INTERACTION ENERGY ANALYSIS

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Abstract

Membrane-filtration is promising for treating the voluminous oily wastewater, especially when the oil emulsions are smaller than 20 μm . However, studies on the inevitable membrane fouling phenomenon by oil are rather scarce. In particular, a question that remained to be addressed was whether the DLVO or XDLVO model provides better predictions of the oil-membrane interfacial interactions and thereby the extent of fouling. Accordingly, this study investigated four oil types (namely, hexadecane, soybean oil, fish oil and crude oil) that were stabilized by the same non-ionic surfactant (namely, Tween 20) and had similar mean droplet diameters. The direct observation through the membrane (DOTM) technique was used to quantify the critical flux of the different emulsions, and both the XDLVO and DLVO models were used to quantify the foulant-membrane and foulant-foulant interactions. DOTM results indicated that the critical flux values were similar for all oils under the conditions tested, except crude oil. Although the XDLVO model appears to be more comprehensive than the DLVO in terms of accounting for the additional Lewis acid-base polar (AB)

interaction that is acknowledged to be important in membrane-filtration, results indicate that the dominance of the AB component drowns out the other interactions like that of electrostatics (EL) in this case, which impedes accurate prediction of the different fouling tendencies by the different oil types.

Keywords: Membrane fouling; interfacial interaction energy; critical flux; oil-water separation; DLVO model

3.1. Introduction

Due to the simplicity in operation, high oil removal capability, smaller footprint, and lower capital and operational costs [1, 2], membrane technology is a promising method for treating the large volumes of oily wastewater found in the oil and gas, food processing, and metal processing industries [3]. Particularly for oil emulsions smaller than 20 μm , conventional technologies such as gravity-based, hydro-cyclone, centrifugation or dissolved air floatation (DAF) become inefficient in separating oil from water [2], which makes it challenging to satisfy the regulations governing discharge into the environment [4]. As with all membrane-filtration processes, membrane fouling is a major drawback impeding the more widespread use of membrane-based separation systems. This necessitates more mechanistic understanding dedicated to the membrane fouling phenomena by oil emulsions, which are distinct from other particulate foulants in terms of deformation and coalescence [5].

The experimental study of fouling has benefited remarkably from techniques that allow for non-intrusive, real-time observation of the evolution of the fouling phenomenon. Such techniques have only recently been applied to oil emulsions. In particular, the Direct Observation through the Membrane (DOTM) method has been used for revealing

various fouling behaviors by oil-in-water emulsions. Tummons et al. [5] unveiled three characteristic stages of membrane fouling, namely, (1) droplet attachment and clustering, (2) droplet deformation, and (3) droplet coalescence. Oil deformability has also been visualized via a microscope to impact filtration performance [6], and also via the Optical Coherence Microscopy (OCT) to cause internal pore fouling even when the oil emulsions were two orders-of-magnitude larger than the pore [7]. Subsequently, DOTM showed that the effect of salt was such that it not only decreased the solubility of the surfactant, but also decreased the interfacial tension and zeta potential of the oil emulsion, resulting in increased coalescence and thereby larger droplets that are easily sheared off by cross-flow [8]. In Chapter 2, we quantified using DOTM the effect of oil concentration, cross flow velocity (CFV) and salinity on the critical flux of oil emulsions. It was also found that the shear-induced diffusion model [9] did not predict well for oil emulsions due to the highly oleophobic membrane used, which suggests expectedly the need to account for interfacial interactions on top of the hydrodynamic effects [10].

As with other foulants, the oil-membrane interaction is one of the determinant factors affecting the extent of fouling [11, 12]. To this end, the Derjaguin-Landau-Verwey-Overbeek (DLVO) model, which consists primarily of the Lifshitz – van der Waals (LW) and electrostatic double layer (EL) interactions, is popularly used to elucidate the interfacial interactions [13-15]. Particularly for membrane-filtration applications, because of the acknowledged dominance of the Lewis acid-base polar (AB) component, the extended DLVO (XDLVO) model thus consists of this additional component [15-18]. Brant and Childress [19] compared the predictions by the classical DLVO theory (i.e., consists only of LW and EL interactions) against that of the XDLVO theory (i.e., consists of LW, EL and AB interactions), and found that the classical DLVO theory

indicated that all the foulant-membrane combinations investigated had weak attractions and thereby similar fouling tendencies, whereas the additional AB interactions considered in the XDLVO approach led to marked differences in the total interaction energies. Also, Ahmad et al. [20] showed that the DLVO and XDLVO models provide good explanations as well to the fouling by non-rigid particulate foulants, namely, algae, during microfiltration. In another study, Kuhn et al. [21] experimentally studied the fouling of milk components in the microfiltration (MF) system at various pH values, and found that the flux reduced at lower pH values due to the less repulsive interaction between the casein constituent and the membrane surface, as also quantified by the XDLVO model. Because the hydrophobic and hydration effects represented by the Lewis acid-base (AB) interactions [22-24] are significant for the hydrophobic surfaces in water [22, 23] in membrane-filtration applications, the XDLVO model has become increasingly popular relative to the classical DLVO model in membrane-filtration studies. Surprisingly, in a recent study, He et al. [13] reported that, due to the apolarity of crude oil, the DLVO model sufficed to explain the interaction of crude oil emulsion with PVDF membrane at various salt concentrations. This interesting result on oil emulsions that appears to counter previous fouling studies that tend towards XDLVO theory warrants a closer look.

To contribute towards an enhanced mechanistic understanding of membrane fouling by oil emulsion and address the question regarding the relevance of the AB interactions for apolar oil foulants, this study investigated four oil types (namely, hexadecane, soybean oil, fish oil and crude oil) that were stabilized by the same non-ionic surfactant (namely, Tween 20) and had similar mean droplet diameters. Tween 20 was chosen as the surfactant due to its non-ionic nature, thus it did not give additional charge on the oil droplet's surface. Oil concentrations in the range of 250 – 750 ppm and crossflow

velocities in the range of 0.1 – 0.4 m/s were studied. The direct observation through the membrane (DOTM) technique was used to quantify the critical flux of the different emulsions, and both the XDLVO and DLVO models were used to quantify the foulant-membrane and foulant-foulant interactions. The agreement or lack thereof of the experimental results and predictions by the two models were assessed and discussed.

3.2. Theory

3.2.1. DLVO and extended DLVO (XDLVO)

The classical DLVO theory states that the total interaction energy is the sum of the Lifshitz-van der Waals (LW) and electrostatic (EL) components, with the Brownian (BR) component negligible for the micron-sized foulant considered here:

$$U_{mlo}^{DLVO} = U_{mlo}^{LW} + U_{mlo}^{EL} \quad (3.1)$$

where U_{mlo} denotes the interaction energy between the membrane and the oil emulsion, with the subscripts m , l and o denote respectively the membrane, liquid environment in the bulk feed and oil emulsion. On the other hand, the extended DLVO theory stipulates an additional polar Lewis acid-base (AB) component [25]:

$$U_{mlo}^{XDLVO} = U_{mlo}^{LW} + U_{mlo}^{EL} + U_{mlo}^{AB} \quad (3.2)$$

3.2.1.1. LW interaction

The LW (Lifshitz-van der Waals) interaction energy represents the non-polar interaction between two surfaces, specifically in this case between the membrane and oil emulsion, which can be expressed as the free energy of adhesion per unit area (ΔG^{LW}) between two infinite planar surfaces [15]:

$$\Delta G_{y_0}^{LW} = 2(\sqrt{\gamma_l^{LW}} + \sqrt{\gamma_m^{LW}})(\sqrt{\gamma_o^{LW}} + \sqrt{\gamma_l^{LW}}) \quad (3.3)$$

where γ denotes the surface tension (i.e., surface free energy per unit area) of a medium (i.e., liquid or membrane or oil), and the subscript y_0 denotes the minimum separation distance of the two surfaces and is usually assigned the value of 0.158 nm [13, 15]. According to Brant and Childress [15], in order to get the actual interaction energy between the membrane surface (assumed to be an infinite planar surface) and oil droplet (assumed to be a sphere), the Derjaguin's technique can be applied to scale the interaction energy to a required geometry. By applying this technique, the LW interaction energy as a function of separation distance (h) between the membrane and oil emulsion is expressed as:

$$U_{mlo}^{LW}(h) = 2\pi\Delta G_{y_0}^{LW} \frac{y_0^2 a_c}{h} \quad (3.4)$$

where a_c is the radius of the oil droplet.

3.2.1.2. EL interaction

The EL interaction is a function of the electrostatic or the zeta potential, and the free energy per unit area (ΔG^{EL}) between two infinite planar surfaces is given by [15]:

$$\Delta G_{y_0}^{EL} = \frac{\varepsilon_0 \varepsilon_r \kappa}{2} (\zeta_m^2 + \zeta_o^2) [1 - \coth(\kappa h)] + \frac{2\zeta_m \zeta_o}{(\zeta_m^2 + \zeta_o^2)} \text{csch}(\kappa h) \quad (3.5)$$

where ζ_m and ζ_o are the zeta potentials of respectively the membrane and the oil, $\varepsilon_0 \varepsilon_r$ is the dielectric permittivity of the liquid environment, κ is the inverse Debye screening length and is equal to 1 μm for DI water [26]. By applying the Derjaguin's technique, the EL interaction energy as a function of the distance between the membrane surface and oil droplet can be obtained by:

$$U_{mlo}^{EL}(h) = \pi \varepsilon_0 \varepsilon_r a_c [2\zeta_m \zeta_o \ln(\frac{1+e^{-\kappa h}}{1-e^{-\kappa h}}) + (\zeta_m^2 + \zeta_o^2) \ln(1 - e^{-2\kappa h})] \quad (3.6)$$

3.2.1.3. AB interaction

The AB interaction is the polar interaction due to the electron-donor and electron-acceptor relationship, and the free energy of adhesion per unit area between two infinite planar surfaces is expressed as a function of the polar components of the surface tension of the membrane (m), bulk feed solution (l), and oil droplet (o):

$$\Delta G_{y_0}^{AB} = 2\sqrt{\gamma_l^+}(\sqrt{\gamma_m^-} + \sqrt{\gamma_o^-} - \sqrt{\gamma_l^-}) + 2\sqrt{\gamma_l^-}(\sqrt{\gamma_m^+} + \sqrt{\gamma_o^+} - \sqrt{\gamma_l^+}) - 2(\sqrt{\gamma_m^+ \gamma_o^-} + \sqrt{\gamma_m^- \gamma_o^+}) \quad (3.7)$$

where the superscripts + and – represent the electron-donor and electron-acceptor. By applying the Derjaguin's technique, the AB interaction energy as a function of separation distance (h) between the membrane and oil emulsion is expressed as:

$$U_{mlo}^{AB}(h) = 2\pi a_c \lambda \Delta G_{y_0}^{AB} \exp \left[\frac{y_0 - h}{\lambda} \right] \quad (3.8)$$

where λ is the characteristic decay length of the AB interaction in water and the commonly used value for aqueous medium is 0.6 nm [27].

3.3. Materials and Methods

3.3.1. Oil-in-Water Emulsions and Characterization

Four different oils were used in this study, namely, hexadecane, fish oil (Menhaden), soybean oil and crude oil (NIST 2722), which were all purchased from Sigma Aldrich. The specific gravity, surface tension (γ) and zeta potential (ζ) values of the oils are listed in Table 3.1. For each oil, a highly concentrated (namely, 25,000 ppm) stock solution of oil emulsion (more specifically, oil-in-water emulsion) was made by mixing 10 ml of oil, 2 ml of Tween 20 (Sigma Aldrich) and 388 ml of DI water (Millipore) in a blender (Warring 8011 S) for one minute at 18,000 rpm. The size distribution of each oil

emulsion stock solution was measured by the Focused Beam Reflectance Measurement system (FBRM; Lasentec S400, PI-14/206), as shown in Fig. 3.1, which indicates the mean droplet diameters among the four oil emulsions were similar and ranged from 8.2 - 10.1 μm . Before each experiment, the stock solution was diluted to the desired oil concentration (i.e. 250, 500, or 750 ppm) by adding DI water. In order to ascertain that the distributions remained similar throughout each experiment, the FBRM was used to monitor the droplet size distributions of the oil emulsion in the feed tank throughout every experiment.

Table 3. 1. Properties of Hexadecane, Fish oil, Soybean oil and Crude Oil

Parameter	Hexadecane	Fish Oil	Soybean Oil	Crude Oil
^a Specific Gravity, SG (-)	0.77	0.93	0.92	0.91 (°API = 23.7°)
^b Surface Tension, γ (mN/m)	27.0	33.9	33.4	22.5 [13]
^c Zeta Potential, ζ (mV)	-39.92	-39.2	-38.2	-32.84
^d pH	7.2	7.3	7.2	6.7

^aData provided from Sigma Aldrich

^bData measured using tensiometer (Dataphysics DCAT 11)

^cData measured using Zetasizer (Phase Analysis Light Scattering Zetasizer, Brookhaven Instruments Corporation, New York, USA)

^dData measured using pH meter (Hanna Instruments, HI 9811-5) for oil emulsion of 500 ppm

^eThis is the American Petroleum Institute (API) Gravity value at 15.6 °C, which is a measure of how heavy the oil is compared to water and is a common standard for crude oil. A value of greater than 10 indicates the oil will float in water. $^{\circ}\text{API} = \frac{141.5}{\text{SG}} - 131.5$

Figure 3. 1. Number-based droplet size distribution of 25,000 ppm of each oil emulsion stabilized by the Tween 20 surfactant.

3.3.2. Direct Observation Through the Membrane (DOTM)

The Direct Observation through the Membrane (DOTM) method was used here, as with the previous study on oil emulsion (Chapter 2). The experimental setup, as shown in Fig. 3.2, consisted of a video camera (Axiocam 105 Color) integrated with a light microscope (Zeiss Imager; A2 m), a membrane cross-flow module, a gear pump (Micropump Inc; GJ-N25. PF/S.A) to propel the feed flow, a peristaltic pump (Cole Palmer; Masterflex L/S 7519-20/85) to propel the permeate flow, a weighing balance (Kern; 572), and a computer to log data during experiments. For the measurement of transmembrane pressure (TMP), three pressure transmitters (Cole Palmer) were used to characterize the pressures in the membrane cell (namely, feed inlet pressure, feed outlet pressure, and permeate inlet pressure) and connected to the computer. The feed tank (600 mL beaker) containing the targeted oil-in-water emulsion sat atop a magnetic stirrer plate (Heidolph; MR Hei-Mix S) to keep the suspension well-mixed. The permeate tank (100 ml beaker) sat atop a weighing balance (Mettler-Toledo) to measure

the permeate flux and every 20 ml of permeate collected was returned to the feed tank to maintain the feed concentration.

Figure 3. 2. Direct Observation Through the Membrane (DOTM) Setup

The membrane module had dimensions of 105 mm length by 35 mm width by 3 mm height, with 2 mm being the feed channel height and 1 mm being the permeate channel height, and the permeate channel being atop the feed channel. The membrane used for every experiment was a new circular Anopore membrane with a diameter of 47 mm and a mean pore size of 0.2 μm . The membrane was glued in between two rectangular (55 mm $\times$ 135 mm) pieces of paper, each with a square cut-out (27 mm by 27 mm) in the center to expose the membrane that served as mechanical support. The membrane was transparent when wetted, thus allowing the light from the microscope to pass through the permeate channel then the membrane, and thereby the focal plane to be at the feed-membrane interface.

3.3.3. Critical Flux Determination

The critical flux (J_{crit}) is the flux at which foulant deposition onsets [28]. In this study, the J_{crit} was determined using the flux-stepping method, starting at a constant permeate

flux of 5 L/m²h, then followed by increments by 5 L/m²h every 10 minutes. During each 10 minutes at the constant permeate flux, two images were taken at the 2nd and 10th minute, and the images were analysed using ImageJ to determine the extent of deposition by the oil emulsion. Specifically, the surface coverage at the feed-membrane interface by the oil droplets (C , %) was obtained, then the rate of change of coverage between the two images at the 2nd and 10th minute ($\frac{\Delta C}{\Delta t}$) was calculated using the following equation:

$$\frac{\Delta C}{\Delta t} = \frac{C_{10\text{th minute}} - C_{2\text{nd minute}}}{8 \text{ minutes}} \quad (3.9)$$

The critical flux (J_{crit}) was determined as the flux at which the $\frac{\Delta C}{\Delta t}$ value exceeds the threshold value of 0.2 %/min, as verified in our previous studies for both oil emulsion and latex particles [26].

3.3.4. Surface Tension Components

The overall surface tension (γ), which was measured using a tensiometer (Dataphysics DCAT 11), is the sum of the non-polar (LW) and polar (AB) components:

$$\gamma = \gamma^{LW} + \gamma^{AB} \quad (3.10)$$

whereby the polar component (γ^{AB}) is a function of two more components, namely, the electron-donor (γ^+) and electron-acceptor (γ^-) components [25]:

$$\gamma^{AB} = 2\sqrt{\gamma^+\gamma^-} \quad (3.11)$$

The surface tension components are usually quantified through measuring the contact angle (θ) and using the extended Young equation:

$$(1 + \cos \theta) \gamma_l = 2[\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_s^-\gamma_l^+}] \quad (3.12)$$

where the subscripts s and l denote solid and liquid, respectively.

For the oils whose surface tension components were not readily available (namely, fish oil and soybean oil), the surface tension components were quantified by the contact angle instrument (Dataphysics Contact Angle System OCA 15EC) using the pendant drop method. Specifically, 5 μL of the oil tested was dropped on top of the parafilm (Whatman PM996 M roll) and the contact angle was measured by analyzing the image from a camera; this was repeated five times for each oil and averaged. Parafilm was used based on a previous study [29], where it was used as the solid reference material due to the apolarity of the material, which means that the polar (i.e., AB) component is equal to zero and Eq. (3.12) can be simplified to the following to determine the LW component of the oil:

$$\gamma_o^{LW} = \frac{[(1 + \cos \theta)\gamma]^2}{4\gamma_{parafilm}^{LW}} \quad (3.13)$$

where θ is the contact angle of the oil on the parafilm, γ is the overall surface tension, and $\gamma_{parafilm}^{LW}$ is the LW surface tension component of the parafilm (which is 25.5 mN/m [29]).

3.4. Results and Discussions

3.4.1. Critical Flux

3.4.1.1. Effect of Crossflow Velocity (CFV)

Increasing the crossflow velocity (CFV) increases the liquid shear on the membrane and thereby mitigates fouling, but this comes at an increased energy cost [26, 30-32]. Fig. 3.3 shows the critical flux values of 500 ppm of the four oils investigated at three CFV values ranging from 0.1 to 0.4 m/s.

Figure 3. 3. Critical flux (J_{crit}) of 500 ppm of each of the four oil emulsions stabilized by the same surfactant (namely, Tween 20) at CFV values between 0.1 – 0.4 m/s. Each error bar represents the range of J_{crit} values from repeated experiments.

As expected, the J_{crit} values increased as the crossflow velocity (CFV) increased due to the increased shear on the membrane. Interestingly, the J_{crit} values for the hexadecane, fish oil and soybean oil were similar at all three CFV values, while that for crude oil was only slightly lower at the two lower CFVs. Specifically, because the same membrane (with a reported streaming potential of approximately -23 mV (Chapter 2) at the conditions tested) was used in all cases, (i) the similar zeta potential (ζ) values (Table 3.1) among hexadecane, fish oil and soybean oil indicate similar foulant-membrane affinity and thereby similar J_{crit} values; and (ii) the less negative zeta potential (ζ) of the crude oil, which probably caused by the presence of mixed natural surfactant in crude oil [33], imply greater foulant-membrane affinity, and thereby slightly lower J_{crit} values at the lower CFVs and similar J_{crit} values at the highest CFV as hydrodynamics effects dominate over interfacial interactions [26].

