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Chemically Stabilized Oil-in-water Emulsion Separation Using a Custom Aquaporin-based Polyethersulfone (PES) Forward Osmosis Membrane System

AnnMarie Ricchino
University of Central Florida

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CHEMICALLY STABILIZED OIL-IN-WATER EMULSION SEPARATION USING A
CUSTOM AQUAPORIN-BASED PLOYETHERSULFONE (PES) FORWARD OSMOSIS
MEMBRANE SYSTEM

by

ANNMARIE LYNN RICCHINO
B.S. University of Central Florida, 2016

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Civil, Environmental, and Construction Engineering.
College of Engineering and Computer Science
University of Central Florida
Orlando, Florida

Spring Term
2020

Major Professor: Woo Hyoung Lee

ABSTRACT

Forward osmosis (FO) for wastewater treatment applications became popular around the 1960s due to the low energy consumption and relatively low associated operational costs. In recent decades, this technique has been proposed as a means of reclaiming freshwater from oily wastewater emulsions that can result from a number of activities; such as bilgewater discharge, runoff from industrial processing plants, and fracking. However, there are many variables associated with oil emulsion stability that can affect the FO process, such as pH, temperature and salinity. Additionally, membrane components and permeability play a large role in the efficiency of the FO process for waste removal, especially in regards to oil-in-water emulsions due to the small size of the oil particles. Nonetheless, the FO process has shown to be a great prospect for this type of wastewater treatment due to the efficiency of removing small organic particles and low cost associations.

The stability of oil-in-water emulsions is enhanced by the presence of surfactants in the water, thereby increasing difficulty of remediation. In this study, mineral oil and a standard bilge mix (SBM) were used as model oils for forward osmosis (FO) performance evaluation and two different high-concentration feed solutions (FS) were tested: 10,000 and 100,000 ppm oil/surfactant (9:1 Oil/Surfactant, wt %). *It was hypothesized that the charge-charge interactions between the surfactant portion of the micelles and the membrane would play an important role in membrane fouling.* Therefore, the effects of both an anionic surfactant (sodium dodecyl sulfate [SDS]) and a nonionic surfactant (Type 1) on fouling propensity as well as water and reverse salt flux (RSF) rates were evaluated. Water flux rates as high as 12.7 and 10.1 LMH ($L\,m^{-2}\,h^{-1}$) were achieved for emulsion solutions using SDS as the emulsifier and containing mineral oil and SBM at concentrations of 10,000 ppm (9:1, oil/SDS), respectively, over a one-hour run-time.

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Furthermore, a 98% flux recovery resulting from a three-hour physical membrane cleaning using deionized (DI) water was observed for solutions containing 10,000 ppm mineral oil/SDS when run under FO mode, and an 87% recovery when run under pressure-retarded osmosis (PRO) mode following a 10-hour run time. Salt (NaCl) addition in the FS demonstrated a destabilization effect of the emulsions, which led to increased water permeation across the membrane when the osmotic pressure gradient was restored. These combined qualities endorse potential use of this FO membrane system as a potential low-cost treatment technology for bilgewater.

ACKNOWLEDGMENTS

I am beyond grateful for having completed this thesis and thank all who supported me in accomplishing my research. Firstly, I would like to thank my graduate advisor, Dr. Woo Hyoung Lee for giving me this opportunity to grow as a researcher and expand my knowledge beyond basic environmental engineering practices. The experience that I have gained in his lab will serve as a guide for many years to come and I am beyond grateful for the guidance and mentorship that I received. I would also like to express my gratitude to the rest of my defense committee members, Dr. Andrew Randall and Dr. A H M Anwar Sadmani, for investing their time in my professional development as well as aiding in the achievement of this thesis.

Special thanks go out to Mrs. Jill Lloyd and Mrs. Kathryn Bylsma, who stimulated my interest in science and environmental practices at a young age, for which I will be forever grateful. Their passion for teaching and the environment inspired me to want to educate myself and others about the importance of the environment and what we can do to limit negative environmental impacts from humans. Above all, they inspired me to want to contribute and make a difference in the world.

My gratitude is also given to all of the members, past and present, of Dr. Lee's lab whose support and guidance helped lead the way in all of my research endeavors. In particular, working with Dr. Jae Hoon Hwang and Daniela Diaz enriched my research experiences here at UCF and compelled me to be the best that I can be through their everlasting support and encouragement.

Finally, I must express my very profound appreciation to my family and friends, inside and outside of the department for providing me with their unfailing support and continuous encouragement throughout my years of study, as this accomplishment would not have been possible without them. I'd like to thank my sisters, Michelle and Roselee for their love and

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LIST OF ABBREVIATIONS AND ACRONYMS