3.4.1.2. Effect of Oil Concentration

Analogous to Fig. 3.3, Fig. 3.4 displays the J_{crit} values for the four oil emulsions stabilized by Tween 20 at three oil concentrations, i.e., 250, 500 and 750 ppm, at a CFV of 0.1 m/s. Clearly, as the oil concentration (C_{oil}) increased, the J_{crit} values decreased, because the increased number of emulsion droplets increased the fouling propensity. Similar to Fig. 3.3, Fig. 3.4 indicates that (i) the J_{crit} values were similar among hexadecane, fish oil and soybean oil; and (ii) the J_{crit} values for crude oil were significantly lower at the lower concentrations of 250 and 500 ppm, but more similar to the other three oils at the highest concentration. The similar trends suggest similar links to zeta potential (ζ) values (Table 3.1).

Figure 3. 4. Critical flux (J_{crit}) of various concentrations between 250 – 750 ppm of each of the four oil emulsions stabilized by the same surfactant (namely, Tween 20) at a CFV of 0.1 m/s. Each error bar represents the range of J_{crit} values from repeated experiments.

In agreement with the previous DOTM study on hexadecane emulsions stabilized by Tween 20 in Chapter 2, striping was consistently observed despite the different oil types used here. Specifically, as shown in Fig. 3.5, the oil emulsions deposited in stripes instead of a more uniform membrane surface coverage. This has been attributed to

hydrodynamic instability stemmed in the balance of the mass transfer rate (permeate drag force) and CFV (shear force) [34, 35], and the stripes has been found to only form at higher oil concentrations (C_{oil}) and lower crossflow velocities (CFV) same as in Chapter 2. The coverage for the crude oil was distinctly greater due to the lower critical flux (J_{crit}).

Figure 3. 5. Striping phenomena for 500 ppm of oil emulsions of different oil types stabilized by Tween 20 at a CFV of 0.1 m/s. Each image was taken at the 10th minute at the flux step of 40 L/m²h.

3.4.2. Effect of Permeate Flux

Since constant-flux operation, rather than constant-pressure operation, is more practically relevant, the evolution of the fouling phenomena at two constant fluxes was investigated here. Fig. 3.6 presents the surface coverage on the membrane for 500 ppm of each oil emulsion analyzed via ImageJ at a CFV of 0.25 m/s over 30 minutes, wherein an image was taken at the end of every minute. Each condition was assessed two to three times. The two constant fluxes studied were 50 and 125 L/m²h, such that one was below

the J_{crit} values of these oils that ranged from 73 - 85 L/m²h and one was above. At 50 L/m²h, the percentage surface coverage remained constantly low for all four oil emulsion types throughout the 30 minutes because of the lack of foulant deposition below the critical flux (J_{crit}). At the higher permeate flux of 125 L/m²h, the surface coverage generally increased with time, but at different rates for the different oil emulsion types. Two observations are worth noting. Firstly, although the surface coverage generally increased with time, the fluctuations of the surface coverage were significant for three of the four oils (namely, hexadecane, soybean oil and crude oil). This was because, instead of solely incremental deposition of the oil emulsion with time, the oil emulsion concurrently deposited onto and detached from the membrane dynamically due in part to the oleophobicity of the Anopore membranes used [5]. Moving cake layers [36], which appeared as clusters of oil droplets that deposited at times and moved along the membrane surface at other times, were clearly observed. The moving cake layers enlarged progressively and were such that the entire layer moved even at full coverage of the membrane. Secondly, the rates of increase of surface coverage varied among the oils, with the increase being fastest for crude oil (Fig. 3.6d) due to the relatively lower critical flux of crude oil (Figs. 3.3 – 3.4). These observations reflect the different foulant-membrane and foulant-foulant affinities.

Figure 3. 6. Percentage coverage of the membrane surface (C , %) over 30 minutes at a CFV of 0.25 m/s for 500 ppm of each oil emulsion: (a) hexadecane, (b) fish oil, (c) soybean oil, and (d) crude oil. The J_{crit} values for these oils ranged from 73 - 85 L/m²h. Each data point represents the average of the images taken at the end of every minute, and each error bar represents the range of coverage over the two - three repeats.

To further substantiate the DOTM observations, Fig. 3.7 displays the evolution of the transmembrane pressure (TMP) versus permeate volume for the same conditions as that in Fig. 3.6. Similar to Fig. 3.6, the TMP profile stayed constant throughout the process for all oil emulsions at the lower flux of 50 L/m²h (below J_{crit}), while the membrane fouling by crude oil (Fig. 3.7d) was at the fastest rate initially compared to other oils at the higher flux (125 L/m²h; above J_{crit}). The latter agrees with the steep increase in TMP also for crude oil observed by He et al. [37].

Figure 3. 7. Transmembrane pressure (TMP) profile over the permeate volume per membrane unit area (cm) at CFV of 0.25 m/s for 500 ppm of each oil emulsion: (a) hexadecane, (b) fish oil, (c) soybean oil, and (d) crude oil. The J_{crit} values for these oils ranged from 73 - 85 L/m²h. Membrane area was 7.29 cm².

3.4.3. Interaction Energy

The DLVO and extended DLVO (XDLVO) interaction energy concepts are becoming increasingly popular recently to explain membrane fouling tendencies in membrane filtration applications [15-17, 38, 39], and therefore this study adopted these two models to provide more insights on the interactions between foulant-membrane and foulant-foulant. Particularly for membrane filtration, the XDLVO model has gained more traction due to the additional consideration of the Lewis polar Acid Base (AB) interaction, which is not included in the original DLVO model and is reported to be important for accounting for the hydration of surfaces [40]. The inclusion of the shorter-range (i.e., smaller separation distances between the surfaces) AB interaction was found

to explain the discrepancies between the experimental results and the predictions by the extended DLVO (XDLVO) model [15-18]. Both the DLVO and XDLVO models were assessed in this study. Table 3.2 displays the surface tension and the corresponding components of the membrane used, water and the four oils investigated. Notably, the AB components of the oils are zero, which agree with a recent study that used the DLVO instead of XDLVO theory in the filtration of oil emulsion, based on the argument that oil emulsions are apolar and thereby the AB term was superfluous [13].

Table 3. 2. Surface tension and the corresponding components for the membrane, water and each oil

Material	γ	γ^{LW}	γ^{AB}	γ^+	γ^-	Ref.
Anopore membrane	39.6	31.6	8	0.6	27.2	[26, 41]
Water	72.8	21.8	51	25.5	25.5	[13, 26]
Hexadecane	27.0	27.0	0	0	0	[25]
Fish Oil	33.9	33.6	0	0	0	Measured
Soybean Oil	33.4	33	0	0	0	Measured
Crude Oil	22.5	21.7	0	0	0	[13]

Note : Units are mJ/m²

Fig. 3.8 shows the profiles of the interaction energy between each of the four oil emulsion and the membrane as a function of separation distance. Specifically, Figs. 3.8a, b and c present respectively the LW, EL and AB interaction energies, while Figs. 3.8d and e present respectively the overall XDLVO and DVLO interaction energies. The LW, EL and AB interaction energies were calculated using Eqs. 3.7, 3.11 and 3.9, respectively, and the surface tension component values in Table 3.2. The range of separation distance is between 0.158 nm (i.e., minimum cut-off or separation distance) and 1000 nm [13-15, 20]. Fig. 3.8 indicates that the AB interaction energy (Fig. 3.8c) was orders-of-magnitude greater than the LW (Fig. 3.8a) and EL (Fig. 3.8b) interactions

at the lower range of separation distance. Furthermore, the LW and AB interaction energies were attractive, whereas the EL interaction energy was repulsive, which culminated in attractive XDLVO interactions (Fig. 3.8d) and repulsive DLVO interactions (Fig. 3.8e). The apparent contradiction between the XDLVO and DLVO energies stem agree with Brant and Childress [15], which found repulsive XDLVO interactions and attractive DLVO interactions between silica particles and three different membranes. Because the only difference between XDLVO and DLVO lies in the respective presence and absence of the AB component (Fig. 3.8c), more scrutiny on the AB component was warranted.

Figure 3. 8. Interaction energy between oil emulsion and membrane: (a) LW interaction, (b) EL interaction, (c) AB interaction, (d) XDLVO, and (e) DLVO.

Fig. 3.8c shows that the AB interaction energy was significant only for separation distances below 7 nm, above which EL interactions dominated over AB interactions.

This indicates that the AB interaction played an important role when the two surfaces were close (less than 7 nm apart), but LW and EL dominated at greater distances. This in turn implies that the separation distance considered dictates the relevance of the two models. Recalling that the critical flux results in Figs. 3.4 – 3.5 that showed that crude oil had a greater fouling tendency than the similar fouling tendencies of the other three oils, it appears that Fig. 3.8e (i.e., the DLVO model) is able to provide a cogent explanation in terms of the lower repulsive interaction energy of the crude oil compared to the other three oils, while Fig. 3.8d (i.e., XDLVO) falls short. This suggests that (i) EL interactions was more dominant, which suggests that the zeta potential values (Table 3.2) could provide useful indications of the fouling tendencies of oil emulsions; and (ii) agrees with He et al. [13], which indicated that the DLVO rather than XDLVO model was adequate for oil emulsions. It should be noted that this does not imply that the XDLVO model is wrong, but that the dominant AB interactions drowned out the EL components that dictated the fouling tendencies (Figs. 3.3 and 3.4).

Figure 3. 9. Interaction energy between oil emulsions: (a) LW interaction, (b) EL interaction, (c) AB interaction, (d) XDLVO, and (e) DLVO.

Analogous to Fig. 3.8 for the interactions between the oil emulsion and the membrane, Fig. 3.9 presents the profiles for the interactions among the oil emulsions of each oil type. The same equations were used, but the surface tension components of the membrane were substituted by that of oil. Interestingly, the XDLVO energies between the oil emulsions (Fig. 3.8d- e) were more attractive than that between the oil emulsion and the membrane (Figs. 3.9d – e) at the lower range of separation distance. This underlies the phenomena of the moving cake layer, which was presumed to cause the fluctuations in the surface coverage in Fig. 3.6 and was attributed to the greater foulant-foulant affinity relative to the foulant-membrane affinity [26]. Similar to Fig. 3.8, Fig. 3.9 indicates that (i) the AB interactions were orders-of-magnitude greater (Fig. 3.9c) than the other two interactions (Figs. 3.9a - b); and (ii) while the XDLVO model (Fig. 3.9d) gave similar interactions among the four oils due to the dominance of the AB component, the DLVO model (Fig. 3.9e) indicated differences among the four oils. In particular regarding (ii), the greater repulsion of hexadecane and soybean oil at the lower range of separation distance coincides with the greater fluctuations of surface coverage in Fig. 3.6. This suggests that the fluctuations of surface coverage may be tied to the greater mobility of the moving cake due to the greater repulsion.

Collectively, Figs. 3.8 and 3.9 demonstrate that, although the AB component was indeed the most dominant, the fouling tendencies for the oil emulsions investigated here were more clearly tied to the DLVO model that does not incorporate the AB component. This agrees with the surprising finding in He et al. [13] and is because the AB components were similar among the oils due to the apolarity (the polar surface tension

component, γ^+ and γ^- , was zero), but the orders-of-magnitude greater values relative to the LW and EL components drowned out the differences in these latter components in the XDLVO model. Between the LW and EL components, the greater values of the latter implies that the zeta potential values mattered, as evident in the analysis of the similar critical fluxes of three of the oils (Figs. 3.3 – 3.4).

3.5. Conclusions

To understand the influence of oil properties on membrane fouling during microfiltration of oily feeds, four different oil emulsions (namely, hexadecane, fish oil, soybean oil and crude oil) stabilized by the same Tween 20 surfactant were studied at various crossflow velocities (CFV; in the range of 0.1 – 0.4 m/s) and oil concentrations (C_{oil} ; in the range of 250 – 750 ppm). The direct observation through the membrane (DOTM) technique was used to characterize critical flux and visually observe fouling, while the DLVO and extended DLVO models were used to explore the interaction energies underlying the fouling phenomena.

Although the oil emulsions had similar mean diameters and varying oil properties (i.e., specific gravity, surface tension, zeta potential), the critical flux (J_{crit}) values were similar for hexadecane, fish oil and soybean oil over the ranges of CFV and C_{oil} assessed, while that of crude oil was lower. DOTM observations indicated all four oil types (i) deposited initially in stripes instead of more uniform coverages, which agree with an earlier study on oil emulsions in Chapter 2; and (ii) exhibited the moving cake layer phenomena, which agree with an earlier study that attractive foulant-foulant interactions causes this [26] and presumably underlie the fluctuations of the surface coverage with time when the flux was above the corresponding critical flux.

The DLVO model accounts for LW and EL interactions, while the XDLVO accounts in addition for the AB interactions. Quantitatively, the AB interaction energies are greater than either the LW or EL component by two orders-of-magnitude at smaller separation distances. Among these three components, while the magnitudes of AB interaction energies are similar for all four oils, variations in magnitudes of LW and EL interactions among the oils are clear. Regarding foulant-membrane interactions, the XDLVO model indicates that the interactions are similar among the four oils due to the dominance of the AB component, whereas the DLVO model indicates that the crude oil has the least repulsive interactions, which agrees with the lowest critical flux values exhibited by crude oil. Similarly, for the foulant-foulant interactions, the variations among the oils are masked by the dominant AB component in the XDLVO predictions, but are clear in the DLVO predictions. The less repulsive DLVO interaction energy of the fish oil, relative to that of hexadecane and crude oil with similar critical flux values, gave a smoother increase of surface coverage with time at a flux above the critical flux. Also, the more attractive foulant-foulant XDLVO interactions relative to that of foulant-membrane led to the flowing cake phenomenon, which agrees with a previous study [26].

The key highlight is therefore that, although XDLVO is a more comprehensive model that incorporates the dominant influence of the AB interactions in membrane filtration applications, the dominant magnitude of AB leads to the drowning out of the other interactions like that of EL in this case, which leads to the inability to predict the different tendencies of the different foulants.

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CHAPTER 4: STRIPING PHENOMENON DURING CROSS-FLOW MICROFILTRATION OF OIL-IN-WATER EMULSIONS

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Abstract

The striping phenomenon in membrane filtration, whereby the foulants deposit as regular streaks rather than a more uniform layer, was first observed more than 30 years ago [1], but the understanding has remained limited to a few subsequent studies [2-5]. In view of the potential practical implications of the stripes in terms of membrane fouling and fouling mitigation, this study was targeted at an in-depth characterization of the stripes. The direct observation through the membrane (DOTM) technique was employed to observe the conditions when the stripes formed by oil emulsions stabilized by three Tween surfactants at a lower cross-flow velocity, and higher oil concentrations and permeate fluxes. The results indicate that (i) other than hydrodynamic factors (e.g., permeate drag, tangential shear), foulant-membrane and foulant-foulant interactions played a role in stripe formation or disappearance, as evident in the formation of stripes only by the oil emulsion stabilized by the Tween surfactants and the effect of pH; (ii) stripes made up of oil droplets appeared to be easier to remove than the more uniform

layer of oil droplets, as evident in the shorter time taken for the former to detach; and (iii) among the three Tween surfactants, the striping characteristics investigated were largely similar, except for the time taken for the deposits to detach.

Keywords : Membrane Fouling, DOTM, Critical Flux, Oil-Water Emulsion, Fouling mitigation

4.1. Introduction

Because membrane fouling remains the Achilles heel of membrane filtration, studies related to obtaining mechanistic understandings of the fouling behavior and correspondingly advancing means of fouling mitigation are widespread. Specifically for microfiltration, which is a pressure-driven membrane process in which suspended colloids and particles larger than approximately 0.1 μm are retained by microporous membranes, the deposition of such particulates/macrosolutes on the membrane is well-acknowledged to be a key limitation [6]. The deposition of foulants on the membrane hinges on a balance between the attractive drag towards the membrane (typically attributed predominantly to permeate drag and foulant-membrane affinity) and repulsive drag away from the membrane (typically attributed predominantly to hydrodynamic shear and foulant-membrane repulsion). A particularly interesting phenomenon of such fouling is that of the stripes, in which the foulants self-arrange into regular streaks of several microns wide that are parallel to the flow direction, reported in just a few membrane-filtration studies thus far [1-5].

The deposition of the foulants as stripes is particularly intriguing, because such particulate/macrosolute foulants are generally known to either deposit as a uniform layer or as clusters depending on the interaction energies at the foulant-membrane and foulant-foulant interfaces [7]. The stripes were first observed by Jonsson [1] during the

study of boundary layer phenomena in ultrafiltration of macrosolutes, namely, dextran and whey protein. Subsequently, Larsen [3] observed striping by the blue dextran solution and proposed a stability model to describe the phenomenon. Larsen [3] found that the appearance of stripes was a slow process; in contrast, the removal of stripes, which can be achieved by increasing the cross-flow velocity (CFV) or relaxing the permeate flux, was rapid. Stripes were also observed by Henriksen and Hassager [2] in the simulation of the macrosolute deposit layer on the membrane surface. Tarabara et al. [5] found via a two-dimensional on-lattice deposition model that stripes formed for cohesive particles under conditions of high Peclet number, and concluded that chemical heterogeneity of the suspensions can lead to fouling layers with different substructures. Another report on stripes was by Li et al. [4] in the study of colloidal fouling using silica and bentonite via Optical Coherence Tomography (OCT), which, consistent with Henriksen and Hassager [2], found the stripes on the fouled layer atop the membrane. Li et al. [4] further used the model developed by Larsen [3] to calculate the spacing between the stripes. In our recent study [8], we also observed the striping pattern formed by deposition of oil emulsions on the membrane via the Direct Observation Through the Membrane (DOTM) technique.

The stripes are reminiscent of the clusters prevalently observed in gas-solid fluidization [9, 10] and also granular flows [11, 12], although the patterns are more disordered than the parallel ones observed here. In gas-solid flows, clusters are understood to result from inelastic collisions leading to decreased kinetic energy and thereby lower local pressure regions that attracts surrounding particles [9]. In granular flows, Royer et al. [11] found that clustering was enhanced by increased inter-particle cohesion. For membrane-filtration processes, the underlying mechanisms leading to the stripes have been hypothesized to be the hydrodynamic instability caused by the flow

along the channel [1] and perturbation in the mass transfer boundary layer, in which the variation of the local permeate flux due to the build up of the deposit (boundary layer resistance) on the membrane surface led to a wave-like hydrodynamic profile [3]. Regarding the boundary layer, nonlinear instability has been reported to lead to stripes or streaks [13, 14]. Another study further stated that the hydrodynamic instability in the flow channel was linked to the viscosity variation, and a critical thickness in the polarization layer and Reynolds number must be attained before the stripes appeared [15]. The stripes therefore appear due to a delicate balance of forces (mainly understood to be permeate drag and hydrodynamic shear), and any disturbance to the balance would result in the disappearance of the stripes [1, 3, 15]. Accordingly, seeking a more in-depth understanding of the striping phenomenon, particularly the characteristics of the stripes, underlies one of the goals of the current study.

The stripes are not merely an interesting research topic, but also have broader practical implications for the membrane-filtration process, particularly with regards to their deposition mechanism and removal from the membrane. Therefore, this study was targeted at systematically characterizing the stripes and evaluating its effect on membrane fouling. The DOTM technique was used to enable non-intrusive, real-time observation of the striping phenomenon by oil emulsion stabilized by surfactants. The specific objectives were to: (i) determine if stripes appeared for oil emulsions regardless of surfactant types, since only the Tween 20 surfactant was used in the previous chapter that observed stripes (Chapter 2); (ii) characterize the stripes in terms of the flux at which they appeared vis-à-vis critical flux, the stripe parameters (namely, width, lateral velocity and number density), influence of pH and ease of detachment. This latter characteristic could have implications for fouling control and mitigation.