Cake enhanced concentration polarization	CECP
Confocal Laser Scanning Microscope	CLSM
Cross flow velocities	CFV
Dissolved air flotation	DAF
Draw solution	DS
External concentration polarization	ECP
Feed solution	FS
Forward osmosis	FO
Grams per meter square per hour; $G\ m^{-2}\ h^{-1}$	GMH
Internal concentration polarization	ICP
Liter per meter square per hour; $L\ m^{-2}\ h^{-1}$	LMH
Nanofiltration	NF
Oil-in-water emulsion	O/W
Parts per million	PPM
Polyacrilonitrile-thin film composite	PAN-TFC
Polydopamine	PDA
Polyethersulfone	PES
Pressure-retarded osmosis	PRO
Reverse osmosis	RO
Reverse salt flux	RSF
Scanning electron microscope	SEM
Sodium dodecyl sulfate	SDS
Standard bilge mix	SBM
Suspended solids	SS
Total acid number	TAN
Thin film composite	TFC
Total organic carbon	TOC
Ultrafiltration	UF
Weight percentage	wt %

Water-in-oil emulsion   W/O

CHAPTER ONE : INTRODUCTION

Oily wastewater from industry and domestic sewage is considered one of the main environmental pollutants worldwide, and is rapidly increasing with increased transportation and use of oil and gas drilling processes [1]. Specific sources of this oily waste include discharge of shipboard bilgewater, food and metal processing plants, as well as other various industrial sources, that contain oil concentrations upwards of 200,000 ppm [2]. Bilgewater is solely responsible for approximately 20%, several million gallons, of the total oil discharge into oceans annually [3]. Due to a recent increase in knowledge about the negative environmental impacts of oily wastewater discharge, it is now becoming strictly regulated by governments globally, with acceptable oil discharge concentrations from ships regulated at <15 ppm [4, 5]. These restrictions have therefore initiated a search for efficient and low-cost treatment options in order to comply.

Oil droplets in water exist in three forms and are classified based on particle size: free oil (>150 µm), dispersed (150 > droplet size >20 µm) and emulsified (< 20 µm) [2]. Free and dispersed oil can be easily removed using basic physical methods, such as skimming and oil-water separator (OWS), while chemically emulsified particles will remain in solution for extensive periods of time, depending on stability [6]. The difficulty in separating these emulsified particles is a result of their small size and resistance to coalesce, which is directly affected by the presence of surfactants in the water. The most common form of removal of wastewaters containing high concentrations of emulsified oil is by deep-well injection, however this method also removes large volumes of water that could otherwise be recycled and reused [7]. Moreover, a conventional treatment method involves the addition of chemicals for demulsification, though while effective, incurs high costs associated with chemical storage and application [2].

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Advanced membrane separation technologies such as nanofiltration (NF) and reverse osmosis (RO) have shown to be effective at producing high quality water from these oily wastes, though demonstrated a high fouling frequency of the membranes that cannot be easily reversed due to the tightly packed layer resulting from the hydraulic pressure, thereby leading to a high energy demand and cost associations for frequent extensive cleaning and membrane replacement [8, 9]. Conversely, forward osmosis (FO) systems have demonstrated completely reversible fouling of the membranes as well as a fouling behavior controllable by varying the cross flow velocity (CFV) of the system [10-12]. Additionally, the FO method relies on the natural osmotic pressure gradient as the driving force as opposed to the RO process, which requires the application of a hydraulic pressure that necessitates higher energy costs [13].

The objective of this study was to investigate the efficiency of an FO system utilizing an aquaporin-based polyethersulfone (PES) membrane on separating these chemically stabilized oil-in-water emulsions. The application of this method for bilgewater treatment, specifically, is investigated in this study using a standard oil mixture as a representative oil as well as oil and surfactant concentrations typically found in raw bilgewater [6]. This method of treatment is proposed as a potential shipboard and pier-side water treatment process capable of producing a water consistent with discharge regulations.
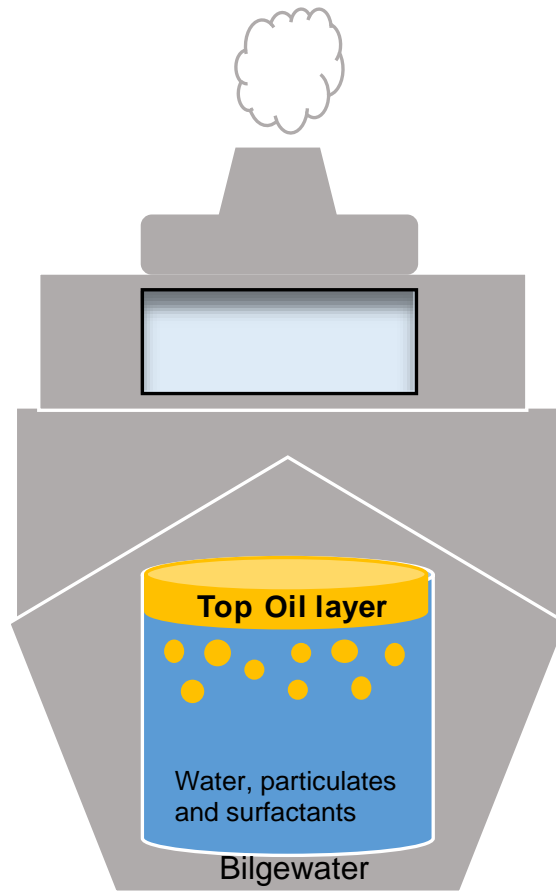
Figure 1-1: Schematic diagram demonstrating where bilgewater is found on a ship as well as constituents that are often present.

CHAPTER TWO : LITERATURE REVIEW

2.1 Oil-in-Water Emulsions (O/W)

The term emulsion refers to the colloidal dispersion of a liquid-in-liquid solution [14, 15]. This

can be especially observed in water solutions where a hydrophobic liquid is added. For instance,

the mixture of oil and water causes emulsions to form due to the extremely hydrophobic nature

of the oil. When discussing emulsions, the "continuous phase" term refers to the liquid to which

the other is added, and therefore presents the larger volume, and the "dispersed phase" refers to

the liquid being added. When water is added to a continuous oil phase, the formation of water-in-

oil emulsions (W/O) occurs, while the addition of oil to water causes oil-in-water emulsion

(O/W) formation [14]. The mixing speed, duration and presence of chemicals or suspended

solids (SS) in the continuous phase greatly affects emulsion formation and particle sizes. Oil

droplets in water exist in three forms and are classified based on particle size: free oil (>150 µm),

dispersed (150 > droplet size >20 µm) and emulsified (< 20 µm) [2]. The small size associated

with emulsified oil particles contributes to their stability and therefore, difficulty in separating

them from oily wastewater.

2.1.1 Surfactant-stabilized Emulsions

One of the main differences between the various oil droplet size classifications is their

kinetic stability, which determined the time they will remain in suspension as opposed to a

tendency towards coalescence. More stable droplets will remain in suspension for longer periods

of time while less stable will coalesce and float to the top due to their low density compared to

water. O/W emulsion stability can be affected by a number of water conditions including

temperature and pH, as well as the presence of surfactants, salinity or SS in the solution.

The presence of surfactants in solutions leads to emulsion formation by the adsorption of the surfactant onto the oil particle surface at the oil/water interface. When emulsions are stabilized by surfactants, they are termed chemically stabilized emulsions. The basic structure of these types of emulsions are demonstrated in Figure 2-1. As shown in the figure, the hydrophobic region (tail) of the surfactant is present inside the emulsified particles, while the hydrophilic head remains on the outside. Together, the head portions of the surfactant form an interfacial film that can be difficult to break down, resulting in stable emulsions [16, 17]. When using Figure 2-1 as a reference, it can be seen that the O/W emulsion on the right demonstrates a tightly packed interfacial film layer, where gaps can be seen in the interfacial layer of the left. These gaps are weaknesses in this boundary layer and contribute to lower kinetic stability compared to that of the particle on the right. The difference in the two layers can occur as a result of surfactant chemistry (ionic strength, chemical structure, etc.) as well as concentration of surfactant in solution. Generally, if surfactant is abundant, tighter, more stable emulsions with smaller particle sizes can be formed.
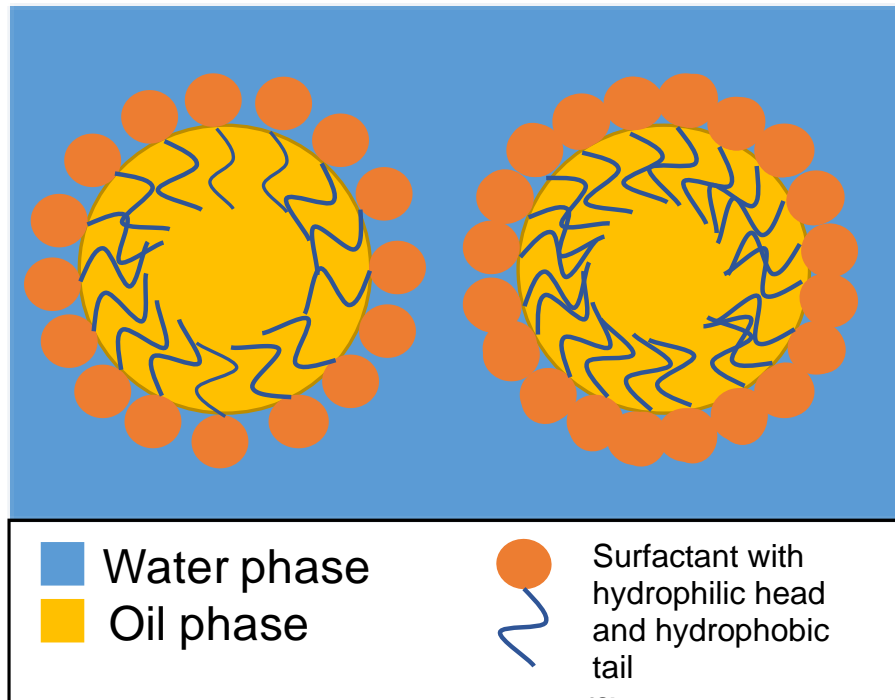
Figure 2-1: Oil-in-water emulsion structure caused by the presence of surfactants in the water.

2.2 Forward Osmosis (FO) to Reclaim Water from Emulsified Oily Wastewater

In recent years, increased knowledge and concern about the health of the environment and climate change has led to a shift in research that focuses on reducing negative environmental impacts from anthropogenic sources. In relation, oily wastewater from industry and domestic sewage is considered one of the main environmental pollutants worldwide, and is rapidly increasing with increased use of oil and gas drilling processes [1]. As the discharge of this oily wastewater is now strictly prohibited by governments, the most common form of removal is by deep-well injections due to their low costs [7]. However, this method removes large volumes of water that could otherwise be recycled and reused; therefore, researchers have started looking into alternative treatment options for water reclamation of these wastes.