4.2. Experimental Methods

4.2.1. Oil-in-water emulsion

The oil-in-water emulsions were prepared by dispersing hexadecane ($C_{16}H_{34}$) ($\geq 99\%$ purity, Sigma Aldrich) in deionized (DI) water (Millipore) with either Tween 20, Tween 40 or Tween 80 surfactants (Sigma Aldrich). The properties (namely, structure, molecular weight (MW), density (ρ), critical micelle concentration (CMC) at 20 – 25 °C, hydrophile-lyophile balance (HLB) and surface tension (γ)) of the three surfactants are listed in Table 4.1. All the properties were provided by Sigma Aldrich; only the surface tension was measured with 100 ppm of surfactant at ambient conditions using a tensiometer (Dataphysics DCAT 11). 500 ml of oil emulsion stock was prepared for each surfactant (each containing 25,000 mg/L of hexadecane, each surfactant at a concentration of 100 times of the CMC value in DI water) using a blender (Warring 8011 S) at 18,000 rpm for 10 s. Before each experiment, a fresh feed solution was made by diluting the stock solution to a desired oil concentration (250 ppm, 500 ppm, or 750 ppm). The Focused Beam Reflectance Measurement system (FBRM; Lasentec S400, PI-14/206) was used to monitor the droplet size distributions of the oil emulsions in the feed throughout each experiment to ascertain that the distributions did not undergo significant changes. Fig. 4.1 presents droplet size distributions of the three oil emulsion stocks with 25,000 ppm of oil. Regardless of which Tween surfactant was used, the number-based means of the oil droplet diameter were in the range of 6-8 μm , and 90% of the droplets had diameter in the 1–20 μm range.

Table 4. 1. Properties of Tween (Polyoxyethylene Sorbitan) 20, 40 and 80 (provided by Sigma-Aldrich).

	Tween 20	Tween 40	Tween 80
Structure
Acid ^a	Lauric Acid (C ₁₂ H ₂₄ O ₂)	Palmitic Acid (C ₁₆ H ₃₂ O ₂)	Oleic Acid (C ₁₈ H ₃₄ O ₂)
MW	1228 g/mol	1277 g/mol	1310 g/mol
ρ	1.095 g/ml	1.08 g/ml	1.064 g/ml
CMC	0.06 mM	0.027 mM	0.012 mM
HLB	16.7	15.6	15
γ	40.0 mN/m	41.3 mN/m	41.5 mN/m

^a the added acid during the ethoxylation of sorbitan.

Figure 4. 1. Number-based droplet size distribution of 25,000 ppm of oil emulsion stabilized by each Tween surfactant.

4.2.2. Direct Observation Through the Membrane (DOTM) setup

The schematic of Direct Observation Through Membrane (DOTM) setup, based on the study by Li et al. [16], is shown in Fig. 4.2. Specifically, a video camera (Axiocam 105 Color) integrated with a light microscope (Zeiss Imager. A2 m) was used in the experiments for non-invasive, real-time observation of the interface between the

membrane and the feed during the cross-flow membrane filtration. In view of the differences in fouling extents at different positions of the membrane [17], the focus was fixed at the center of the membrane for every experiment. The feed solution was contained in a 600 mL glass beaker and continuously mixed using a magnetic stirrer (Heidolph, MR Hei-Mix S) throughout each experiment, and a gear pump (Micropump Inc, GJ-N25. PF/S.A) circulated the feed solution through the feed channel of the membrane module at crossflow velocities (CFV) of 0.1, 0.25 or 0.4 m/s. A peristaltic pump (Cole Palmer; Masterflex L/S 7519-20/85) installed in the permeate line controlled the permeate flux during the flux-stepping method to determine critical flux (J_{crit}). A mass balance (Kern; 572) was used to quantify the permeate flux.

The membrane used in the experiments was the Anopore inorganic membrane (Anodisc, Whatman) with a diameter of 47 mm and a nominal pore diameter of 200 nm. The membrane, when wetted, had sufficient optical transparency for DOTM experiments. The cross-flow channel had dimensions of 105 mm length by 35 mm width by 3 mm height, with 2 mm being the feed channel height and 1 mm being the permeate channel height. The circular membrane disc was fitted with glue (Araldite) between two rectangular (55 mm × 135 mm) pieces of paper with a square (27 mm × 27 mm) gap in the center. The permeate channel of the transparent membrane module was on top, and the focal plane of the microscope was adjusted through the permeate channel and the membrane to be right at the feed-membrane interface. Three pressure transmitters (Cole Palmer; Transducer 206) were used to measure the pressures in the feed inlet, feed outlet and permeate inlet of the membrane module. The images from the camera, the pressure signals from the pressure transmitters and the mass from the balance were recorded on a computer throughout each DOTM test. The focus of the observation was placed at the center of the membrane for each experiment.

Figure 4. 2. Schematic of the Direct Observation Through the Membrane (DOTM) setup.

4.2.3. Critical flux (J_{crit}) determination

The critical flux (J_{crit}), which is the permeate flux above which fouling occurs, was determined by the flux-stepping method [18]. In every flux-stepping experiment, the permeate flux was set at 5 L/m²h for 10 min at the beginning, and after that the flux was increased by 5 L/m²h every 10 min. Two DOTM images were taken at the end of the 2nd minute and 10th minute for every 10 min of constant flux to determine the extent of fouling, which can be quantified by the percentage of the image covered by the oil droplets (C , %) using the ImageJ software. The rate of change of coverage between these two images ($\frac{\Delta C}{\Delta t}$) was calculated using the following equation:

$$\frac{\Delta C}{\Delta t} = \frac{C_{10th\ minute} - C_{2nd\ minute}}{8\ minutes} \quad (4.1)$$

The critical flux (J_{crit}) was determined as the flux at which the $\frac{\Delta C}{\Delta t}$ value exceeds the threshold value of 0.2 %/min, as verified in our previous studies for both oil emulsion and latex particles (Chapter 2 and Appendix).

4.2.4. Characterizing the Stripes

The characteristics of the stripes were studied as comprehensively as possible to shed light on the underlying mechanisms leading to their formation and subsequent disappearance. The parameters quantified include the permeate flux at which the stripes first appeared (J_{stripe}), the time taken for the stripes to appear at above the critical flux (t_{stripe}), width (w_{stripe}), the lateral velocity of the stripes (v_{stripe}), the number of stripes per unit membrane area (n_{stripe}), the time taken for the stripes to detach (t_{detach} ; which provides an indication of the ease of membrane fouling mitigation), as well as the influence of pH on the stripping phenomenon.

Similar to the determination of critical flux (J_{crit}), the flux-stepping method was used to determine the flux at which the stripes first appeared, typically in the bulk feed (J_{stripe}) first before deposition. Specifically, the permeate flux was set to 5 L/m²h for 10 min initially, and then the flux was increased by 5 L/m²h every 10 min until the stripes appeared. The determination of the J_{stripe} was based on the first observation of the appearance of stripes in the span of 10 minutes of the permeate flux step. To determine time taken for the stripes to appear (t_{stripe}), the permeate flux was set at 10 L/m²h above the critical flux (J_{crit}) and the time needed before the stripes appeared was measured. Video images were taken at a frequency of 6 fps (frames per second) over 10 minutes, after which the images were analyzed using ImageJ to pinpoint the time when stripes were first observed. The same videos were used to quantify the width of the stripes

(w_{stripe}), number of stripes per unit membrane area (n_{stripe}) and lateral velocity of the stripes (v_{stripe}). At least 1000 stripes were characterized for each parameter.

In the detachment study, the permeate flux was first set at 5 L/m²h above the critical flux (J_{crit}) for 20 minutes for the stripes to deposit on the membrane, then the permeate flux was set to 0 L/m²h and a video was recorded at a frequency of 6 fps for up to 5 minutes to determine how long it took for the stripes to detach (note that the stripes typically disappeared as they detached).

The pH of the feed was adjusted to understand its effect on the stripping phenomenon. The pH of 500 ppm of oil emulsion in DI water was approximately 7.7. Either 500 μ L of acetic acid (CH₃COOH; Sigma Aldrich) was added to modify the pH to 3, or 750 μ L of ammonium hydroxide (NH₄OH; Sigma Aldrich) was added to adjust the pH to 10. The addition was made immediately upon the appearance of the stripes at a permeate flux of 5 L/m²h above the critical flux (J_{crit}). The zeta potentials of the oil droplets at the three different pH values were measured using Zetasizer (Phase Analysis Light Scattering Zetasizer, Brookhaven Instruments Corporation, New York, USA).

4.3. Results and Discussions

4.3.1. Critical Flux (J_{crit})

Motivated by the observation of stripes in earlier study on oil emulsions stabilized by Tween 20 (Chapter 2), the present study was targeted at further understanding the striping phenomenon. Such stripes, which are highly structured with distinct gaps in between, have only been reported in a few previous membrane filtration studies [1-5]. For reasons yet unclear, the stripes were only observed with surfactant from the Tween family and not with other surfactants such as polyvinyl alcohol (PVA; non-ionic),

cetyltrimethylammonium bromide (CTAB; cationic), and sodium dodecyl sulfate (SDS; anionic). Accordingly, the present work focused on the differences among the three different Tween surfactants.

As a first step, the critical flux was characterized. Fig. 4.3 displays the critical flux (J_{crit}) versus CFV trends for the three oil-in-water emulsions stabilized by Tween 20, Tween 40 and Tween 80 surfactants for the same oil concentration of 500 ppm. The CFV values used in this study were in the range from 0.1 m/s to 0.4 m/s, which translates to Reynold number of 419, 1048, and 1677, respectively; the lower bound was such that the DOTM images were still sufficiently clear to be analyzed, while the upper bound was to avoid membrane vibration observed at higher CFV values. Regardless of surfactant (i.e., Tween 20, Tween 40 or Tween 80), the critical flux (J_{crit}) of the oil emulsions (i) increased as the CFV increased, which agrees with the previous study on oil emulsions (Chapter 2) and general behaviors of particulate foulants [19], and (ii) had similar values at each CFV, presumably because of similar droplet sizes (Fig. 4.1) as well as similar interactions between the oil droplets and membrane. J_{crit} will be compared with the flux at which stripes firstly appeared (J_{stripe}), as will be elaborated in Section 3.3.

Figure 4. 3. Critical flux (J_{crit}) versus cross-flow velocity (CFV) trends of the oil emulsions stabilized with Tween 20, Tween 40 or Tween 80 at the oil concentration of 500 ppm.

To further explore how the onset of the stripes affects the transmembrane pressure (TMP) and thereby membrane fouling, Fig. 4.4 presents the evolution of flux and TMP at a cross-flow velocity (CFV) of 0.1 m/s, and also images taken at permeate fluxes of 10, 30 and 50 L/m²h. Per the flux-stepping protocol, the permeate flux was increased by 5 L/m²h increments every 10 minutes. Fig. 4.4 shows that the TMP increased slightly at lower fluxes then started to gradually increase when the flux approached 20 L/m²h, signalling that $J_{crit} \approx 20$ L/m²h, after which the TMP steeply increased at higher fluxes. The similarity of the critical flux (J_{crit}) value obtained via both TMP and DOTM (Fig. 4.4) of 20 L/m²h agrees with the previous study on oil emulsions (Chapter 2). Notably, the stripes were not visible at 10 L/m²h, that is ~ 10 L/m²h below the critical flux (J_{crit}) and not affecting the TMP. Above the critical flux (J_{crit}) of 30 L/m²h, the stripes became in focus since they have deposited on the membrane, which was the focal plane. This means that the oil droplets deposited as stripes instead of individual droplets, which is

somewhat counter-intuitive, since the stripes are larger ‘particles’ which would be expected to be more readily back-transported from the membrane. Deposition of particulate foulants on the membrane surface can take on various forms, like individual particles [7], clusters [16], and cake layer [20], and Figs. 4.4 indicate clearly via the TMP increase and DOTM images that the stripes constitute another form of membrane fouling. At the flux of 50 L/m²h, which was beyond the critical flux (J_{crit}), full coverage of the membrane with oil droplets was observed because the permeate drag became dominant, and the TMP started to increase steeply which indicates that this is the threshold flux ($J_{threshold}$) [21]. The exponential increase in TMP due to the formation of the cake layer on the membrane surface is well-acknowledged [22]. It should be noted that it was not possible via DOTM to observe if the stripes were still present on the deposited layer of oil droplets. Such trends were consistent for the other two surfactants (namely, Tween 20 and Tween 80).

Figure 4. 4. Evolution of permeate flux and transmembrane pressure (TMP) for 500 ppm of oil emulsion stabilized with Tween 40 at a CFV of 0.1 m/s; and images were taken at the end of the 10 minutes at the permeate fluxes of (a) 10, (b) 30 and (c) 50 $\text{L/m}^2\text{h}$. J_{crit} determined by DOTM was $22.3 \text{ L/m}^2\text{h}$.

4.3.2. Stripping phenomenon by oil emulsions stabilized by Tween 20, 40 and 80

Fig. 4.5 shows the stripes observed at a cross-flow velocity (CFV) of 0.1 m/s (which was in the laminar regime with a Reynolds number of 419), oil concentration of 500 ppm for the three surfactants, and permeate flux corresponding to $10 \text{ L/m}^2\text{h}$ above the critical flux (J_{crit}). Two observations are noteworthy. Firstly, the stripes were approximately parallel to the direction of the feed flow, and appeared to be somewhat different (e.g., width of stripe, gap between stripes) among the surfactants. Secondly, at this condition, stripes appeared for all three surfactants. The stripes did not appear at

higher cross-flow velocities (CFV). At the same CFV of 0.1 m/s, stripes appeared too for all three surfactants at the higher oil concentration of 750 ppm, but stripes only appeared for two of the surfactants (namely, Tween 20 and Tween 40) at the lower oil concentration of 250 ppm. This agrees with the previous study which found that stripes formed at conditions of lower CFV and higher oil concentrations (Chapter 2), and also the study by Henriksen and Hassager [2] that stripes only appeared in the low Reynolds number (400 - 800) regime.

Figure 4. 5. Striping phenomenon for the oil emulsions stabilized by Tween surfactants (at a concentration of 10 times the CMC) at a cross-flow velocity (CFV) of 0.1 m/s and oil concentration of 500 ppm. Images were taken at the end of 10 minutes at fluxes corresponding to of $J_{crit}+10$ L/m²h; the direction of flow was from left to right.

The studies to date have collectively implied that the appearance of stripes hinged on a delicate balance of forces (namely, permeate drag and hydrodynamic shear), and that any perturbation to the balance would cause the stripes to disappear [1, 3, 15]. This agrees with Fig. 4.4 as well as our study in Chapter 2, specifically in that the stripes only appeared under conditions that coupled low cross-flow velocities (CFV) with sufficiently high permeate drag and oil concentration. Regarding why the stripes were not observed at higher CFVs, the increased secondary flows generated can enhance solute and foulant back-transport from the membrane [23], and therefore the stripes may

not be observable because the focal plane of the DOTM technique was at the feed-membrane interface. Notably, because the stripes only occurred for the oil emulsions stabilized by the Tween family of surfactants (and not other surfactants tested), inter-particle interactions (e.g., electrostatic due to the differently charged hydrophilic head group of the surfactants) among the oil droplets seem to play a key role too.

Accordingly, regarding inter-particle interactions specific to the oil emulsion stabilized by Tweens, we hypothesize the following mechanistic picture. The formation of regular stripes rather than more random structures suggests directional attractive interactions at play, akin to that observed in polymerization, during which monomers will only attract each other at specific spots while exhibiting repulsion at other spots [24-27]. Each oil droplet had surfactants dynamically (i.e., not rigidly) aligned at the oil-water interface, such that the hydrophobic and hydrophilic parts of the surfactants exclusively interacted respectively with oil and water. The oil droplet surface may not be fully covered with the surfactants and the surfactants are dynamic, so as two oil droplets approach, the oil components may still be able to interact with each other [28, 29]. Between the surfactants, the hydrophobic moieties only interact with hydrophobic moieties, but, for the hydrophilic parts, the charges on the hydrophilic moieties would dictate whether the interaction is attractive or repulsive. The non-ionic hydrophilic part of the Tween family of surfactants, as opposed to the cationic hydrophilic part of CTAB or the anionic part of SDS, may be more subjected to directional attraction and thereby alignment of the oil droplets. Note though that the oil emulsion stabilized by non-ionic PVA surfactant was found not to exhibit striping, so further investigations are needed. Therefore, the combination of the various attractive-repulsive interactions may lead to the alignment of the oil droplets in rows along the flow direction with lateral widths of a few droplets (Fig. 4.8) as the most stable configuration.

4.3.3. Characterization of stripes

Because the stripes did not necessarily appear at critical flux (J_{crit}), as seen in Fig. 4.4, it was necessary to assess the flux at which these stripes appear. Fig. 4.6 displays the flux at which stripes were first observed (J_{stripe}) vis-à-vis critical flux (J_{crit}) with respect to oil concentration in the range between 250 and 750 ppm at the cross-flow velocity (CFV) of 0.1 m/s, with each error bar representing the span of the repeats. Three observations are highlighted from Fig. 4.6. Firstly, the J_{stripe} and J_{crit} values were generally similar, which indicate the similarity of the underlying mechanisms. Stripes were observed to sometimes form in the bulk feed prior to any deposition (i.e., at $J_{stripe} < J_{crit}$, as seen in Fig. 4.4) and at other times form only after deposition was observed (i.e., $J_{stripe} > J_{crit}$). Secondly, expectedly, the critical flux (J_{crit}) (i) decreased as the oil concentration increased, which agrees with previous studies [30], and (ii) were similar among the surfactants, which agree with Fig. 4.3. Thirdly, at the same conditions, Tween 80 was the only surfactant that did not exhibit stripes at the oil concentration of 250 ppm (Fig. 4.6c), which suggests a different interaction behavior among the surfactants since the hydrodynamics, the membrane and oil were the same. A plausible reason may be the relatively longer fatty acid chain of Tween 80 (Table 4.1) that caused more repulsion between the oil molecules and thereby reducing the likelihood of stripe formation.

Figure 4. 6. Flux at which stripes appear (J_{stripe}) and Critical Flux (J_{crit}) with respect to oil concentration at CFV = 0.1 m/s for oil emulsions stabilized with (a) Tween 20, (b) Tween 40, and (c) Tween 80.

Furthermore, it was observed that the stripes did not appear immediately when the permeate flux was set at or above J_{stripe} , but instead took a few minutes to form. Therefore, Fig. 4.7 shows the time taken for the stripes to form after the flux was set at 10 $\text{L/m}^2\text{h}$ above the critical flux (J_{crit}) with respect to oil concentration at the cross-flow velocity (CFV) of 0.1 m/s. Generally, it took between 1.5 to 3 minutes for the stripes to form, which implies that the time needed for the forces to balance for the genesis of the stripes was on the order of minutes. Larsen [3] also mentioned that the process leading to the appearance of stripes was slow due to the time needed to attain the balance between permeate drag force and shear force.

Figure 4. 7. Time taken for the stripes to form after the flux was set at $J_{crit}+10$ L/m²h (t_{stripe}) with respect to oil concentration at a CFV of 0.1 m/s.