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While conventional removal techniques such as skimming, dissolved air flotation (DAF) and flocculation are efficient at removing the free oil particles, they have no effect on emulsified oil [2]. The difficulty in separating emulsified oil lies in its small particle size [18, 19]. Advanced separation technologies such as ultrafiltration (UF) membranes with pore sizes between 0.001 and 0.1 µm have previously been used to separate relatively clean water from these emulsions, but were unable to provide a water quality adequate for reuse when used to treat wastewater with low oil concentrations (~100 ppm) [20, 21]. Furthermore, the nanofiltration (NF) method has shown to be effective at producing high quality water from these oily wastes, though showed a high fouling frequency of the membranes, thereby leading to high cost associations for frequent cleaning or replacement [8]. Conversely, the FO system has demonstrated completely reversible fouling of the membranes [11] as well as a fouling behavior controllable by the cross flow velocity (CFV) [10]. Osmosis refers to the net movement of water across a semipermeable membrane from an area of low solute concentration to an area of high solute concentration. For water treatment practices, reverse osmosis (RO) has been extensively used and is considered the more familiar process of the two. However, the RO process has high energy costs associated with it as it requires the application of a hydraulic pressure (e.g., 125 – 1,000 psi) to force the solution through the membrane, whereas the FO process relies on natural osmotic pressures [13]. Therefore, FO is increasingly becoming popular among water treatment officials.

2.2.1 Draw Solution Characteristics and General System Design

The main difference between FO and RO processes is that RO requires the application of an outside hydraulic pressure to force the solution through the membrane against the concentration gradient for water purification, while FO relies on natural osmotic pressure. The system is comprised of a flow/membrane cell, a feed solution (oily wastewater in this study) and

a single salt solution as a draw solution (DS). The concentrated draw solution flows on one side of the membrane while the feed solution flows counter-currently on the other. Furthermore, the FO system can be operated in two modes: pressure retarded osmosis (PRO) and FO [7]. The difference between these two modes is the direction in which the membrane faces. In PRO mode, the rejection layer of the membrane faces the draw solution, whereas in FO mode, the rejection layer would face the feed solution. It has been demonstrated that when the system is operated in PRO mode, the effects of internal concentration polarization (ICP) are less significant than those when operating under FO mode [7]. However, higher fouling tendencies resulting from operation under PRO mode generally hinder its application.

The intention of FO membrane separation is for only the water molecules from the feed solution to be pulled through the semipermeable membrane towards the draw solution due to the natural osmotic pressure gradient. The draw solution salt and concentration are selected based on their solubility and ability to generate high osmotic pressures. Common salts used are ammonium bicarbonate (NH_4HCO_3) [22] and sodium chloride ($NaCl$), though it depends on the application of the FO process. Concentrations of the single salt draw solution are also important, with better results being reported with higher concentrations (2.0 to 4.0 M) [22, 23]. However, one must take into consideration the dilution of the draw solution during experimentation. As water molecules are pulled through the membrane and into the draw solution, it may cause a dilution effect, leading to a lower osmotic pressure and therefore lower efficiency of the system [24]. For this reason, it is important to continuously monitor the salinity of the draw solution throughout experimentation and supplement salts when necessary. This can easily be done using a conductivity meter [25]. This phenomenon can also be avoided in bench-scale tests by using a

high starting volume of the draw solution and a low volume feed solution, resulting in decreased dilution effects by the addition of water from the feed solution.

2.2.2 Membrane Compatibility

Another important consideration in forward osmosis (FO) systems is the type of membrane and composition to be used. The permeability and pore size of the membrane is of vital importance, especially when applied to oil emulsions with a particle diameter of < 20 µm. Though there are many studies in literature that focus on membrane structure and design for optimal separation of emulsified oil [7, 18, 26, 27], this is still a relatively new research topic and none of them provide conclusive results. For example, the work of Duong and Chung (2014) showed that a polyacrilonitrile-thin film composite (PAN-TFC) membrane was successful at removing these small oil particles up to 99.88% from a 200,000 ppm solution over a 30 minute run-time, however the membranes demonstrated fouling quickly, which hindered the efficiency for long-term use [27]. There have also been studies that focus on developing systems with lower fouling tendencies of membranes by applying special coatings to the membranes or by increasing the cross-flow velocities (CFVs) of the system. For instance, it has been proven that the application of a polydopamine (PDA) coating to thin film composite membranes can decrease surface pore size as well as increase hydrophilicity of the membranes, leading to more efficient oil separation via FO [18]. Additionally, the effect of CFV on water flux demonstrated that higher oil concentrations in the feed solution require increased flow rate to increase water flux, which is most likely a result of decreased fouling on the membrane surface [27].

2.2.3 Flux Determinations and Efficiency of the System

The efficiency of the system can be determined by a number of fluxes; water flux (J_v) expressed in units of "LMH" (L m^{-2} h^{-1}), reverse salt flux (J_s) expressed as GMH (g m^{-2} h^{-1}), and oil flux (J_o) as gMH [27]. The equations used to determine these values are given as:

$$J_v = \frac{\Delta V}{A_{eff}\Delta t} \qquad \text{Eq. (1)}$$

$$\text{Eq. (2)}$$
$$J_s = \frac{\Delta(C_{t-f}V_{t-f})}{A_{eff}\Delta t}$$

$$\text{Eq. (3)}$$
$$J_o = \frac{\Delta(C_{t-d}V_{t-d})}{A_{eff}\Delta t}$$

where ΔV (L) is the change in volume, A_{eff} is the effective membrane surface area (m^2), and C_{t-f} and V_{t-f} are the salt concentration and volume of the feed solution (L) at the end of the FO tests [27]. Additional testing for efficiency includes using a total organic carbon (TOC) analyzer to ensure that no oil particles have passed through the membrane and into the draw solution during experimentation [27].

The overall objective of this study was to investigate the efficiency of a custom-made FO system

utilizing an aquaporin-based polyethersulfone (PES) membrane on separating chemically

stabilized oil-in-water emulsions. This was achieved by the following tasks:

I. **Compare FO system performance between mineral oil (as a control) and standard bilge**

mix (as a representative bilgewater) in the FS. Mineral oil was used as a control oil in this

experiment for a number of reasons. Firstly, the density of mineral oil is similar to that of

SBM, ~0.87g/mL. In addition, pure mineral oil does not have any additives that could affect

emulsion stability, whereas SBM does. The acidity of crude oils, a major component of

SBM, is an important consideration for their use, as acidic oils can cause problems with

corrosion and obstruction due to oil sludge buildup. Therefore, each oil is given a TAN, or

total acid number. The acidity, and therefore TAN, of an oil can be manipulated with the

addition of alkaline additives, though these additives have shown to increase emulsion

stability [28, 29]. Therefore, the use of both emulsified mineral oil and SBM feed solutions in

this system was important in that it provided insight into how emulsion stabilization affects

membrane performance as well as providing results more representative of those that could

be expected utilizing this treatment method for real bilgewater samples.

II. **Determine the effects of membrane orientation and surfactant chemistry on fouling**

propensity. The orientation in which an FO system is operated is always an important

consideration as the operation under different orientations will undoubtedly provide differing

water permeation rates as well as RSF. In order to determine the differences caused by

membrane orientation for this novel membrane system, the system was run under both FO

and PRO mode. Furthermore, surfactant chemistry and surface charge play a large role in

membrane fouling. Therefore, a nonionic and an anionic surfactant were used as the emulsifiers in this study to determine the effects of the charge-charge interactions between the interfacial boundary of surfactants on the oil droplet surface and the active layer of the membrane.

III. **Evaluate the effects of salt addition in the FS on water and RSF rates.** The presence of salt in solutions has demonstrated an emulsion destabilization affect when dosed at high concentrations [30]. This is important to consider for this study, as bilgewater contains NaCl in the form of seawater. Therefore, the effects of salt addition in the FS on membrane system performance were also evaluated to provide a more comprehensive analysis of membrane system performance and to aid in the proposal of this system as a potential pier-side bilgewater treatment process.

CHAPTER THREE : MATERIALS AND METHODS

3.1 Materials and Chemicals

A standard bilge mix (SBM) provided by the Naval Surface Warfare Center Carderock Division (NSWCCD) (West Bethesda, MD) was used for preparing the oil-in-water emulsion feed solutions (FS) imitating bilgewater, while mineral oil was used as a control. Two types of surfactants, sodium dodecyl sulfate (SDS) as an anionic surfactant and Type 1 as a nonionic surfactant, were used as the emulsifiers for the oil-in-water emulsion FS. The draw solutions (DS) were prepared using DI water and sodium chloride (NaCl) at concentrations of 2.0 and 5.0 M, 116.9 and 292.0 g/L, respectively. Nile red (Cat. No. 72485, Sigma-Aldrich, Milwaukee, WI) was used to stain mineral oil prior to oil particle size characterization while a cationic Methylene Blue (LOT 995195B, Fisher Scientific) solution made using a standard method (5540-C, Standard Methods 19th Edition, 1995) was used to stain anionic SDS.

3.2 FO Membrane System

A previously defined, custom-made FO system utilizing a novel PES membrane (Aquaporin-Sterlitech, Kent, WA) with an active surface area of 12.5 cm^2 was used for this study [25]. Briefly, the system consisted of a 0.5 L FS tank, 15 L DS tank, a peristaltic pump, and the custom FO cell (Figure 3-1). The cell was forged using ¾" plexiglass (ePlastics, San Diego, CA), with matching flow channels on either side of the membrane, and separated by a 5-mm thick rubber gasket (50A, Rubber-Cal, Santa Ana, CA). A 0.33 mm thick polypropylene permeable mesh (FM100, Diversified Biotech, Dedham) was also placed on the DS side in order to provide support for the membrane and to prevent rupture. The volume of the FO flow chamber was 3.75 cm^3 (12.5 cm^2 [A] × 0.3 cm [H]). The peristaltic pump (Masterflex L/S economy pump drive, Cole Parmer, Vernon Hills, IL) circulated the FS and DS in counter-current directions with the