Characterization of the various parameters of the stripes like width (w_{stripe}), number per unit membrane area (n_{stripe}) and lateral velocity (v_{stripe}) was possible by using ImageJ to analyze the DOTM images. Fig. 4.8 presents the evolution of the average width of the stripes (w_{stripe}), with each error bar representing the span of the values in each minute, for an oil concentration of 500 ppm, cross-flow velocity (CFV) of 0.1 m/s and permeate flux of 10 L/m²h above J_{crit} . The widths attained a steady-state value quickly once the stripes formed. All three surfactants gave similar average w_{stripe} values, with that by Tween 20 slightly narrower, which suggests that the balance of forces leading to the stripping phenomenon was similar among the three surfactants. The average width of the stripes (w_{stripe}) ranged between 15 and 25 μ m, which correspond to between two and three oil droplets, and the span of the w_{stripe} values was quite large at between 10 and 60 μ m. The asymmetry of the error bars implies that the larger w_{stripe} values were less prevalent than the smaller ones. The dynamic changes in the w_{stripe} values lie in the lateral (i.e., perpendicular to the feed flow direction) movement of the stripes, which led

to their merging and splitting, as depicted in Fig. 4.9. Fig. 4.9 shows that the two stripes in the boxed part of Fig. 4.9a progressively merged in 20 s (Fig. 4.9c), then splitted to result in the two stripes in Fig. 4.9e appearing similar to that in Fig. 4.9a. Similar phenomena were observed for the other two surfactants. Such merging behaviors are inevitably due to the different lateral velocities of the stripes, which are examined in Fig. 4.10.

Figure 4. 8. Evolution of the width of stripes (w_{stripe}) for the oil emulsions stabilized by (a) Tween 20, (b) Tween 40, and (c) Tween 80. Each error bar represents the span of values in each minute. The oil concentration was 500 ppm, CFV was 0.1 m/s, and permeate flux was $J_{crit}+10$ L/m²h.

Figure 4. 9. Images depicting the evolution of the stripes, which indicate their merging at $t = 7 \text{ min } 20 \text{ s}$ and subsequent splitting. of the stripes. The surfactant used was Tween 80, oil concentration was 500 ppm, CFV was 0.1 m/s, and flux was $J_{crit}+10$ L/m²h. The smaller images in (b) and (e) show only the boxed portion in (a).

Fig. 4.10 displays the lateral velocity of the stripes (v_{stripe}) formed by the oil emulsions stabilized by the three surfactants when the oil concentration was 500 ppm, cross-flow velocity (CFV) 0.1 m/s and permeate flux 10 L/m²h above the critical flux (J_{crit}). The average v_{stripe} magnitudes were similar at between 12 and 14 $\mu\text{m/s}$, and the span of v_{stripe} values range between 9 and 20 $\mu\text{m/s}$, the variation of which underlies the merging and splitting phenomenon in Fig. 4.9. It is interesting to note that the average v_{stripe} was four orders-of-magnitude lower than the cross-flow velocity (CFV).

Figure 4. 10. Lateral velocity of stripes (v_{stripe}) formed by oil emulsions stabilized by Tween 20, 40 and 80. The oil concentration was 500 ppm, CFV was 0.1 m/s and permeate flux was $J_{crit}+10$ L/m²h.

Analogous to Fig. 4.8, Fig. 4.11 presents the evolution of the number of stripes per unit membrane area (n_{stripe}) when the oil concentration was 500 ppm, cross-flow velocity (CFV) was 0.1 m/s and permeate flux was $J_{crit}+10$ L/m²h. As understood from Fig. 4.7, it took a few minutes for the stripes to form. However, in contrast to w_{stripe} in Fig. 4.8, the average n_{stripe} took a longer time to attain the steady-state value. This may be tied to the merging and splitting phenomenon seen in Fig. 4.9, which also took some time to reach a steady-state value after the stripes formed. Fig. 4.11 indicates that the steady-

state average n_{stripe} values were also similar for all three surfactants, with that for Tween 40 (Fig. 4.11b) being somewhat lower, and ranged between 35 and 50 mm^{-2} . For pH=7, Tween 40-stabilized oil emulsion has the less negative zeta potential in comparison to Tween 20 and 80. This reason could be the probable reason why the oil emulsion stabilized with Tween has higher attraction force to interact with the membrane surface and also with other particle during the merging-demerging of stripes. With less repulsive force, the stripes with Tween 40 has a higher tendency to merge and faster to create cake compared to other Tween, this leads to the decrease of the number of stripes at the later time.

Figure 4. 11. Evolution of the number of stripes per unit membrane area (n_{stripe}) for the oil emulsions stabilized by (a) Tween 20, (b) Tween 40, and (c) Tween 80. Each error bar represents the span of values in each minute. The oil concentration was 500 ppm, CFV was 0.1 m/s, and permeate flux was $J_{crit}+10$ $\text{L}/\text{m}^2\text{h}$.

For membrane-filtration applications, the more pertinent question is, compared to the more typical deposition of a more uniform layer of deposits, whether the stripes observed here are easier or more difficult to remove after deposition. This affects the ease of membrane cleaning or fouling mitigation. Accordingly, the stripes were allowed to deposit for 20 minutes at a permeate flux of 5 $\text{L}/\text{m}^2\text{h}$ above the critical flux (J_{crit}), after which the permeate flux was set to 0 $\text{L}/\text{m}^2\text{h}$ and the time taken for the deposits to detach (t_{detach}) was determined. Fig. 4.12 shows the t_{detach} values for the oil emulsions

stabilized by the three Tween surfactants at an oil concentration of 500 ppm and cross-flow velocity (CFV) of 0.1 m/s. Although the striping parameters were observed to be similar among all three surfactants in Figs. 4.6 – 4.11, Fig. 4.12 indicates that the t_{detach} values were distinctly different, which likely signifies different emulsion-membrane interactions despite similar emulsion-emulsion interactions. Specifically, the oil emulsions stabilized by Tween 20 and Tween 80 exhibited more similar average t_{detach} values of less than a minute, whereas that by Tween 40 was more than twofold at approximately 2.5 minutes. This indicates greater emulsion-membrane affinity when Tween 40 was used, and thereby greater difficulty in the removal of the deposits. It should be noted that, after 20 minutes at the constant flux of $J_{crit}+5$ L/m²h, the deposits for Tween 40 appeared as a cake rather than stripes, whereas stripes still prevailed for Tween 20 and Tween 80. This is reminiscent of the previous study in which greater foulant-membrane affinity led to more uniform deposition of foulants on the membrane, while greater foulant-foulant affinity led to clustering of foulants and non-uniform deposition on the membrane [7]. In view of the different types of deposits (i.e., uniform layer for Tween 40 versus stripes for Tween 20 and Tween 80) at the point of relaxation and the different t_{detach} values associated with each type, the results here indicate that the stripes are beneficial in terms of their deposits being easier to shear off the membrane.

Figure 4. 12. Time taken for deposits to detach (t_{detach}) upon relaxation after 20 minutes of a permeate flux of $J_{crit}+5$ L/m²h. The oil concentration was 500 ppm and CFV was 0.1 m/s.

4.3.4. Effect of pH on the stripping phenomenon

To further explore the emulsion-emulsion interactions leading to the formation of the stripes, the pH values of the feed containing 500 ppm of oil were adjusted from 7.7 to 3 and 11 by adding respectively acid and base. Specifically, acid or base was added after stripes were observed. Consistently in all cases, the stripes disappeared, although the subsequent behaviors were different between the acid and base additions. As the stripes disappeared, the oil emulsion started to deposit as clusters in the presence of the acid, whereas the oil emulsion were repelled from the membrane in the presence of the base. This is likely linked to the shifts in the zeta potential that affected the emulsion-emulsion and also emulsion-membrane interactions. As Fig. 4.13 shows, the zeta potentials were similar for all three surfactants in both the presence and absence of oil in the range of pH values investigated. Whereas the zeta potentials of the surfactants only were invariant with pH, the zeta potentials of the oil emulsion stabilized by the

surfactants decreased significantly as the pH increased. Specifically, the emulsions were only slightly negative at the low pH of 3, and became increasingly negative as the pH increased. As for the Anopore membrane, it has been reported that the streaming potential was 4 mV at a pH of 3, and -4 mV at a pH of greater than 7 [31]. Therefore, relative to that at pH of 7.7, the emulsion-membrane interactions were more attractive and the emulsion-emulsion interactions less repulsive relative at the pH of 3, which caused the emulsion to preferentially adhere to the membrane and disrupt the stripes that were based on a delicate balance of forces. Conversely, compared to that at pH of 7.7, both the emulsion-membrane and emulsion-emulsion interactions were more repulsive at the pH of 11, which disrupted the stripes and also repelled the emulsion from the membrane. At an approximately neutral pH, the unique interactions of the oil emulsions stabilized by the Tween family of surfactants caused stripes to form, but stripes were not observed for the other surfactants tested (namely, CTAB, SDS and PVA). The results here thereby affirm that, other than the shear force and permeate drag force that are responsible for the formation of the stripes as studied by Jonsson [1] and Larsen [3], foulant-membrane and foulant-foulant interactions also play a non-negligible role on stripe formation or disappearance.

Figure 4. 13. Zeta potentials of the oil emulsions stabilized by the different Tween surfactants and also of Tween surfactants only in the range of pH values between 3 and 11.

4.4. Conclusions

The striping phenomenon in membrane-filtration processes was observed more than 30 years ago [1], but the understanding of this phenomenon remains limited to six studies [1-5, 8], despite the attendant non-negligible impact on the filtration performance. To bridge the gap in the knowledge base, this study systematically investigated the striping phenomenon using the Direct Observation through the Membrane (DOTM) technique. Oil emulsions stabilized by three Tween surfactants (namely, Tween 20, Tween 40 and Tween 80) were studied over a range of oil concentrations, cross-flow velocities (CFV) and permeate fluxes to determine the range of conditions at which stripes appeared. The Tween family of surfactants were used because stripes did not form for the other surfactants tested in this study (namely, SDS, CTAB and PVA). Then the stripes were characterized in terms of the flux at which they appeared (J_{stripe}) vis-à-vis critical flux (J_{crit}), the stripe parameters (namely, width

(w_{stripe}), lateral velocity (v_{stripe}) and number density (n_{stripe})), ease of detachment (t_{detach}), and influence of pH.

Firstly, other than the permeate drag and hydrodynamic shear reported to be responsible for the formation of the stripes [1, 3], foulant-membrane and foulant-foulant interactions was observed to also play a non-negligible role in stripe formation or disappearance. Specifically, (i) the oil emulsion only formed stripes when stabilized by the Tween family of surfactants but not other surfactants tested (i.e., SDS, CTAB and PVA), (ii) the different detachment time (t_{detach}) observed for deposited oil emulsions (either as stripes or a uniform layer) stabilized by the different Tween surfactants; and (iii) the disappearance of the stripes upon the addition of acid or base. Secondly, the stripes affected the transmembrane pressure (TMP), which increased when the stripes contacted the membrane surface, thus indicating that the stripes are a unique manifestation of membrane fouling. As a form of fouling, stripes appeared to be easier to remove than the more uniform layer of deposited oil. At the set permeate flux of 5 L/m²h above the critical flux (J_{crit}), the oil emulsion stabilized by Tween 20 and Tween 80 formed striped deposits while that by Tween 40 formed a more uniform layer, then upon relaxation, the time taken to detach the stripes was shorter. Thirdly, among the three Tween surfactants, the striping characteristics investigated (namely, J_{stripe} , w_{stripe} , v_{stripe} and n_{stripe}) were largely similar, except for t_{detach} . Generally, the J_{stripe} values were similar to J_{crit} , and the stripes took between 1.5 to 3 minutes to form at J_{stripe} , after which the stripe parameters attain steady-state values within a minute. At steady-state, (i) the average w_{stripe} corresponded to between two and three oil droplets, (ii) the stripes continuously merged and splitted, (iii) the average v_{stripe} was four orders-of-magnitude lower than the cross-flow velocity (CFV), and (iv) the average n_{stripe} ranged between 35 and 50 mm⁻².

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CHAPTER 5: CRITICAL FLUX AND FOULING MECHANISM IN CROSS FLOW MICROFILTRATION OF OIL EMULSION: EFFECT OF VISCOSITY AND BIDISPERSITY

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Abstract

Membrane-based filtration is promising for applications in the food industry, for example, for processing dairy products, but membrane fouling restricts the efficiency of the process. The deposition of the main constituents in skim milk of casein, lactose and milk fat globules onto the membrane due to the permeate drag is inevitable, which necessitates a mechanistic study of the fouling phenomena. The Direct Observation through the Membrane (DOTM) technique was used to understand the effects of viscosity and bidispersity on the microfiltration of oil emulsions. Deposits at the feed-membrane interface clearly slowed down as the feed viscosity increased. The higher drag to the crossflow as a result of the higher viscosity caused more oil droplets to foul the membrane. However, although both casein and lactose increased the feed and permeate viscosity, the presence of lactose did not alter the fouling phenomena of a moving cake layer of oil droplets much, but the presence of casein caused the oil droplets

to deposit instead as clusters. Addition of casein changed the oil feed to bidisperse solution, which its smaller size, coupled with increased viscosity, promoted a higher fouling propensity of the oil emulsion. Agreement between the experimental data and the shear-induced diffusion model was good at the lower cross-flow velocities (CFVs) but poorer at higher CFVs, which indicate that the effect of viscosity appeared negligible at the lower CFVs but more dominant at the higher CFVs. DLVO model confirmed the results of J_{crit} and TMP, with the mixture of oil and casein was the least repulsive for foulant-membrane interaction energy. This study sheds light on the membrane fouling phenomena for viscous feeds, and are expected to be useful particularly for food applications.

Keywords : Membrane fouling; Critical flux; Viscous; Bidisperse; Direct Observation through the Membrane (DOTM); cross-flow velocity (CFV), DLVO

5.1. Introduction

In recent years, the application of membrane technology in food processing has been become increasingly popular. Particularly, microfiltration (MF) is used in the milk and dairy industry for removing bacteria and also concentrating casein (usually exists as micellar casein with a particle size range between 0.18 – 0.5 μm) from skim milk [1], in which the fat content is below 0.1% (1000 ppm), and casein (approximately 26 g/l) and lactose (approximately 50 g/l) are the major components along with serum protein (approximately 7 g/l) and minerals (approximately 8 g/l) [2]. Via MF, two main valuable products are produced from skim milk, namely, the micellar casein concentrate in the retentate and the serum protein in the permeate. While the micellar casein concentrate is used in cheese production [3, 4] due to its higher heat stability (up to 100 °C) [5], the

serum protein can be further concentrated using ultrafiltration (UF) and used as an alternative for whey protein concentrate [6]. Because of good selectivity and mild operating conditions, MF provides a superior way to separate the skim milk constituents in comparison to the conventional methods like ultra-heat treatment (UHT), pH lowering, or CaCl_2 addition [7, 8]. Unfortunately, membrane fouling impedes the wider proliferation of the process.

Specifically, with skim milk as the feed in MF, due to the difference in the size of the constituents, casein is retained together with milk fat globules and part of the dissolved lactose, while serum proteins, minerals and part of the dissolved lactose pass through the membrane into the permeate. Correspondingly, the accumulation of casein, lactose and milk fat globules on the feed-membrane interface due to the permeate drag fouls the membrane, thereby causing the permeation rate to deteriorate. Past studies have provided some mechanistic understandings on the membrane fouling phenomena by oil emulsions [9-11], but the effects of viscosity and bidispersity (that is particularly pertinent in food processing, e.g., skim milk) on the microfiltration of oil emulsions is yet unknown.

Past studies have shown that the casein micelles were the major actors dictating membrane fouling during the microfiltration of skim milk [2, 12-14]. Steinhauer et al. [12] reported three different types of casein micelle deposits, namely, (i) a dominant porous and loosely attached structure; (ii) reversible gel-like layer; and (iii) non-reversible internal fouling. In addition, Jimenez-Lopez et al. [2] found that, during the microfiltration (MF) of skim milk, an irreversible gel-like structure formed on the membrane surface, which became more cohesive and difficult to remove with the addition of salt, because of the increased ionic strength of casein. Furthermore, Qu et al. [13] observed from the deposit formation on the membrane surface that membrane

fouling was most likely linked to the colloidal nature of the casein micelle. Also, Kuhn et al. [14] found that membrane fouling was more affected by protein hydrophilicity rather than the electrostatic interactions between proteins, especially for fluids with high ionic strength such as milk. As for lactose, the role lactose plays in membrane fouling has been much less studied in comparison to that by casein. Adams et al. [15] observed that the addition of lactose to the feed increased feed and permeate viscosity, which reduced the limiting flux. Moreover, Bouzid et al. [16] observed that the retention of lactose was not affected by the change in pH, while Rao et al. [17] observed that a significant decrease in the flux in the presence of lactose. These studies shed some light on the effect of casein and lactose, but the link between the physical properties of the feed (e.g., viscosity and polydispersity) and membrane fouling remains amiss, which stymies wider application.

In order to understand the individual role and interplay of the major constituents of skim milk on membrane fouling during microfiltration, model feeds containing mixtures of casein, lactose and Tween 20 – stabilized oil emulsion were studied using the Direct Observation through the Membrane (DOTM) method. Four different feeds were studied, namely, oil alone; oil and casein; oil and lactose; and oil, casein and lactose. The effect of cross-flow velocity, viscosity, bidispersity and concentration were studied. Experimental data were also compared to model predictions to enhance the physical understanding.

5.2. Materials and Methods

5.2.1. Casein Suspension, Lactose Solution and Oil-in-Water Emulsion

The casein suspension was prepared by mixing 13 g of casein from bovine milk powder (Sigma-Aldrich) with 500 ml of 0.015 M NaOH, and also 97.5 mg of Sodium Azide (Sigma Aldrich) to prevent bacterial growth. This gave a total concentration of 26 g/l casein, which is the average concentration of casein in skim milk [2, 18], and a pH of 7.0. The mixture was stirred overnight at room temperature, and then kept in the fridge. The mean size of casein was determined by the Zetasizer (Phase Analysis Light Scattering Zetasizer, Brookhaven Instruments Corporation, New York, USA) to be 376.9 nm.

The stock solution of oil emulsion with an oil concentration of 25,000 ppm was prepared by blending 10 ml of soybean oil (Sigma Aldrich), 2 ml of Tween 20 (Sigma Aldrich) and 388 ml of DI water (Millipore) in a blender (Waring 8011 S) for one minute at 18,000 rpm. For each experiment, a constant 500 ppm of soybean oil emulsion was prepared by diluting 10 ml of the stock solution with 490 ml of DI water. Casein (Sigma Aldrich) concentrations used were 2.6, 6.5, and 13 g/l, while the lactose (Sigma Aldrich) concentrations used were 5, 12.5 and 25 g/l. The concentrations were chosen with reference to that in skim milk (Table 5.1), such that the ratios of the concentration used to that reported for either casein ($C_{N,casein}$) or lactose ($C_{N,lactose}$) were between 0.1 – 0.5. The maximum C_N value was limited to 0.5 for clarity in the visual observation via DOTM.

The oil droplet size distributions of the soybean oil emulsions shown in Fig. 5.1 were characterized using the Focused Beam Reflectance Measurement (FBRM; Lasentec S400, PI-14/206) instrument. The distributions of the oil emulsions alone and that in the presence of lactose were similar because lactose dissolved completely, while that in the

presence of casein had two peaks, the smaller of which was the casein particulates that did not dissolve.

Table 5. 1. Skim milk components and concentration [2]

Component	Concentration (g/l)
Casein	26
Serum protein (SP)	7
Minerals	8
Lactose	50
Milk fat	0.1

Figure 5. 1. Number-based droplet size distributions of three types of 500 ppm soybean oil emulsions stabilized by the Tween 20 surfactant, namely, oil alone, oil with casein ($C_{N,casein}=0.5$) and oil with lactose ($C_{N,lactose}=0.5$). The mean droplet sizes were 13.6, 12.7, 14.4 μm , respectively for oil, oil+casein, and oil+lactose.

It should be noted that although salt is also an important component in milk, it was not used in the feed in this study, because it has been well-reported that it worsened fouling and reduced permeate flux more [19, 20]. In Chapter 2, salt was observed to alter the interaction between oil and membrane, because the zeta potential of the oil emulsion became less negative while the streaming potential of the membrane remained similarly negative.