same cross-flow velocity (CFV) of 5 cm s^{-1}. This CFV was previously determined to be sufficient in separating organic material using this particular membrane system, and was therefore used for all flux analyses in this study [12].
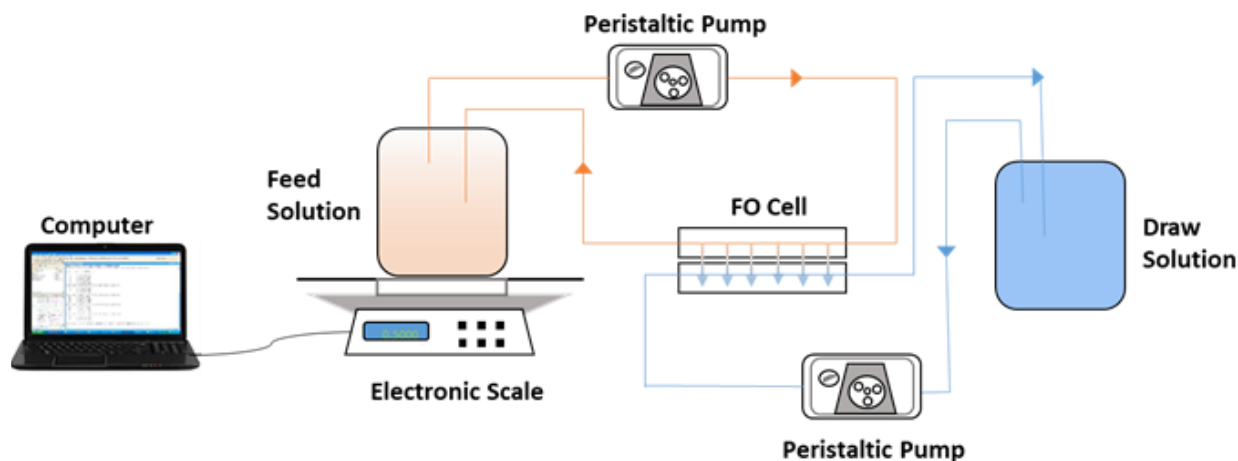
Figure 3-1: Schematic diagram of lab-scale FO system used for emulsified oil separation. Adapted from source [12].

To assess oil separation performance of the system, 10,000 and 100,000 ppm oil/surfactant (9:1, wt%) mixtures with initial volumes of 0.5 L were used as the FS along with a DS containing NaCl at concentrations of 2 M and 5 M. DS of 8 L were used for all water flux evaluation experiments to minimize dilution effects of the DS on FO performance. After addition of NaCl, the DS was manually mixed for one minute or until NaCl particles were no longer visible in solution. Conductivity of the DS was measured using a portable multimeter (HQ40d, Hach, Loveland, CO) before each test to ensure that it was of the desired concentration of NaCl. The high concentration FS were used to represent untreated bilgewater, which can contain total organic concentrations upwards of 100,000ppm [6]. All FS were under continuously stirred conditions (~ 200 rpm) to ensure homogeneity of the solution and to prevent coalescence during testing. Temperatures of FS and DS remained at 23 °C ± 0.2 °C for all experiments.

3.3 Emulsion Preparation and Characterization

To simulate oily wastewater, a method similar to that previously described by Han et al. (2014) was used in which oil and surfactant were mixed at a 9:1 (wt %) ratio with a high-speed blender. A characteristic preparation process involved first dissolving the surfactant in a predetermined amount of DI water dependent on the concentration being tested. Then, the representative oil was added at a concentration consistent with the respective oil/surfactant ratio, and the solution was mixed with the high-speed blender for three minutes to form the stable emulsions. Operation of the FO system was performed directly after mixing to ensure that no settling would occur.

Micrographs were taken immediately following mixing using a microscope (M83EZ-C50S, OMAX) integrated with a digital camera (A355OS, OMAX) at magnifications of both 100X and 400X. A minimum of six images were taken per sample in order to guarantee representative results. These images were later imported into an image analysis software (MIPAR, Worthington, OH) for oil particle size characterization. Mineral oil solutions using SDS as the emulsifier were also analyzed using Confocal Laser Scanning Microscopy (CLSM) to demonstrate micelle structure. Before CLSM analysis, mineral oil was dyed with 100 mg/L Nile Red and SDS was dyed with the standard Methylene Blue solution. CLSM analysis was performed within 1 hour of sample preparation using a Leica TCS SP8 (Leica Microsystems, Buffalo Grove, IL) with an argon laser operating at 496 and 633 nm excitation wavelengths. Each line of pixels in an image was scanned for both Methylene Blue and Nile Red in sequence in order to avoid cross-fluorescence effects. Emission was detected between 507 and 574 nm for the Nile Red, and between 665 and 715 nm for the Methylene Blue [31]. As Methylene Blue is a

cationic dye, it is unable to stain nonionic Type 1, therefore Type 1 solutions were not analyzed