5.2.2. Direct Observation Through the Membrane (DOTM)

The Direct Observation through the Membrane (DOTM) setup, which has similarly been employed to observe membrane fouling by oil emulsion [10, 11], is depicted in Fig. 5.2. Specifically, the DOTM system had a light microscope (Zeiss Imager; A2 m) focused at the feed-membrane interface plane that was integrated with a video camera (Axiocam 105 Color) and connected to a computer to record images. The membrane cell had dimensions of 105 mm length by 35 mm width by 3 mm height, with 2 mm being the feed channel height and 1 mm being the permeate channel height, and the permeate channel being atop the feed channel. The feed was contained in a 600 ml beaker that sat atop a magnetic stirrer plate (Heidolph; MR Hei-Mix S) to keep the suspension well-mixed. A gear pump (Micropump Inc; GJ-N25. PF/S.A) was used to channel the feed solution between the membrane cell and feed beaker, while a peristaltic pump (Cole Palmer; Masterflex L/S 7519-20/85) circulated the permeate. The permeate beaker (100 ml) sat atop a mass balance (Mettler-Toledo) to quantify the permeate flux, and every 20 ml of permeate collected was returned to the feed tank to maintain the feed concentration. For the measurement of transmembrane pressure (TMP), three pressure transmitters (Cole Palmer) were used to characterize the pressures in the membrane cell (namely, feed inlet pressure, feed outlet pressure, and permeate inlet pressure).

Figure 5. 2. Direct Observation through the Membrane (DOTM) Setup

The DOTM setup required a membrane that was transparent when wetted to allow light to pass through to enable visualization of the feed-membrane interface, and thereby the Anopore membrane (Whatman; 50% porosity; nominal pore size of 0.2 μm) was used. The membrane was glued in between two rectangular (55 mm by 135 mm) pieces of paper for mechanical support, each with a square cut-out (27 mm by 27 mm) in the center to expose the membrane. After the gluing, the membrane was placed in between two sheets of parafilm (Whatman PM996 M roll) and a weight (3 kg) was placed atop for drying over three days.

5.2.3. Critical Flux Determination

In every experiment, the critical flux (J_{crit}) was measured using the flux-stepping method starting from an initial permeate flux of 5 $\text{L}/\text{m}^2\text{h}$. Specifically, critical flux is the flux whereby the foulant starts to deposit on the membrane surface, and below which no deposition occurs [21]. To characterize J_{crit} , each flux was held constant for 10 minutes,

during which two images were taken at the 2nd and 10th minutes. It should be noted that the duration of 10 min has been ascertained in our earlier studies, which used the same protocol, to be sufficient (Chapter 2-4). The images were then binarized and the concentration of deposits at the feed-membrane interface (C ; i.e., number of black pixels with respect to the total number of pixels) quantified using ImageJ. The rate of change of membrane surface coverage was calculated using Eq. 1 (Chapter 2):

$$\frac{\Delta C}{\Delta t} = \frac{C_{10\text{th minute}} - C_{2\text{nd minute}}}{8 \text{ minutes}} \quad (5.1)$$

The critical flux (J_{crit}) was determined as the flux at which the $\frac{\Delta C}{\Delta t}$ value exceeds the threshold value of 0.2 %/min, as verified in our previous studies for both oil emulsion and latex particles (Chapter 2 and Appendix).

5.3. Results and Discussion

The individual role of casein and lactose in influencing membrane fouling was investigated by observing the deposition of the Tween 20 – stabilized soybean oil emulsion using DOTM, since all three components are present in skim milk. In the MF of skim milk, casein and oil emulsion are in the retentate, while lactose is partly retained and partly permeated.

5.3.1. Effect of cross-flow velocity (CFV)

Cross-flow is the mainstay in microfiltration due to the beneficial membrane fouling mitigation effects. The effect of cross-flow velocity (CFV) on membrane fouling by three different feeds containing Tween 20 – stabilized soybean oil emulsion (namely, oil alone, oil and casein, and oil and lactose) at two concentrations of casein and lactose is presented in Fig. 5.3. As expected, the J_{crit} values generally increased with CFV.

Interestingly, the feed containing soybean oil emulsion alone consistently had the greatest J_{crit} values, followed by that in the presence of lactose and then casein. At both concentrations of casein and lactose in Fig. 5.3, vis-à-vis soybean oil emulsion alone, the presence of lactose insignificantly affected J_{crit} at the lower CFV values, whereas the presence of casein significantly depressed the J_{crit} values at all the CFV conditions investigated. The much depressed J_{crit} values in the presence of casein was at least in part because of the casein particulates, the smaller sizes (Fig. 5.1) of which made them more prone to foul than the larger oil droplets, as reported by previous studies on bidisperse systems [22].

Figure 5. 3. Critical flux (J_{crit}) of three different solutions (namely, soybean oil emulsion; soybean oil emulsion and casein; and soybean oil emulsion and lactose) at various cross-flow velocities (CFV). The oil concentration was 500 ppm and C_N values were (a) 0.1 and (b) 0.5.

Fig. 5.4 shows the TMP profiles versus permeate volume per unit area for the three systems (namely, soybean oil emulsion, soybean oil emulsion and 13 g/l casein ($C_N = 0.5$), and soybean oil emulsion and 25 g/l lactose ($C_N = 0.5$)) at a permeate flux below J_{crit} and a permeate flux above J_{crit} . At the permeate flux of below J_{crit} , the TMP values

expectedly remained low throughout the filtration. On the other hand, at the permeate flux of above the J_{crit} of the respective systems, two different TMP trends were observed. For soybean oil emulsion alone (Fig. 5.4a), the TMP increased gradually initially, then more rapidly before plateauing. The trend is similar in the presence of lactose (Fig. 5.4c). In contrast, for the system with soybean oil emulsion and casein (Fig. 5.4b), the TMP increased rapidly initially, then more gradually before plateauing, which is more similar to that reported by He et al. [9] for crude oil emulsions. The steeper increase was due to the augmented deposition of the smaller casein particulates (Fig. 5.1), as also reflected in the lowered J_{crit} values (Fig. 5.3).

Figure 5. 4. Transmembrane pressure (TMP) as a function of cumulative permeate volume per unit membrane area for (a) soybean oil emulsion, (b) soybean oil emulsion and 13 g/l casein ($C_{N,casein} = 0.5$), and (c) soybean oil emulsion and 25 g/l lactose ($C_{N,lactose} = 0.5$). Two permeate fluxes (namely, one below J_{crit} and one above J_{crit}) were imposed at the oil concentration of 500 ppm and CFV of 0.25 m/s.

Fig. 5.5 shows the DOTM images of the feed-membrane interface of the various systems, namely, soybean oil emulsion (Fig. 5.5a); soybean oil emulsion and 2.6 g/l casein (Fig. 5.5b); soybean oil emulsion and 5 g/l lactose (Fig. 5.5c); and soybean oil emulsion, 2.6 g/l casein and 5 g/l lactose (Fig. 5.5d). For the soybean oil emulsion alone (Fig. 5.5a), the fouling mechanism appeared to be the moving cake layer

whereby clusters of the oil droplets move along the membrane surface with the cross-flow. A similar phenomenon was observed in the presence of lactose (Fig. 5.5c) despite the higher viscosity (Fig. 5.7), which suggests that viscosity is not a dominant factor dictating the fouling mechanism. However, Figs. 5.5b and d contrast that of Figs. 5.5a and c, which indicate that the presence of casein changed the fouling mechanisms. Specifically, in the presence of casein alone, Fig. 5.5b shows some clustering of the oil droplets but not a moving cake layer (as shown by the smaller dark patches compared to Fig. 5.5a and c). The dominant effect of casein also was seen in the mixture of all three components in Fig. 5.5d, which similarly shows clustering deposition without the moving oil cake layer per Fig. 5.5b. Past studies [2, 12, 13] reported that casein deposited as a compressible, deformable gel, which resulted from the inter-micellar bond between the casein micelles. Due presumably to the higher viscosity of the feed and the stickiness of the casein gel, the movement of the oil droplets distinctly slowed down both in the bulk and on the membrane surface. As the casein particulates were smaller than the oil droplets (Fig. 1), they had a higher tendency to deposit on the membrane surface [22], and their presence on the membrane surface created the porous, gel-like structure that increased the local viscosity near the membrane surface, which in turn reduced the movement of oil droplets significantly near the membrane surface and worsened fouling. Fig. 5.6 presents the DOTM images taken at the feed-membrane interface for two different feeds (namely, one with only the oil emulsion, and the other with oil and casein ($C_{N,casein} = 0.25$)) at different time intervals. The relative slower motion of the deposits in the presence of casein is clear. In the absence of casein, previous studies have also shown that the particulate foulants of either oil emulsions (Chapter 2) or latex particles (Appendix) did not appear to slow down drastically as they approached the membrane surface. For the oil emulsion, those

which contacted the membrane were observed to roll together with other oil droplets until a moving cake layer was created that at times deposited on the membrane surface, which agrees with Chapter 2.

Figure 5. 5. DOTM images taken of the feed-membrane interface at the end of the 10th minute at the permeate flux of $J_{crit} + 15 \text{ L/m}^2\text{h}$ for four different feeds containing (a) soybean oil emulsion, (b) soybean oil emulsion and 2.6 g/l casein ($C_{N,casein} = 0.1$), (c) soybean oil emulsion and 5 g/l lactose ($C_{N,lactose} = 0.1$), and (d) soybean oil emulsion, 2.6 g/l casein ($C_{N,casein} = 0.1$) and 5 g/l lactose ($C_{N,lactose} = 0.1$). The oil concentration was 500 ppm and CFV was 0.25 m/s. The deposited oil droplets are shown as darker pixels, and the same magnification of 200 $\times$ was used.

Figure 5. 6. DOTM images of the feed-membrane interface at three time intervals for two feed types (namely, oil only at CFV = 0.1 m/s, and oil and casein ($C_{N,casein} = 0.25$) at CFV = 0.25 m/s). The oil concentration was 500 ppm and permeate flux was 5 L/m²h above J_{crit} . The images were taken at 6 frames per second at the 10th minute at the target flux. The dashed circles highlight two oil clusters at $t = 0$ for each feed, with the images at subsequent time steps indicating that the identified oil clusters moved faster for the feed containing oil alone such that they disappeared from the images, whereas that for the feed containing oil and casein remained relatively stagnant.

5.3.2. Effect of viscosity

The viscosity values of the feeds containing the Tween 20 - stabilized soybean oil emulsion in the presence of either casein or lactose with respect to the concentration ratio (C_N) are displayed in Fig. 5.7. In view of the twofold difference in the concentrations of casein and lactose in skim milk (Table 1), each x -axis denotes the concentration ratio (C_N), which is the ratio of the concentration of casein or lactose used in the experiment to that of the concentration in skim milk of respectively 26 g/l and 50 g/l. Specifically, the casein and lactose concentrations used were between 2.6 - 13 g/l and 5 - 25 g/l, respectively. Fig. 5.7 indicates that the viscosity values were negligibly

affected at the lowest C_N value of 0.1, but increased significantly at higher C_N values, with the increase being steeper for the casein case. To understand the effect of viscosity (μ) on membrane fouling, Fig. 5.8 presents the critical flux (J_{crit}) as a function of viscosity (μ). Notably, at the lower C_N of 0.1 (Fig. 7a), although the viscosity values were similar to that of soybean oil emulsion alone (Fig. 7), the J_{crit} value in the presence of lactose was slightly lower than soybean oil emulsion alone, while that in the presence of casein was severely depressed. The effect of viscosity in worsening membrane fouling agrees with previous studies. Adams et al. [15] found that the increase of viscosity due to the presence of lactose in the feed solution led to the decrease of the limiting flux of skim milk, while Rao et al. [17] also found a decrease in the permeate flux by 24% at 25 °C when 4.5 wt% lactose was added. This is because, as the viscosity of the solution increases, the drag on the flow increases and thereby the shear on the membrane surface decreases, which thus increases the likelihood for the oil emulsion to deposit. This was evident in Fig. 5.6. As the concentration further increased, although the viscosity increased more drastically for casein (Fig. 5.7), the extents of decrease of critical flux with viscosity was similar for both cases (Fig. 5.8). The results in Figs. 5.7 and 5.8 therefore imply that viscosity (μ) alone is not a dominant factor dictating the extent of fouling, but the presence of small particulates in the case of casein (Fig. 5.1) appeared to exhibit a more significant influence.

Figure 5. 7. Kinematic viscosity of Tween 20 – stabilized soybean oil emulsion in the presence of casein and lactose at an oil concentration of 500 ppm and CFV of 0.25 m/s.

Figure 5. 8. Critical flux (J_{crit}) of the Tween 20 – stabilized soybean oil emulsion in the presence of casein and lactose versus kinematic viscosity. The experiments were at $C_{N,casein}$ or $C_{N,lactose}$ of 0 - 0.5, CFV of 0.25 m/s, and oil concentration of 500 ppm.

5.3.3. Effect of concentration and bidispersity

Fig. 5.9 shows the critical flux (J_{crit}) of the Tween 20 – stabilized soybean oil emulsion in the presence of casein and lactose at an oil concentration of 500 ppm and cross-flow velocity (CFV) of 0.25 m/s. As explicit in Fig. 5.8, the presence of either casein or lactose reduced the J_{crit} values, with the impact being more severe for the former. To further understand skim milk filtration, all three components (namely, casein, lactose and soybean oil emulsion) were investigated for an oil concentration of 500 ppm and CFV of 0.25 m/s. Fig. 5.10a displays the normalized critical flux ($J_{crit}/J_{crit0,lactose}$), which is the critical flux measured at the targeted condition normalized with respect to the critical flux at a fixed casein concentration of 2.6 g/l ($C_{N,casein} = 0.1$) and no lactose, as a function of the concentration ratio of lactose ($C_{N,lactose}$). Analogously, Fig. 5.10b shows the normalized critical flux ($J_{crit}/J_{crit0,casein}$) at a fixed lactose concentration of 5 g/l ($C_{N,lactose} = 0.1$) and various casein concentrations. Two observations are clear. Firstly, the presence of traces of the third component (either lactose or casein) significantly depreciated the critical flux (J_{crit}), then the addition of more negligibly affected J_{crit} . Secondly, between lactose and casein, the presence of casein had a more detrimental effect on membrane fouling. Consistently, the results indicate that viscosity (Fig. 5.7) had a lesser influence on membrane fouling than foulant particulate size (Fig. 5.1). As shown also in Fig. 5.1, the presence of lactose did not affect the oil size distribution that much in comparison to the addition of casein. The main reason was the solubility of lactose in water, meanwhile casein was in the state of suspension, thus its size became notable for the fouling mechanism. Bidispersity of the mixture solution with the addition of casein is shown by the double peak size distribution for the mixture of casein and soybean oil emulsion (Fig. 5.1), which affected the fouling mechanism more than the effect of viscosity. Kromkamp et al [23] observed that the smaller particle in the

bidisperse mixture controlled the overall flux or the fouling mechanism in their study of Shear-induced Diffusion (SID) model for polydisperse solution. This result then was confirmed by the study of Zhang et al [22], which they used three different sizes of latex particle, to study the critical flux (J_{crit}) of the monodisperse solution and the bidisperse solution with DOTM system at different particle concentration. They found out that the particle deposition was governed by the smaller particle in the mixture, with only the smaller particle deposited on the membrane surface as the flux exceeded the J_{crit} . They also observed that the presence of the 3 μm latex particle in the suspension of 10 μm lowered down the J_{crit} value of the monodisperse 10 μm suspension, and the other way around if the comparison was based on the J_{crit} value of the monodisperse 3 μm . The previous study with bidisperse latex particle solution with various CFV value (Appendix) also confirmed that the results from these two studies, which could explain that the presence of the casein was not just increasing the viscosity but also the overall particle dispersity. The bidispersity caused by the presence of casein lowered down the J_{crit} even more, compared to the addition of lactose, due to the higher number of casein presented in the mixture which deposited on the membrane surface first then increased the viscosity, thus slowed down the movement of the oil emulsion and promote its earlier deposition.

Figure 5. 9. Critical flux of Tween 20 – stabilized soybean oil emulsion in the presence of casein and lactose at an oil concentration of 500 ppm and CFV of 0.25 m/s.

Figure 5. 10. Normalized critical flux (J_{crit}/J_{crit0}) of the feed containing all three components (namely, casein, lactose, and soybean oil emulsion) at (a) a fixed casein concentration of 2.6 g/l ($C_{N,casein} = 0.1$) and various lactose concentrations; and (b) a fixed lactose concentration of 5 g/l ($C_{N,lactose} = 0.1$) and various casein concentrations. The oil concentration was 500 ppm and CFV was 0.25 m/s. $J_{crit0,lactose}$ was 15.5 L/m²h and $J_{crit0,casein}$ was 79.0 L/m²h.

5.3.4. Shear-induced diffusion and DLVO model

Since the diameters of the oil emulsion and casein particulates were respectively around 10 and 0.369 μm , the back-transport mechanism is linked to shear-induced diffusion (SID) and Brownian diffusion [24]. However, Samuelsson et al. [25] observed that the SID model had better predictability for casein than the Brownian diffusion model. Therefore, to compare against the experimental results here, the SID correlation reported by Li et al. [26] was used:

$$J = 0.0595 \gamma_o \left(\frac{a^4}{L}\right)^{\frac{1}{3}} \ln \left(\frac{\phi_w}{\phi_b}\right) \quad (5.2)$$

where J represents length-averaged flux ($\text{L}/\text{m}^2\text{h}$), γ_o represents shear rate at the membrane surface (s^{-1}), a represents particle radius (m), L represents membrane length (m), ϕ_w represents particle volume fraction at the membrane surface (-), and ϕ_b represents particle volume fraction in the bulk suspension.

Fig. 5.11 shows the flux predicted by the SID model vis-à-vis the experimental data for the four feed types containing Tween 20 – stabilized oil emulsions, namely, oil alone, oil and casein ($C_{N,\text{casein}} = 0.1$), oil and lactose ($C_{N,\text{lactose}} = 0.1$), and oil, casein ($C_{N,\text{casein}} = 0.1$) and lactose ($C_{N,\text{lactose}} = 0.1$). Despite the higher viscosity, the agreements for all feed types were good at the lower CFV values. Because the SID model (Eq. (5.2)) does not explicitly account for viscosity, the good agreement indicate the insignificant influence of feed viscosity at low CFVs. On the other hand, at the higher CFVs, the discrepancies between the experimental data and model prediction were greater. At the higher CFVs, the experimental critical flux (J_{crit}) was lower than that predicted by the SID model for the case of oil alone (Fig. 5.11a), and even more severely depressed in the presence of both oil and lactose (Fig. 5.11c). For the latter case, the higher viscosity of the feed posed a greater resistance to the cross-flow shear that exacerbated deposition (Fig. 5.6).

On the other hand, for the feed containing oil and casein (Fig. 5.11b), the experimental critical flux (J_{crit}) was greater than that predicted by the model, which was due to the presence of the small casein particulates (Fig. 5.1), which was accounted more in the SID model calculation due to its higher number of particle. The coupling of the J_{crit} depression due to the higher viscosity and the enhancement due to the smaller casein particulates experimentally led to better agreement with the model prediction in Fig. 5.11d. Therefore, Fig. 5.11 indicates that the effect of viscosity appeared negligible at lower CFVs but more prominent at higher CFVs.

Figure 5. 11. Comparison of critical flux (J_{crit}) values of experiments and that predicted by the SID model [26] for the various feeds of Tween 20 – stabilized oil emulsion: (a) oil alone; (b) oil and casein ($C_{N,casein} = 0.1$), (c) oil and lactose ($C_{N,lactose} = 0.1$); and (d) oil, casein ($C_{N,casein} = 0.1$) and lactose ($C_{N,lactose} = 0.1$). The oil concentration was 500 ppm.

The interaction between the oil emulsion and the membrane inevitably plays an important role in governing the results [27, 28]. It has been demonstrated that the Derjaguin-Landau-Verwey-Overbeek (DLVO) model was better correlated with the fouling trends for various oils than the extended DLVO (XDLVO) model [29], so the DLVO model was used to calculate the interaction energies (equations listed in Chapter 3) for the various systems investigated. Fig. 5.12 shows that the interaction energy for the soybean oil emulsion only was the most repulsive to the membrane surface, followed by the soybean oil with lactose, and then the soybean oil with casein, which agrees with the TMP and J_{crit} results.

Figure 5. 12. DLVO interaction energy of three different solutions (namely, soybean oil emulsion; soybean oil emulsion and casein; and soybean oil emulsion and lactose) with the membrane surface at various separation distance of two surfaces (particle and membrane).

5.4. Conclusion

In order to understand the individual role and interplay of the major constituents of skim milk on membrane fouling during microfiltration, model feeds containing mixtures of casein, lactose and Tween 20 – stabilized oil emulsion were studied using the Direct Observation through the Membrane (DOTM) method. Past studies have provided mechanistic understandings on the membrane fouling phenomena by oil emulsions [9-11], but the effects of viscosity and bidispersity (that is particularly pertinent in the processing of skim milk) on the microfiltration of oil emulsions is yet unknown.

Regarding the lesser reported effect of viscosity, DOTM images affirmed that the deposits at the feed-membrane interface clearly slowed down as the feed viscosity increased. Interestingly, although both casein and lactose increased the feed viscosity, the presence of lactose did not alter the fouling phenomena of a moving cake layer of oil droplets much, but the presence of casein had a twin effect (increasing the viscosity and particle dispersity) caused the oil droplets to deposit earlier as cluster.

Comparison was made between the experimental data and the predictions from the shear-induced diffusion model. Agreement was good at the lower cross-flow velocities (CFVs) but poorer at higher CFVs, which indicate that the effect of viscosity appeared negligible at the lower CFVs but more dominant at the higher CFVs. DLVO model confirmed the results where the interaction energy between oil emulsion and membrane surface was the least repulsive with the presence of casein.

Collectively, the results shed light on the membrane fouling phenomena for viscous feeds, and are expected to be useful for improving the membrane's efficiency in food applications such as the microfiltration of skim milk.

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CHAPTER 6: IN-SITU CHARACTERIZATION OF CAKE LAYER FOULING DURING CROSSFLOW MICROFILTRATION OF OIL-IN-WATER EMULSION

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Abstract

In view of membrane-filtration being a promising means for treating the large volumes of oily wastewater, much efforts have been dedicated to understand membrane fouling by oil emulsions. This study focused on characterizing the evolution of the oil-emulsion cake layer characteristics on hollow fiber (HF) membranes in real time using the direct observation through the membrane (DOTM) technique. The more well-studied latex particles were studied alongside to provide a benchmark for comparison. Despite the same feed concentration and crossflow velocity used, the transmembrane pressure (TMP) and cake layer resistance magnitudes were greater for oil emulsion than for latex particles at the same permeate flux. DOTM images revealed that this was linked to the following behaviors: (i) oil tended to deposit as a moving cake layer, whereas latex as scattered deposits; and (ii) oil gave a thinner yet denser cake layer. Although, real images of oil and latex fouling evolution have been studied before by looking the top

flat sheet membrane surface, this study showed the other perspective of the fouling from different angle of observation by using hollow fiber membrane. Moreover, it was observed that the cake thickness and porosity fluctuated significantly with respect to permeate volume for the oil emulsions, because the moving cake layer gave greater variations of cake thicknesses along the membrane. Finally, the interfacial interaction energy predicted by the XDLVO model gave higher oil-membrane and oil-oil affinities compared to that of latex, which underlie respectively the more extensive fouling and denser cake exhibited by oil. The unique characteristics of the cake layer of oil emulsion vis-à-vis the well-studied particulate foulant (i.e., latex) shown here provides new perspectives on the monitoring and control of oil fouling.

Keywords: Membrane fouling; DOTM; oil emulsion; cake thickness and porosity; XDLVO model

6.1. Introduction

For membrane-based separation processes, membrane fouling remains the key drawback. The blocking law describes that fouling can take various forms, namely, the foulant sits on the top of the pore opening, the foulant penetrates into the pore, or a cake of foulants forms on the membrane surface [1]. In particular, the cake layer deserves more understanding since it is the presiding form of fouling throughout the membrane-filtration process. The initial cake layer forms upon sufficient accumulation of deposited foulants (larger than membrane pores) on the membrane surface with time, and the cake progressively thickens as more foulants deposit due to the permeate drag [2]. As the cake layer builds up, the mass transfer resistance to the permeation process inevitably increases, thus leading to either a drop in the permeate flux for processes operated at constant TMP (transmembrane pressure) or an increase in TMP for processes operated

at constant flux [3]. In practical systems employing crossflow of the feed, moving cake layers have been observed for oil emulsions [4], biofilms [5] and also glass particles [6]. Past studies have attempted at a more in-depth understanding of the cake in order to benefit the corresponding mitigation. Both the cake layer thickness and porosity affect the filtration performance [7], with a study further showing that the cake had a porosity gradient across the cake thickness, with the lower porosity being near the membrane [8]. Interestingly, it has been reported that the gel fouling layer gave high filtration resistance despite a high porosity [9-11], which was linked to the water bound in the gel layer that had a low state of chemical potential and thereby gave higher mass transfer resistance to the permeation of water. Fortunato et al. [12] utilized the Optical Coherence Tomography (OCT) to visualize the formation of the biofilm, and also its growth and structure, and found two distinctly different layers, namely, a stagnant bottom layer and a moving upper layer that was more porous. Marselina et al. [13] studied the bentonite cake layer on the membrane surface using the Direct Observation (DO) method, and saw in real time a stagnant cake and a fluidized cake on the membrane surface during filtration, and cake expansion and erosion during backwashing. Zamani et al. [6] showed using the direct observation through the membrane (DOTM) technique that the phenomenon of a flowing cake layer was observed at a lower cross-flow velocity (CFV) for glass but not for latex (also known as polystyrene), the different phenomena of which was attributed to the greater inter-particle cohesion of the glass particles. Because fouling is affected by the nature of the foulants, studies dedicated to specific foulants are warranted.

In view of the vast volumes of oily wastewater from various industries (such as oil and gas, food and beverage, and metal processing) and the promising treatment means by membranes [14], it is necessary to understand the formation and characteristics of the

cake formed by oil emulsions. Inferences of the oil cake layer have been made through TMP or flux data, UTDR (ultrasonic time-domain reflectometry), SEM (scanning electron microscope) images and model predictions [4, 14-21]. As a complementary tool, direct observation techniques allowed for the unveiling of the cake layer buildup in real time. The direct observation of membrane fouling by oil emulsion has been revealed to be different from that expected of other particulate foulants by DOTM [22, 23] (Chapter 2-5) and OCT [24]. DOTM images has been further coupled with the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) model to link the interfacial interaction between the membrane and foulant to membrane fouling (Chapter 3) [6]. Correspondingly, specifically with respect to cake characteristics, more investigations are needed for oil emulsions, which formed the goal of the current study.

In this study, the focus was on the cake-fouling on HF membranes by oil emulsions. The well-studied latex particles were studied alongside as a reference for comparison. A constant feed concentration of 100 ppm and crossflow velocity (CFV) of 0.035 m/s were employed. The TMP and corresponding resistance of the cake layer were obtained with respect to permeate flux, then DOTM images were taken to quantify the cake layer thickness and porosity. The XDLVO model was also used to quantify the interfacial interaction energies to explain the fouling phenomena observed.

6.2. Materials and Methods

6.2.1. Oil-in-Water Emulsion and Latex Particle Solution

Two model feeds, namely, oil emulsion (specifically, oil-in-water emulsion) and latex (polystyrene) particles, were investigated in this study. Stock solutions for each were first made, then diluted for use in the experiments. For the oil emulsion, (i) the oil emulsion stock solution with a concentration of 25,000 ppm was prepared by blending

10 ml of soybean oil (Sigma Aldrich), 2 ml of Tween 20 (Sigma Aldrich) and 388 ml of deionized (DI) water (Millipore) in a blender (Warring 8011 S) for one minute at 18,000 rpm; then (ii) the stock solution was diluted to 100 ppm by mixing 2 ml to 498 ml of DI water. As for the latex particles, (i) the stock solution of 1000 ppm was prepared by diluting the 10 ml of 10% latex particle (Sigma Aldrich) in 990 ml of DI Water then kept in the fridge (4 °C); and (ii) for the experiments, 50 ml of stock solution was added to 450 ml of DI water to a concentration of 100 ppm. The mean diameters of the oil emulsion and latex particles were measured using the Focused Beam Reflectance Measurement system (FBRM; Lasentec S400, PI-14/206) to be 9.5 and 10.5 μm , respectively; the particle size distributions can be found in Chapter 2 and an earlier study [6].

6.2.2. Direct Observation Through the Membrane (DOTM)

The Direct Observation through the Membrane (DOTM) setup, which has similarly been employed for observing membrane fouling by oil emulsion and latex particles (Chapter 2-5, Appendix), is depicted in Fig. 6.1. Specifically, the main component was the light microscope (Zeiss Imager; A2 m) that was focused at the feed-membrane interface plane and integrated with a video camera (Axiocam 105 Color) to record the images. The feed was contained in a 600-ml beaker that sat atop a magnetic stirrer plate (Heidolph; MR Hei-Mix S) to keep it well-mixed, and the feed circulation between the feed beaker and membrane cell was enabled by a gear pump (Micropump Inc; GJ-N25. PF/S.A). For the permeate side, a peristaltic pump (Cole Palmer; Masterflex L/S 7519-20/85) was employed to circulate the stream between the membrane cell and the permeate beaker (100 ml), which sat atop a mass balance (Kern; 572). For the

measurement of transmembrane pressure (TMP), three pressure transmitters (Cole Palmer) were used to characterize the pressures in the membrane cell (namely, feed inlet pressure (P_1), feed outlet pressure (P_2) and permeate inlet pressure (P_3)).

Figure 6. 1. Direct Observation through the Membrane (DOTM) Setup.

The acrylic membrane cell used, as displayed in Fig. 6.2, was designed and fabricated in-house to accommodate three hollow-fiber (HF) membranes (Tritech Permamax Reinforced Brand). The membrane material was PVDF, which is the most common in practice due to its chemical resistance, thermal stability and mechanical strength [25]. The cell had a length of 105 mm, and consisted of two parts, with the bottom part with dimensions of 35 mm width and 3 mm height, and top part with dimensions of 24 mm width and 4 mm; the two parts were dissimilar because the bottom was previously used for flat-sheet membranes and the top was newly fabricated to adapt for HF membranes. The HF membranes were hydrophilic PVDF membranes with a nominal pore size of 0.1 μm , and with internal diameters (ID) and outer diameters (OD) of 1 and 1.8 mm, respectively. Each HF membrane, with a length of 10 cm and the distance between the

HF membranes of 5 mm, was glued (Epoxy glue, Araldite) to two holders, one at each end of the membrane, giving a total active length of 8.5 cm. The holders were then placed at the two ends of the membrane cell. The focal plane of the microscope was positioned at the feed-membrane interface at the outer wall of the middle HF membrane to enable observation of the fouling in real time. The crossflow velocity (CFV) used was 0.035 m/s throughout all experiments.

Figure 6. 2. Schematic of the membrane cell: (a) side view; and (b) top view.

6.2.3. Flux-stepping and constant-flux protocols

Two modes of operation, namely, flux-stepping and constant-flux, were used in this study. For the flux-stepping mode, the permeate flux was increased from 0 L/m²h to 100 L/m²h incrementally by 10 L/m²h every 10 minutes. This was used to characterize (i) the TMP profiles for both foulant types (namely, oil emulsion and latex particles), with the TMP profile for a DI water feed serving as the benchmark for comparison; and (ii) the change in mass transfer resistance due to fouling (R_f). As for the constant-flux mode, a constant permeate flux of 50 L/m²h was imposed over the cumulative permeate

volume from 0 to 50 ml. This was targeted at evaluating the growth of the membrane fouling layer thickness and also the evolution of TMP.

6.2.4. Image analysis to assess local fouling layer thickness

Real-time observation and measurement of the growth of the fouling layer thickness was enabled by the DOTM technique (Fig. 6.1). A constant flux of 50 L/m²h was implemented for each of the two foulants. The experiments were carried out at the same feed concentration of 100 ppm and CFV of 0.035 m/s, and stopped when the cumulative permeate volume reached 50 ml. Images of the membranes were taken every 2.5 ml of permeate volume, then analyzed using ImageJ to quantify the thickness of the fouling layer. Specifically, each image was compared to the image of the initial clean membrane to obtain the difference that constituted the fouling layer. The local cake layer thickness was averaged over the entire length of the examined image since the thickness was not uniform throughout.

6.3. Results and Discussion

6.3.1. Mass Transfer Resistance

Fig. 6.3 shows the change in TMP values as the permeate flux was stepped up incrementally by 10 L/m²h every 10 minutes from 0 L/m²h to 100 L/m²h. The three feeds investigated were DI water, 100 ppm oil emulsion and 100 ppm latex particles, and the CFV was consistently at 0.035 m/s. Fig. 6.3a shows the whole TMP value of each flux step throughout the operation time and the other figure (Fig. 6.3b) shows the average TMP value for each flux step for clearer observation of the TMP line deviation of oil and latex from DI water. For the DI water feed, the TMP expectedly increased

approximately linearly with permeate flux. As for the feeds containing oil or latex, the TMPs values were similar to that of DI water at zero or low permeate fluxes, but greater at higher fluxes (≥ 20 L/m²h for oil and ≥ 30 L/m²h for latex, which implies a lower critical flux associated with the former) due to the increased extents of fouling. It is shown also in Fig. 6.3a that in the higher permeate flux with the duration of 10 minutes, TMP of oil was still in the unsteady state region, meanwhile for latex, it could reach steady state region even in the higher permeate flux, which suggested there was a difference in the characteristic of the fouling layer of oil and latex. Similar trend of TMP increase for oil emulsion filtration was observed also by Miller et al [26], where they did the comparison between constant flux and TMP operation. Between oil and latex, the TMP values for oil were greater for the former at the higher fluxes (≥ 30 L/m²h), which suggests greater resistance caused by the oil deposits. The discrepancy in fouling phenomena despite similar mean diameters agree with previous studies (Chapter 2-5) that showed that oil droplets behaved differently from the well-studied rigid particulates [22-24].

Figure 6. 3. Transmembrane pressure (TMP) versus time (a) and permeate flux (b) for DI water, oil and latex. The permeate flux was stepped up incrementally by 10 L/m²h every 10 minutes from 0 L/m²h to 100 L/m²h at a constant CFV of 0.035 m/s. The

TMP points in (b) were the average from 10th minute data for each permeate flux for clearer observation how the TMP of oil and latex started to deviate from DI Water.

According to Darcy's law [27], permeate flux (J) and TMP are related as follows:

$$J = \frac{\text{TMP}}{\mu(R_m + R_f)} \quad (6.1)$$

where μ is the permeate viscosity, R_m is the mass transfer resistance of membrane, and R_f is the mass transfer resistance of the fouling layer (both reversible and irreversible). For all three feeds, the μ values were similar because of the permeates were aqueous (viscosity of water = 0.00089 N/m²s at 25°C), and the R_m values were also the same because the same membranes were used. The R_m value can be obtained by using the TMP value of DI water when $R_f = 0$, and thereby the R_f value at each permeate flux for oil and latex can be calculated using Eq. (6.1) with the TMP value of oil and latex, except when the permeate flux was zero ($J = 0$ L/m²h). When there was no permeate flux applied, the calculation of R_f was based on the assumption that no fouling happened for all cases (DI water, oil, and latex) during the operation with zero permeate flux, thus the $R_f = 0$ for oil and latex.

Fig. 6.4 shows the mass transfer resistance due to fouling (R_f) for both feeds containing oil emulsion and latex particles. Clearly, for both feeds, the R_f values increased gradually with permeate flux at the lower range and more rapidly at the higher range. Agreeing with the TMP trends (Fig. 6.3), the R_f values for oil were greater than that for latex and increased more steeply at the higher permeate fluxes.

Figure 6. 4. Mass transfer resistance due to fouling (R_f) versus permeate flux for oil emulsion and latex particles. The experiments were carried out at a CFV of 0.035 m/s and feed concentration of 100 ppm.

Figs. 6.5 and 6.6 show the fouling phenomena at various permeate fluxes (namely, critical flux (J_{crit}), and 10 L/m²h and 20 L/m²h above J_{crit}) for respectively oil emulsion and latex particle on both HF membranes and flat-sheet membranes [28]. The images were taken at the end of the 10th minute at the specific permeate flux. Fig. 6.5 indicates that the moving cake layer reported for flat-sheet membranes (bottom row of Fig. 6.5 is from Chapter 2) was also evident with the HF membranes (upper row of Fig. 6.5). Zhu et al. [4] also observed a similar formation of a thin layer of oil fouling layer deposited at the beginning and a moving layer at the later stage. Such a moving cake layer has also been observed for biofouling [5]. The previous studies in Chapter 2-4 on flat-sheet membranes found that oil emulsions tended to form a moving cake layer [22-24], whether as a cluster of individual droplets or as stripes of oil droplets or as a moving coalesced droplet, but these results had a commonality whereby the layer covered most of the membrane surface while it moved. By seeing the different angle of observation

of oil fouling layer on HF membrane, it complemented the understanding of the fouling mechanism which has been understood previously on the flat sheet membrane.

Figure 6. 5. Fouling phenomena by oil emulsion observed using DOTM at critical flux (J_{crit}), and 10 L/m²h and 20 L/m²h above J_{crit} : the top row was HF membranes, at a CFV of 0.035 m/s and oil concentration was 100 ppm; while the bottom row was flat-sheet membranes, at a CFV of 0.1 m/s and feed concentration of 200 ppm (Chapter 2). The images were taken at the end of the 10th minute of the permeate flux step.

On the other hand, for the latex particles, Fig. 6.6 indicates that the latex particles remained stagnant once deposited on the membranes, and subsequent deposits occurred near other deposits due to the attractive interaction energy between the particles [6]. Both HF (upper row of Fig. 6.6) and flat-sheet (bottom row of Fig. 6.6) membranes displayed similar fouling phenomena for both oil droplets and latex particles. This agrees with Hai et al. [29], which demonstrated the similarity in fouling trends between the two membrane types for single-constituent feeds, but that flat-sheet membranes were more susceptible to pore blocking whereas hollow fiber to cake layer fouling for more complex (e.g., multi-component) feeds. The fouling phenomena presented in Figs. 6.5 and 6.6 are inextricably related to the TMP trends in Fig. 6.3. The layer formed by the

oil blocked more area of the membrane (Fig. 6.5) and thereby caused a greater increase in TMP, while the scattered depositions by the latex particles allowed more permeation and thus a gentler increase in TMP.

Figure 6. 6. Fouling phenomena by latex particles observed using DOTM at critical flux (J_{crit}), and 10 L/m²h and 20 L/m²h above J_{crit} : the top row was HF membranes, at a CFV of 0.035 m/s and oil concentration was 100 ppm; while the bottom row was flat-sheet membranes, at a CFV of 0.1 m/s and feed concentration of 50 ppm [28]. The images were taken at the end of the 10th minute of the permeate flux step.