using this method.
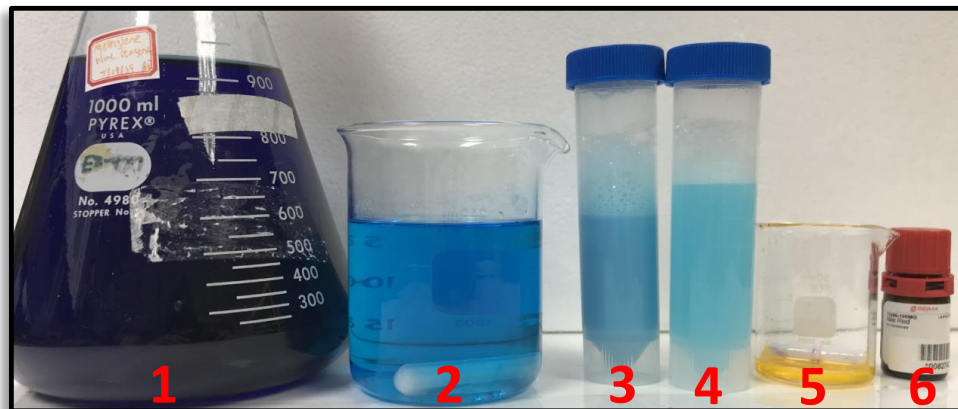
1	Standard Methylene Blue solution
2	10,000ppm SDS + 50% (v/v) Methylene Blue
3	100,000ppm homogeneous Mineral oil + SDS solution
4	10,000ppm homogeneous Mineral oil + SDS solution
5	Mineral oil dyed with Nile red at 100mg/L
6	Nile Red dye

Figure 3-2: Materials used for CLSM analysis.

3.4 FO Performance Analysis

Water permeability (J_w, L m^{-2} h^{-1}, abbreviated as LMH), reverse salt flux (J_s, g m^{-2} h^{-1}, abbreviated as GMH), and organics rejection (oil and surfactant) R_o (%) were determined using the previously described lab-scale FO setup. The weight change of the FS tank was continuously monitored using an electronic analytical balance (PCE-PCS 6 Counting Scale, PCE Americas, Inc., Jupiter, FL) that was connected to logging software (MATLAB) and used for the water permeation flux calculation over a pre-selected experiment duration. This flux (J_w) was calculated using the general equation:

$$J_w = \frac{\Delta V}{A_m \Delta t} \tag{1}$$

where ΔV (L) is the volume of water permeated from the FS to the DS, A_m is the effective membrane surface area (m^2) and Δt is the experiment duration time (hr).

Conductivity in the FS was monitored and then converted to the corresponding salt concentration (g L^{-1}) using the standard curve (Figure A2) to determine J_s values as

$$J_s = \frac{C_{f,t} V_{f,t} - C_{if,i} V_{f,i}}{A_m \Delta t} \tag{2}$$

where $C_{f,t}$ and $V_{f,t}$ are the final concentration and volume of the feed solution, and $C_{i,t}$ and $V_{i,t}$ are the initial concentration and volume of the feed solution, respectively.

The oil and surfactant concentration in the DS was measured using a total organic carbon (TOC) analyzer (TOC, Fusion UV/Persulfate Analyzer, Teledyne Tekmar) to calculate organics rejection by

$$R_o = (1 - \frac{C_p}{C_{f,i}}) \times 100\% \tag{3}$$

where $C_{f,i}$ is the initial concentration in the feed solution and C_p the concentration in the permeate.

3.5 Effects of Membrane Orientation on FO Performance

FO systems can be run under two different orientations due to the asymmetric structure of the membranes: 1) Forward osmosis, or FO mode, in which the active/selective layer of the membrane faces the feed solution (also referred to as AL-FS), and 2) Pressure retarded osmosis, PRO mode, in which the active/selective layer faces the draw solution (AL-DS). It is well-documented that operation of an osmosis system under PRO mode produces higher initial water fluxes than those produced when run under FO mode, however operation under FO mode often demonstrates a more stable flux depending on the concentration of foulant in the FS [7, 32-34]. The variance in flux when operated using the different orientations is a result of internal concentration polarization (ICP) that occurs due to the membrane structure; FO membranes are designed to have both an active layer and a porous/support layer. The active surface of the semi-permeable membrane is constructed to allow only water molecules to pass through, whereas the support layer is not designed to demonstrate this selective characteristic. In this study, the effects of operating under both modes on resulting water permeability flux values were evaluated.

Table 3-1: Summary of experimental parameters used in this study.