6.3.2. Fouling Layer Thickness

Fig. 6.7 depicts the evolution of the normalized TMP (i.e., normalized with respect the initial TMP) and cake layer thickness with respect to the permeate volume per unit membrane area at a constant flux of 50 L/m²h. Both normalized TMP and fouling thickness expectedly increased as more permeate volume was collected. Fig. 6.7a shows that the normalized TMP values were greater for oil than for the latex particles, which agrees with Fig. 6.3. As for Fig. 6.7b, four observations are worth noting. Firstly, Fig. 6.7b indicates an opposite trend, specifically in that the thickness of the cake layer was instead greater for latex than for oil, which is counter-intuitive because cake thickness was expected to correlate positively with TMP. This is likely linked to the higher

polydispersity (i.e., wider size range) of the oil droplets (Chapter 2), which led to denser packing in the cake and thereby greater TMP values (due to greater resistance as shown in Fig. 6.4) and a thinner cake. Secondly, the cake thickness trend for oil fluctuates more, which is due to the more dynamic moving cake layer (Fig. 6.5). Thirdly, the error bars were greater for oil with respect to both TMP and cake thickness, which is also due to the dynamism of the cake. Fourthly, the cake thickness for oil plateaued at approximately 7 μm , whereas that for latex continued to grow beyond the range of permeate flux investigated here. Zhu et al. [4] indicated significant flux decline initially due to the immediate formation of an oil layer and after that the flux decreased slowly due to the formation of a stable dynamic (moving) oil layer with approximately constant thickness.

Figs. 6.8 and 6.9 further present the side views of the cakes formed on the outer walls of the HF membranes by respectively oil and latex particles at various permeate volumes, which shows the progressive growth of the cake. For oil (Fig. 6.8), oil droplets started depositing and the cake became distinct at the permeate volume of 20 ml. It should be noted that both the initial deposited oil droplet and the subsequent cake layer rolled along the membrane with the cross-flow rather than remaining stagnant, as also observed in previous studies (Chapter 2 and 3). The maximum cake thickness increased with permeate volume, and the thickness was not uniform along the membrane. The results here on the evolution of the oil-fouling complemented that by Xu et al [21], wherein the Ultrasonic Time-domain Reflectometry (UTDR) used for the same purpose (i.e., oil-fouling on HF membranes) showed the progressive fouling from a thin oil layer to a thicker one. As for latex particles (Fig. 6.9), the fouling phenomenon was distinctly different, though both had cakes with non-uniform thickness along the membrane. Specifically, scattered deposits were clear from 5 ml, the cake was clearly more granular

compared to that by oil, and the deposits were stagnant rather than rolling along with the cross-flow. The fouling mechanism by latex particles have been described by Zamani et al. [6]. Because of the attractive inter-particle interaction, the latex particles tended to cluster together as they deposit on the membrane.

Figure 6. 7. Normalized TMP (a) and cake thickness (b) of oil and latex particles versus the cumulative permeate volume per unit membrane area. The experiments were carried out at a CFV of 0.035 m/s, feed concentration of 100 ppm and constant permeate flux of 50 L/m²h.

Figure 6. 8. Cake layer growth on the membrane surface for oil over various cumulative permeate volumes. The experiments were carried out at a CFV of 0.035 m/s, feed concentration of 100 ppm and constant permeate flux of 50 L/m²h. The images were taken at the moment each respective volume was collected.

Figure 6. 9. Cake layer growth on the membrane surface for latex particles over various cumulative permeate volumes. The experiments were carried out at a CFV of 0.035 m/s, feed concentration of 100 ppm and constant permeate flux of 50 L/m²h. The images were taken at the moment each respective volume was collected.

6.3.3. Porosity of the Cake Layer

On top of cake thickness, the compressibility or porosity of the cake layer influences the filtration performance too [7]. The interstices in the cake layer would differ depending on the nature of the foulants, with a denser cake layer being more detrimental to the permeate flux. Regarding cake compressibility under different pressures, Mendret et al [3] found that the cake thickness was not linearly correlated to the mass of deposits due to the varying cake layer porosity. The overall cake layer deposited can be calculated based on the local thickness of the cake layer and the overall particle mass balance, with the assumption that the flux and the deposit morphology (i.e., porosity and thickness) were uniform throughout the membrane [3]. Specifically, the mass of deposits (m_d) can be expressed as:

$$m_d = v \cdot c = \rho_d \cdot v_d \cdot (1 - \varepsilon_f) \quad (6.3)$$

where v is the volume of collected permeate, c is the bulk concentration of the feed, ρ_d is the density of the deposited particulate, v_d is the volume of the deposited particulate, and ε_f is the porosity of the cake layer. The volume of the deposited particulate (v_d)

could be calculated from the multiplication of the filtration area (A) and the local cake layer thickness (h_{local}):

$$v_d = A \cdot h_{local} \quad (6.4)$$

Fig. 6.10 shows the cake porosity (ε_f) as a function of permeate volume. Based on the same mass deposited, which was calculated from the density and volume of deposition of each particle, on the membrane surface for oil emulsion and latex particles, the porosity (ε_f) of the oil emulsion layer was lower than that for latex particles over the whole range of permeate volume. In particular, the porosity of latex particle layer stayed between the narrow range of 0.8 to 0.9, whereas that of the oil emulsion layer fluctuated drastically between 0.05 to 0.7. The lower porosity of the oil droplet layer indicates a denser cake, which underlie the higher TMP and thinner cake layer relative to that of the latex particles (Fig. 6.7) and also explains that in the higher permeate flux (above J_{crit}), the TMP of oil could not reach steady state region in the duration of 10 minutes (Fig. 6.3a), as the oil kept filling the gap and increased the TMP. In addition, the denser layer of oil emulsions also made it more prone to result in a moving cake layer due to the inherently greater inter-emulsion cohesion, as observed by Zhu et al [4].

Figure 6. 10. Porosity of the local fouling layer or deposited mass (ϵ_f) of oil droplet and latex particle during the constant flux operation of 50 L/m²h. The feed concentration was 100 ppm and the CFV was 0.035 m/s.

6.3.4. Interaction Energy

Other than the porosity of the cake layer, the foulant-membrane and foulant-foulant interactions inevitably also underlie the different TMP trends between oil and latex (Fig. 6.3). The Derjaguin-Landau-Verwey-Overbeek (DLVO) and the corresponding extended DLVO (XDLVO) models are popularly used to quantify such interactions [30]. Generally, it has been well-acknowledged that the XDLVO model, which considers an additional Lewis acid-base (AB) interaction, is well-suited for membrane-filtration applications [31]. However, particularly for oil emulsion, it has recently been reported that the DLVO model suffices in describing the fouling phenomenon (Chapter 3) [32]. To evaluate the difference between oil and latex, Table 6.1 lists the surface tension components of PVDF [32], water [6, 32], hexadecane (i.e., oil) [33] and latex [6].

Table 6. 1. Surface tension components of the PVDF membrane, water, oil and latex.

Material	γ^{LW}	γ^+	γ^-	Ref.
PVDF	40.4	0.04	61.9	[32]
Water	21.8	25.5	25.5	[6, 32]
Hexadecane	27.0	0	0	[33]
Latex	42.0	0	1.1	[6]

Note: Values are in units of mJ/m²

It should be noted that these values were obtained from literature instead of measured, based on past validation of such a practice for well-studied materials like polymeric membranes [34], inorganic membranes [35], latex particles [35, 36], and silica particles [35, 37]. Fig. 6.11 displays the interaction energy predicted by the XDLVO model versus separation distance profiles for both foulant-membrane and foulant-foulant interactions. For both sub-figures, the minimum separation distance is 0.158 nm [31, 32]. For both foulant-membrane and foulant-foulant interactions, oil was more attractive (i.e., more negative values) than that of latex. While the greater oil-membrane interaction energy substantiates the worse fouling exhibited by oil emulsions evident in the higher TMP values (Fig. 6.3) and cake resistance (Fig. 6.4), the greater oil-oil interaction explains the formation of a cake layer (Fig. 6.8) rather than scattered deposits (Fig. 6.9). Furthermore, the greater oil-oil attraction relative to that of latex-latex also underlie the denser cake formed by oil (Fig. 6.10).

Figure 6. 11. Interaction energy predicted by the XDLVO model versus separation distance for (a) foulant-membrane interactions, and (b) foulant-foulant interactions.

6.4. Conclusion

This study targeted at characterizing the evolution of the oil-emulsion cake layer characteristics on HF membranes in real time using DOTM. As a benchmark for comparison, the more well-studied latex particles were studied alongside.

Interestingly the results show that, at the same feed concentration of 100 ppm and crossflow velocity of 0.035 m/s, (i) the TMP values were greater for oil emulsion than for latex particles at the same permeate flux, which was because oil tended to deposit as a moving cake layer, whereas latex as scattered deposits; (ii) oil gave a thinner cake layer that was denser which resulted in higher cake layer resistance (R_f); (iii) the increase in cake layer thickness was non-monotonic with respect to permeate volume for oil but monotonic for latex, due to the movement of cake layer of the former; (iv) the fluctuations of cake porosity with respect to permeate volume were much more drastic for oil than for latex; and (v) the XDLVO model gave higher oil-membrane and oil-oil interactions compared to that of latex, which underlie respectively the more extensive fouling and denser cake exhibited by oil

The unique characteristics of the cake layer fouling by oil emulsion vis-à-vis a well-studied particulate foulant (i.e., latex) shown here provides new perspectives on the monitoring and control of oil fouling. Notably, on the industrial scale, instruments like the UTDR [38] and the Electrical Impedance Spectroscopy (EIS) [39] that have been shown to be proficient in fouling detection may need to be further developed specifically for oil, in view of the dramatically fluctuating cake layer thickness and the denseness of

the cake. The moving cake layer would make for an interesting case study and refinement for such instruments.

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CHAPTER 7: CONCLUSIONS AND FUTURE PERSPECTIVES

7.1. Conclusions

Membrane filtration technology has gained more attention in the recent years for the oil-water separation, especially for the oil droplet size below 10 μm , where the conventional separation methods become ineffective, but it has an inevitable drawback in terms of membrane fouling. In this studies, we employed Direct Observation through the Membrane (DOTM) method to observe the oil fouling on the membrane surface from the growth, movement, also the comparison with other foulant in various operating parameters, such as cross-flow velocity (CFV), feed concentration, salt concentration, viscosity, and bidispersity.

In the first chapter, we reviewed the need of separate oil emulsion from water, with the development of membrane technology from the novel studies until the commercial membrane used in the real practice. It was also explained how the new study of membrane fouling could be implemented into the industry in order to enhance the membrane performance in oil-water separation.

In the second chapter, we studied the critical flux (J_{crit}) of oil emulsion in various CFV, oil concentration, and salt concentration. It was observed that the J_{crit} increased as the CFV increased, but decreased as the oil concentration increased. The salinity of the feed also decreased the J_{crit} , as the interaction between oil droplet and membrane surface became less repulsive in the presence of salt.

In the third chapter, a more comprehensive study of oil fouling were done by various oil type and it was observed that the J_{crit} was similar for all oils, except for crude oil. This interesting result was confirmed with the interaction energy model of DLVO

and XDLVO. The DLVO model could show the difference between the oils, which explained the J_{crit} result, meanwhile the more comprehensive XDLVO model could not show clearly due to the overwhelming value of AB interaction, which was two-order magnitude higher than EL and LW interaction energy.

In the fourth chapter, the study was continued for explaining the striping phenomenon of oil fouling which was found out during the earlier studies. This interesting phenomenon was observed at the high oil concentration and low CFV, and it was tested with different Tween surfactants. As the stripes appeared, the TMP increased as well, which showed that the stripes were part of the manifestation of the fouling. It was observed clearly also for the stripes movement that the stripes moved along the feed flow and it could merge with other stripes, then demerged.

In the fifth chapter, the study was expanded to the effect of the viscosity and bidispersity for the critical flux of oil-water separation. It was based on the filtration of skim milk where casein, oil emulsion, and lactose were the main foulants. J_{crit} of oil emulsion decreased as the lactose was in the feed, due to the increase of viscosity, but it decreased significantly for casein, due to the twin effect of viscosity and bidispersity.

In the last chapter, fouling by oil emulsion was observed from a different perspective by using a HF membrane. The observation showed the growth of the fouling from oil emulsion which was different from a rigid particle of latex. The oil cake layer was thinner but denser in comparison with the latex particle. The oil fouling also created a moving layer which was also observed in the previous studies, meanwhile the latex particle deposited individually and stayed once it reached the membrane surface.

All in all, these studies revealed more understanding regarding the unique oil fouling on the membrane surface, which could help the development of the more enhanced and efficient membrane filtration technology in the future.

7.2. Future Perspectives

Due to the complexity of membrane fouling especially for oil emulsion, more studies could be done in the future to shed more knowledge of the issue. As these studies were done mainly for the MF system, it could be better if more studies could be done for the direct observation of the oil fouling in UF, NF or RO systems, but it could be done with the development of new transparent membrane. The limitation of DOTM system is the transparency of the membrane, where currently it is limited to the Anopore membrane which is a ceramic membrane with the range of MF to UF system. Novel transparent membrane could open new understanding for the oil fouling as well as enhancing the technology. Multiple spots of observation could be added also to the DOTM system in the future, for more comprehensive representation of the overall phenomena on the membrane surface. The complexity of the feed solution could be increased as well to be studied deeper, such as the effect of metals or bio-organisms to the fouling, due to the various content in the industrial oily wastewater. Other than these suggestion, novel modelling system could be studied also for better prediction of the J_{crit} and fouling, based on the uniqueness of the oil emulsion in the constant pressure or constant flux filtration method, which would prolong the lifespan of the membrane.

APPENDIX : EFFECT OF SPACER AND CROSSFLOW VELOCITY ON THE CRITICAL FLUX OF BIDISPERSE SUSPENSIONS IN MICROFILTRATION

The content of this chapter has been published under the title of *Effect of Spacer and Crossflow Velocity on the Critical Flux of Bidisperse Suspensions in Microfiltration* in *Journal of Membrane Science*, vol. 513, pp. 101-107, Sep 2016 (<https://doi.org/10.1016/j.memsci.2016.04.040>).

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Abstract

Crossflow microfiltration is a popular application spanning various industries. Although the impacts on fouling of feed bidispersity, crossflow velocity (CFV) and spacer, all of which are present in practical operations are known separately, the understanding of the interplay of these three factors on fouling is lacking. Accordingly, this study used the Direct Observation Through the Membrane (DOTM) technique to characterize the critical flux of monodisperse and bidisperse polystyrene particles in both the absence and presence of a spacer over a broad range of CFV values. The results indicate that (i) the combined effects of both bidispersity ($d_p = 3\ \mu\text{m}$ and $10\ \mu\text{m}$) and spacer gave the highest J_{crit} values for the smaller particles throughout the CFV range investigated; (ii) bidispersity was more effective in enhancing J_{crit} at a lower CFV, the presence of a spacer was more effective at a higher CFV; (iii) a higher CFV diminished the enhancement induced by bidispersity more than that by the spacer; and (iv) comparisons between models and experimental data reveal that shear-induced diffusion models based

on monodisperse particles are deficient for bidisperse mixtures, because they cannot allow for particle size segregation effects that occur in flowing mixed systems.

Keywords: Microfiltration; Bidisperse; DOTM; Critical Flux; Shear-induced Diffusion

1. Introduction

Microfiltration has widespread applications including wastewater and food. As with all membrane-based separation processes, membrane fouling is an inevitable problem that needs to be addressed. In practical operations, crossflow of the feed is used to induce shear on the membrane surface to mitigate concentration polarization and fouling [1, 2]. As a means of quantifying the onset of fouling, Field et al. [3] proposed the term ‘Critical Flux’, which is the permeate flux beyond which fouling becomes significant. Subsequently, Bacchin et al. [4] introduced the concept of ‘Sustainable Flux’ to incorporate notions of economic and environmental sustainability. Sustainable flux is qualitatively related to Critical Flux. Notably, the underpinnings of critical flux (J_{crit}), which is a function of various parameters, provide important operational and design heuristics [4-6].

Conventional techniques used to measure J_{crit} are based on indirect measurements (e.g., flux-pressure measurements, mass balance, and fouling rate analysis), which are convenient but not informative of the mechanisms leading to fouling. With the advent of novel non-invasive observation techniques, the precision associated with the determination of J_{crit} and the elucidation of the underlying mechanisms have been significantly improved. The Direct Observation Through the Membrane (DOTM) technique is one such technique allowing for the direct visualization of the interaction

of particulate foulants with the membrane; in particular, it has been verified that the onset of the first deposition occurs earlier than the onset measurable changes in membrane resistance detected via indirect means [4, 7]. DOTM has been proven to be a useful technique for studying the fundamentals of foulant deposition and foulant-membrane interactions, and has been used in characterizing the following particulate foulants: polystyrene (also known as latex) particles [7-12] as particles or mixtures and fractal floc, yeast [7, 8], algae [8, 13], and bacteria (sub-micron) [14].

In a previous DOTM study of bidisperse mixtures of particles it was observed that the presence of the larger particles increased the J_{crit} of the smaller particles, and only the smaller particles were observed on the membrane [9]. The explanation provided was that the enhancement of J_{crit} of the smaller particles was due to augmentation of shear-induced diffusivity of the smaller particles in the boundary layer by the bigger particles. This mechanism would be dependent on crossflow velocity and eddy promotion, as achieved by spacers [14, 15]; neither of these factors were examined in the earlier work. Therefore this study reports on the effect of a range of crossflow velocities and operation with and without spacer. In addition, the results have been compared with models for mono- and bidisperse particle systems.

2. Experimental description

2.1. Experimental setup and materials

The experimental setup using the Direct Observation Through the Membrane (DOTM) technique [7] is shown in Fig. A.1. The setup consisted of a light microscope (Zeiss Imager.A2 m) coupled with a camera (Axiocam 105 Color), a feed pump (Micropump Inc, GJ-N25.PF/S.A), a permeate pump (Cole Palmer; Masterflex L/S

7519-20/85), a cross-flow acrylic membrane cell (with total channel dimensions of 105 mm length by 35 mm width by 3mm height; the feed and permeate channel heights were respectively 2 mm and 1 mm), three pressure transmitters (Cole Palmer; Transducer 206) to characterize the pressures in the membrane cell (namely, feed inlet pressure, feed outlet pressure, and permeate inlet pressure), a feed solution container, a permeate container placed atop a balance (Kern; 572) to quantify permeate flux, and a computer to log pressure signals from the pressure transmitters and mass from the balance via Labview (2014-64 bit).

Figure A. 1. Direct Observation Through the Membrane (DOTM) Experimental Setup

The membrane used was an Anodisc membrane (Whatman, Germany), which was a circular disk with a diameter of 47 mm and had a nominal pore diameter of 0.2 μm . The Anodisc membrane has high porosity and straight-through pores, making it transparent when wet, as required by DOTM. A piece of A4-size paper was cut into a

smaller rectangular area with dimensions of 55 mm by 135 mm, from which a square area of 27 mm by 27 mm was cut in the center. After that, an Anodisc membrane was centered and pasted with glue between two pieces of these cut-outs, such that the active membrane area was 27 mm by 27 mm.

The particles used as model foulants were monodisperse polystyrene (also known as latex) particles (Fluka, Sigma Aldrich) with particle diameters (d_p) of 3 and 10 μm . The particle concentration used in the feed for each experiment was 0.05 g/L, regardless of whether a monodisperse (i.e., 3 μm) or bidisperse mixture (i.e., 3 and 10 μm particles in 1:1 volumetric ratio) was investigated.

The spacer used is shown by Fig. A.2, whereby each grid had dimensions of 3 mm by 3 mm, and was angled at 45° to the feed and permeate streams. A spacer was always used on the permeate side of the membrane to enhance the mechanical integrity of the membrane to enable it to lay flat throughout the experiments. On the other hand for the feed side, a spacer was added only in some of the experiments to understand the effect of a spacer vis-a-vis that without.

Figure A. 2. Photograph of the spacer used. Each grid had dimensions of 3 mm by 3 mm, and was angled at 45° to the feed and permeate streams.

2.2. Method for determining critical flux

Critical flux, defined as the maximum flux above which the membrane fouls [3], was determined by the flux-stepping method. The initial permeate flux was set at 5 l/m²h for 10 minutes, after which the flux was increased by 5 l/m²h every 10 minutes. At each flux, one image was taken at the first minute then another at the ninth minute. Each image was analyzed using ImageJ for the rate of change of surface coverage (C), based on the formula employed by Wicaksana et al. [13]:

$$\frac{\Delta C}{\Delta t} = \frac{C_{9th\ minute} - C_{1st\ minute}}{t_{9th\ minute} - t_{1st\ minute}} \quad (A.1)$$

Two notes are worth highlighting regarding the image area characterized. Firstly, the area had dimensions of 0.416 by 0.556 mm, giving an area of 0.23 mm², which was more than 500 times larger than the 430 μm² characterized in Wicaksana et al [13], thereby expected to confer a more representative reflection of membrane fouling. Secondly, when a spacer was used, the area was within a unit cell of the spacer (Fig. A.2). In view of the observation in Neal et al. [14] regarding the variations in local critical flux within each unit cell of the spacer, care was taken to focus at the center of the unit cell for every experiment. Even so, the variations in critical flux values was observed to be greater when a spacer was used relative to when the spacer was absent. A typical versus permeate flux plot is shown in Fig. A.3. The critical flux (J_{crit}) was determined as the permeate flux at which $\frac{\Delta C}{\Delta t}$ attained a pre-determined threshold. Specifically, to determine an appropriate threshold value, multiple $\frac{\Delta C}{\Delta t}$ versus permeate flux plots obtained under different conditions were examined to identify a consistent point which signified the onset of more rapid deposition (i.e., $\frac{\Delta C}{\Delta t}$ increased more rapidly). In this study, the threshold value was determined as 0.2%/min, which was higher than

the 0.03%/min used previously [13] because of the lower feed concentration studied here and also the greater variability associated with the data obtained when a spacer was present. In particular, a lower threshold value caused greater variations in the J_{crit} values obtained in this study. The reported J_{crit} values are based on duplicate or triplicate experiments, with error bars showing the range of data.

Figure A. 3. Plot of $\frac{\Delta C}{\Delta t}$ versus permeate flux for 0.05 g/L of monodisperse 3 μm particles in the presence of a spacer and at CFV = 0.25 m/s. The critical flux was determined as the permeate flux at which $\frac{\Delta C}{\Delta t}$ attained the threshold value of 0.2. In this case, the critical flux was 60 l/m²h.

Four crossflow velocities (CFV) in the range of 0.1 to 0.25 m/s were investigated. The lower CFV limit of 0.1 m/s was set to avoid the difficulty in distinguishing between deposited and flowing particles (especially for $d_p = 3 \mu\text{m}$) at lower CFVs, and the upper CFV limit of 0.25 m/s was set because higher CFVs tended to break the brittle Anodisc membranes (especially in the absence of a spacer).

3. Results

3.1. Critical flux of monodisperse and bidisperse suspensions

Fig. A.4 shows the critical flux (J_{crit}) versus crossflow velocity (CFV) of monodisperse polystyrene particles with $d_p = 3\ \mu\text{m}$ in the absence of a spacer, which served as the baseline for comparing the effects of CFVs and spacer on the J_{crit} of binary mixtures. In agreement with a previous study [7], as CFV increased, J_{crit} increased monotonically, which indicates expectedly that the enhanced shear on the membrane surface attenuated membrane-fouling.

Figure A. 4. Critical flux (J_{crit}) versus crossflow velocity (CFV) of 0.05 g/l of monodisperse polystyrene particles with $d_p = 3\ \mu\text{m}$ in the absence of a spacer

Armed with the interesting results of Zhang et al. [9] regarding the significant increases in critical flux with the addition of larger particles, presumably due to the enhanced shear-induced diffusion, this study targeted further probing the impact of the larger particles at various crossflow velocities (CFVs) and in the presence of a spacer. The bidisperse mixture was such that the volume ratio of the particles with $d_p = 3\ \mu\text{m}$

and 10 μm was 1:1, and the particle concentration was the same as the monodisperse suspension (Fig. A.4) at 0.05 g/l. Fig. 5 is a plot of J_{crit} versus CFV, which illustrates the impact of a bidisperse particle mixture and a spacer vis-a-vis the monodisperse ($d_p = 3 \mu\text{m}$) system. In general, the combination of bidisperse mixture and spacer performed the best in terms of consistently giving the highest J_{crit} values, while that of monodisperse without spacer performed the worst. To address the question of whether bidispersity or the presence of a spacer was more effective in mitigating membrane-fouling, the answer seems to depend on CFV. Whereas bidispersity was more effective at a lower CFV (which equates to a lower energy requirement), the presence of a spacer was more effective at higher CFV which augmented the turbulence effects. Two more specific observations are worth highlighting. Firstly, for both the monodisperse and bidisperse systems, the presence of a spacer consistently gave higher J_{crit} values at all CFVs, which agrees with the acknowledged benefits of spacers in inducing eddies at the membrane surface to reduce fouling [14-16]. In particular, Sousa et al. [17] found via Computational Fluid Dynamics (CFD) that more eddies were formed and the force towards the membrane due to permeate flux that was received by the particle was reduced at the spacer as the CFV increased. Secondly, in the absence of a spacer, the J_{crit} values of the bidisperse mixture were consistently higher than that of the monodisperse system, which agrees with Madaeni [18] and our previous study [9], because of the enhanced shear-induced diffusion associated with the larger particles. Fig. A.6 shows more explicitly the enhancement possible for systems with bidisperse mixtures and/or spacers with respect to that of a monodisperse mixture without a spacer in terms of $J_{crit}/J_{crit,3\mu\text{m},no\ spacer}$. The enhancement factor (i.e., $J_{crit}/J_{crit,3\mu\text{m},no\ spacer}$) generally diminished as CFV increased. As shown in Fig A.6 at the lowest energy expenditure (i.e., lowest CFV of 0.1 m/s), the combination of both a bidisperse mixture

and a spacer led to a significant five times improvement of J_{crit} , the presence of a bidisperse mixture alone resulted in a 3.5 times improvement, while the presence of a spacer alone resulted in the lowest but non-negligible twofold improvement of J_{crit} . At higher energy expenditures (i.e., $CFV \geq 0.2$ m/s), the highest $J_{crit} / J_{crit, 3\mu m, no\ spacer}$ possible was reduced to a maximum of 2, with the bidisperse mixture in the absence of spacer barely providing an enhancement.

For the enhancement by bidispersity alone (i.e., without spacer), the enhancement factor decreased from greater than 3 to about 1 as CFV increased, presumably because (i) the larger particles tended to segregate towards the center of the channel at higher CFV [19, 20], which meant the concentration of the larger particles close to the membrane surface was reduced, which in turn implied the enhancement of the shear-induced diffusion of the smaller particles by the larger particles was diminished; and (ii) the increased eddy formation in the liquid phase diminished the shear-induced diffusion effects of the particles. Regarding (ii), such an effect can be traced to the particle Reynolds number (Re_p):

$$Re_p = \frac{\rho_p d_p V_l}{\mu_l} \quad (A.2)$$

where ρ_p is particle density, V_l represents CFV, and μ_l is the viscosity of liquid. Physically, Re_p is the ratio of the inertia of the particle to the viscous forces in the liquid. More specifically, both a larger d_p and a larger CFV (hence V_l) lead to larger Re_p , which implies that the larger particles are less likely to follow fluid streamlines, which underlie the shear effects, at higher CFV, thereby the beneficial shear-induced diffusion effects are reduced.

Figure A. 5. Critical flux (J_{crit}) versus crossflow velocity (CFV) of 0.05 g/l of monodisperse ($d_p = 3\ \mu\text{m}$) and bidisperse ($d_p = 3\ \mu\text{m}$ and $10\ \mu\text{m}$) polystyrene particles in the presence and absence of a spacer

Figure A. 6. Enhancement of critical flux (J_{crit}) for systems with bidisperse mixtures and/or spacers with respect to that of a monodisperse system ($d_p = 3\ \mu\text{m}$) without a spacer in terms of $J_{crit} / J_{crit, 3\ \mu\text{m}, \text{no spacer}}$

To further understand the enhancement effects of bidispersity and spacer, Fig. A.7 displays the enhancement effects with respect to the monodisperse particle system and the system without a spacer respectively in Figs. A.7a and b. Both sub-plots have

the same ranges of x - and y -axes for easier comparison. In Fig. A.7, all the values are above one, which implies the expected beneficial effects of bidispersity and spacer. Fig. A.7a shows that $J_{crit,3\mu m+10\mu m}/J_{crit,3\mu m}$ was greater in the absence of spacer at lower CFVs (i.e., < 0.15 m/s), which affirms that the spacer diminished the shear-induced diffusion enhancement of the smaller particles by the larger particles; however, the impact of spacer was negligible at higher CFVs (i.e., > 0.15 m/s). On the other hand, Fig. A.7b shows that $J_{crit,spacer}/J_{crit,no\ spacer}$ was greater for the monodisperse rather than the bidisperse system at lower CFVs, which indicates that the spacer was more effective for the monodisperse system; however, higher CFVs similarly diminished the difference between the two systems. Comparing the two sub-plots in Fig. A.7 reveals that (i) the enhancement induced by bidispersity (Fig. A.7a) was greater than by spacer (Fig. A.7b) at lower CFVs, and (ii) the effect of CFV on diminishing the enhancement induced by bidispersity (Fig. A.7a) was more severe than that by spacer (Fig. A.7b).

Figure A. 7. Enhancement of critical flux (J_{crit}): (a) effect of bidispersity in the presence and absence of a spacer; (b) effect of spacer on monodisperse and bidisperse particle systems.

3.2. Shear-induced diffusion model

The particle back-transport mechanism for micron-sized particulate foulants in the particle diameter range of 0.5 - 30 μm is acknowledged to be shear-induced diffusion [1, 21]. Zydney and Colton [22] provides one of the first expressions of the shear-induced diffusion model in the form of a length-averaged flux, J :

$$J = 0.078 \gamma_0 \left(\frac{a^4}{L}\right)^{\frac{1}{3}} \ln \left(\frac{\phi_w}{\phi_b}\right) \quad (\text{A.3})$$

where γ_0 represents shear rate at the membrane surface (s^{-1}), a represents particle radius (m), L represents membrane length (m), ϕ_w represents particle volume fraction at the membrane surface (-), and ϕ_b represents particle volume fraction in the bulk suspension. Because Eq. A.3 applied to concentrated suspensions such as blood [22], Li et al. [8] modified Eq. A.3 for more dilute suspensions (i.e., $\phi_w = 0.2$) wherein the shear-induced diffusivity (D) was smaller [23]:

$$J = 0.0595 \gamma_0 \left(\frac{a^4}{L}\right)^{\frac{1}{3}} \ln \left(\frac{\phi_w}{\phi_b}\right) \quad (\text{A.4})$$

In view of the poor agreement for the smaller particles ($d_p = 3 \mu\text{m}$), Li et al. [8] used an empirical constant (C_d) to improve the fit with experimental data:

$$J = 0.807 \gamma_0 \left(\frac{C_d^2 \phi_w^2 a^4}{L}\right)^{\frac{1}{3}} \ln \left(\frac{\phi_w}{\phi_b}\right) \quad (\text{A.5})$$

where C_d was found to average 0.31 [8].

Eqs. A.3 – A.5 apply to monodisperse particles. For polydisperse mixtures, Shauly et al. [24] has considered the twin effects of interaction frequency of particles of different sizes and an effective viscosity:

$$J = -k \gamma_0 a' a_i \phi_b \phi_w [\nabla \ln(\gamma_0 \phi_i) + \frac{a'}{a_i} \nabla \ln \mu^\lambda] \quad (\text{A.6})$$

where k represents dimensionless particle migration parameter, a' represents average particle diameter (m), a_i represents the diameter of particle i (m), ϕ_i represents volume

fraction of particle i , μ represents viscosity of the fluid (kg/ms), and λ represents dimensionless particle migration coefficient. Krompkamp et al. [25, 26] adopted Eq. A.6 for bidisperse mixtures by accounting for particle size segregation effects in that the membrane surface is typically enriched with the smaller particles:

$$J = 0.072 \gamma_0 \left(\frac{\phi_w a^4}{\phi_b L} \right)^{\frac{1}{3}} \quad (\text{A.7})$$

where $\phi_b < 0.1$.

Three of the models (namely, Eqs. A.4, A.5 and A.7) presented above are compared below with the experimental data obtained, due to the similarity in the operating parameters (i.e., ϕ_b and d_p). Specifically, Eq. A.2 by Zydney and Colton [22] was not used because the shear-induced diffusivity at higher concentrations failed to agree at more dilute conditions [8]. No model that accounts for the presence of a spacer is available. To account for the effect of a spacer, because the spacer network breaks the channel into short increments with the laminar boundary layer restarting in each mesh of the net [27, 28], it is conceivable that a characteristic hydraulic diameter (d_h) can be used in place of the membrane length (L) [27, 29] in (Eqs. (A.4), (A.5) and A.7). However, Da Costa et al. [27] has concluded that the hydraulic diameter (d_h) defined for a spacer [28] is insufficient to describe the complex flow trajectories induced by the spacer. Hence, the impact of the spacer unfortunately cannot be incorporated into the models readily.

Figure A. 8. Comparison between model predictions and experimental data for the monodisperse particles with $d_p = 3 \mu\text{m}$ in the absence of a spacer.

Fig. A.8 shows the comparisons between model predictions and experimental data for the monodisperse particles with $d_p = 3 \mu\text{m}$ in the absence of a spacer. Two notes are worth highlighting. Firstly, the experimental data agree with Eq. (A.4) at lower CFVs (i.e., $\leq 0.15 \text{ m/s}$) and Eq. (A.5) at higher CFVs (i.e., $\geq 0.2 \text{ m/s}$), the trend of which is consistent with the observations of Li et al. . Li et al. [8] found that Eq. (A.4) significantly under-predicts for the smallest particle investigated of $d_p = 3 \text{ mm}$ at higher CFVs, presumably due to the more dominant electro-kinetic effects and also effects associated with flow that is not fully developed at higher Reynolds number. To correct for the discrepancy specific to the smaller particles, Li et al. [8] hypothesized that the concentration at the membrane surface (ϕ_w) needs to be modified hence used an empirical coefficient (C_d) in Eq. (A.5), which was found to improve the agreement between experimental and model results particularly for higher CFVs. Secondly, the experimental data are consistently lower than that predicted by Eq. (A.7). Kromkamp et al. [25] also found that Eq. (A.7) overpredicted J_{crit} by fivefold, the discrepancy of which

was hypothesized as stemming from a difference in the channel length, L , values between model and experiments.

Figure A. 9. Comparison between model predictions and experimental data for the bidisperse mixture

The same models were applied to the bidisperse mixture investigated; the only difference in the application of the equations was in the ‘effective’ radius a value used, which depends on the particle volume fraction of each species at the membrane surface, as explained below. Krompkamp et al. [26] proposed three scenerios for the behavior of the binary mixture in the feed channel: (i) the shear-induced diffusivity of the smaller particles was not influenced by that of the larger particles; (ii) the shear-induced diffusivity of the smaller particles was influenced by that of the larger particles; and (iii) the larger particles segregated to the center of the channel such that the shear-induced diffusivity was similar to that of the monodisperse smaller particles. Both (i) and (ii) assumed that the volume ratios of the two particle species were similar in the bulk and at the membrane surface, whereas (iii) assumed that the larger particles were of lower

concentrations at the membrane surface than in the bulk. Krompkamp et al. [26] ascertained that (iii) agreed best with the experimental data for dilute suspensions with ϕ_b of 1.8×10^{-5} and high shear rates up to 5000 s^{-1} , which promotes the segregation of the larger particles away from the membrane surface. For the dilute particle concentration of 0.05 g/l and lower shear rate (i.e., maximum magnitude of 250 s^{-1}) used in this study, an arithmetic average was used for the a value (i.e., $a = 3.25 \text{ }\mu\text{m}$). Fig. A.9 compares the model predictions and experimental data for the bidisperse mixture, Eqs. A.4 and A.5 agreed very well with experimental data, which is surprising because the models were developed for monodisperse particle systems. This seems to imply that $\phi_b = \phi_w$, which indicates the lack of particle size segregation effects. However, Eq. A.7, which was developed for bidisperse suspensions, persisted in over-predicting the J_{crit} values, as per the monodisperse case (Fig. A.8), when $a = 3.25 \text{ }\mu\text{m}$, although the agreement with experimental results was good when $a = 1.4 \text{ }\mu\text{m}$ (i.e., when only the $3 \text{ }\mu\text{m}$ particles were at the membrane surface). This implies that Eq. A.7 is valid only based on the premise that the size segregation effects were perfect such that none of the larger particles were found at the membrane surface. Therefore, whereas Eqs. A.4 and A.5 suggest a lack of particle size segregation such that the characteristic a value is the arithmetic average of the two particle radii, Eq. A.7 suggests on the contrary that particle size segregation was so extensive that only the smaller particles were found at the membrane surface. In fact the DOTM images showed that indeed the $3 \text{ }\mu\text{m}$ particles tended to be dominant on the membrane surface (few large particles were observed) and this implies that Eq. A.7 holds more mechanistic understanding for bidisperse mixtures. This is because Eq. A.7 is an adaptation of the Shauly et al. model [24], which is a phenomenological model incorporating flow patterns and particle concentration distributions of polydisperse suspensions.

4. Conclusion

In this study, DOTM was used to understand the effects of bidispersity and spacer on critical flux values in microfiltration (MF) at various crossflow velocities (CFV). The particles investigated was polystyrene (also known as latex); the monodisperse particle had a particle diameter (d_p) of 3 μm , while the bidisperse mixture was an equal volume ratio of $d_p = 3 \mu\text{m}$ and 10 μm .

Four observations are worth highlighting. The results show that: (i) the combined effects of both bidispersity ($d_p = 3 \mu\text{m}$ and 10 μm) and spacer were the most beneficial in mitigating membrane-fouling in terms of the highest J_{crit} values, whereas the case of a monodisperse particle with $d_p = 3 \mu\text{m}$ in the absence of a spacer gave the lowest J_{crit} values; (ii) whereas bidispersity was more effective at enhancing J_{crit} at a lower CFV (which means a lower energy requirement), the presence of a spacer was more effective at a higher CFV which augmented the eddy formation effects; (iii) the enhancement induced by bidispersity was diminished at high CFV and, to a lesser degree, by the spacer; and (iv) comparisons between model predictions and experimental data reveal that shear-induced diffusion models based on monodisperse particles are deficient for bidisperse mixtures, due to the lack of consideration of particle size segregation effects unique to non-monodisperse systems like particle size segregation.

Regarding the impact of bidispersity, the presence of larger particles improved the J_{crit} values due to the associated higher shear-induced diffusivity. However, the beneficial effects are limited to lower CFV magnitudes, because both the Reynolds number and segregation effects dictate the diminished influence of the larger particles at higher CFVs.

With respect to spacer, the presence of a spacer on one hand enhanced the J_{crit} values for both monodisperse and bidisperse mixtures, but on the other hand reduced

the enhancement factor induced by bidispersity (i.e., the enhancement of J_{crit} value for the bidisperse mixture was lowered in the presence of a spacer). It should be noted that the shear-induced diffusion models are largely for laminar flows, so the local eddies induced by spacers are not well characterized by the mechanistic basis of these models.

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Nomenclature

a	Particle radius (m)
a'	Average Particle radius (m)
a_i	Particle radius of i (m)
C_d	Diffusivity Constant
D	Diffusivity (m^2/s)
J_{crit}	Critical Flux ($\text{l}/\text{m}^2/\text{h}$)
k	Dimensionless particle migration parameter for Eq. 6
L	Membrane Length (m)

Greek Symbols

γ_0	Shear rate at the membrane surface (s^{-1})
ϕ_b	Particle volume fraction in the bulk suspension (-)
ϕ_i	Bulk concentration of particle i
ϕ_w	Particle volume fraction at the the membrane surface (-)
λ	Dimensionless particle migration coefficient for Eq. 6

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