Feed Solution (FS) Concentration 9:1 Oil/Surfactant	Draw Solution (DS) Concentration	Cross-Flow Velocity (cm s^{-1})	Mode
DI water	2.0 M NaCl	5.0	FO, PRO
10,000ppm Mineral oil + SDS	2.0M NaCl	5.0	FO, PRO
100,000ppm Mineral oil + SDS	2.0 M NaCl	5.0	FO, PRO
10,000ppm Mineral oil + Type 1	2.0 M NaCl	5.0	FO
100,000ppm Mineral oil + Type 1	2.0 M NaCl	5.0	FO
10,000ppm SBM + SDS	2.0 M NaCl	5.0	FO
100,000ppm SBM + SDS	2.0 M NaCl	5.0	FO
10,000ppm SBM + Type 1	2.0 M NaCl	5.0	FO
100,000ppm SBM + Type 1	2.0 M NaCl	5.0	FO
100,000 ppm SBM + Type 1 + 1.4 M NaCl	2.0 M NaCl, 5.0 M NaCl	5.0	FO

CHAPTER FOUR : RESULTS AND DISCUSSION

4.1 Membrane Fouling Propensity and Orientation

Membrane components and fouling propensity play a large role in the efficiency of the FO process for waste removal, especially in regards to oil-in-water emulsions, due to the small size of the emulsified oil particles (< 20 µm). In fact, one of the main drawbacks to using membrane separation processes for contaminant separation is the fouling propensity of the membranes, which increases both energy and capital costs [35]. Though, as FO operational processes do not necessitate a hydraulic pressure force, cleaning protocols have shown to be effective at reducing fouling due to the less densely packed fouling layers that are often observed in other membrane filtration processes, such as RO. In order to demonstrate flux recovery due to cleaning, the water flux values of the solutions before and after a cleaning protocol were evaluated. The cleaning protocol used in this study consisted of a FS of DI water only, a 2 M NaCl DS, a CFV of 10 cm s^{-1}, and a three-hour operation time operated under both FO and PRO orientations . Fouling was not reversible for the 100,000 ppm mineral oil solution containing SDS or for either of those solutions containing Type 1 as the emulsifier. Conversely, a 98% flux recovery was observed for the 10,000 ppm mineral oil/SDS solution when operated under FO orientation, and an 87% flux recovery when operated under PRO (Figure 4-1). This is in agreement with the hypothesis that a lower flux recovery would result for the PRO orientation due to internal membrane fouling of the porous support layer, which is much more difficult to clean than the selective layer, where most of the oil foulant can be found on the surface (Figure 4-2 (a)) [36, 37].
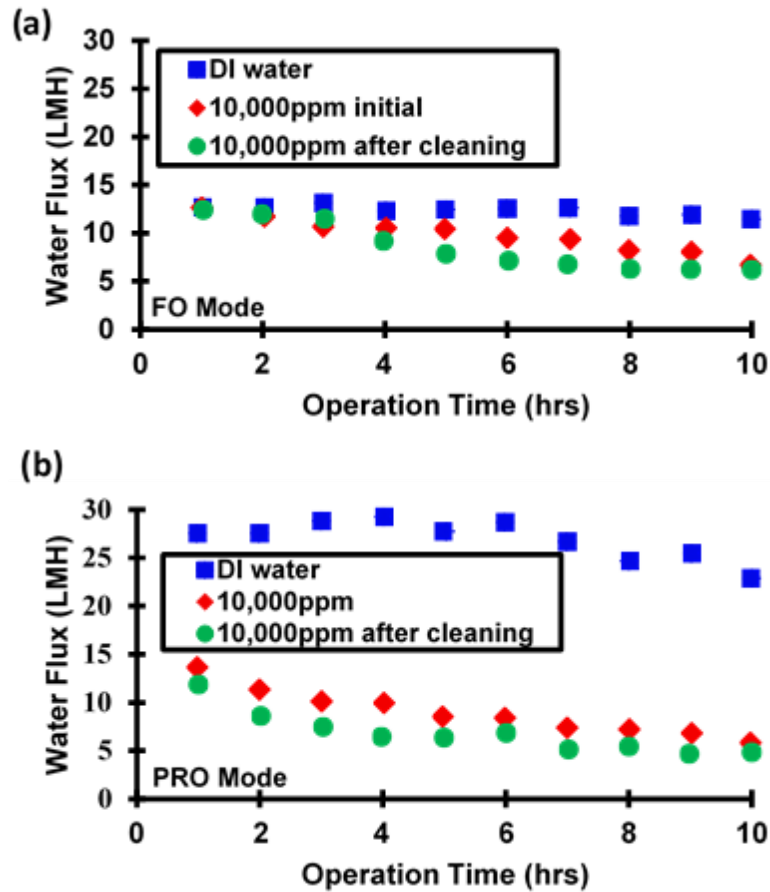
Figure 4-1: Water flux of 10,000 ppm mineral oil/SDS emulsions as a function of operation time before and after undergoing a cleaning protocol, operated under (a) FO mode and (b) PRO mode.

The differences in flux values for membranes before undergoing the cleaning protocol can be explained by ICP. When run under FO orientation, a dilutive ICP occurs in which NaCl ions must travel through the support layer to the underlying surface of the active surface layer, where the concentration becomes diluted by water permeating through the membrane. This is dissimilar than the ICP which occurs when run under PRO orientation, which is referred to as concentrative ICP. In concentrative ICP, NaCl ions are present on the active surface of the

semipermeable membrane, and have low rates of diffusion, thereby leading to a build-up of

contaminant in the underlying support layer due to the high osmotic drive force [33]. This is also

the reason that higher water permeation rates are demonstrated when using DI as the FS for both

FO and PRO orientations (Figure 4-1), as there is not a build-up of foulant that hinders transport

of water across the membrane. Based on these results and for the purpose of this study, all

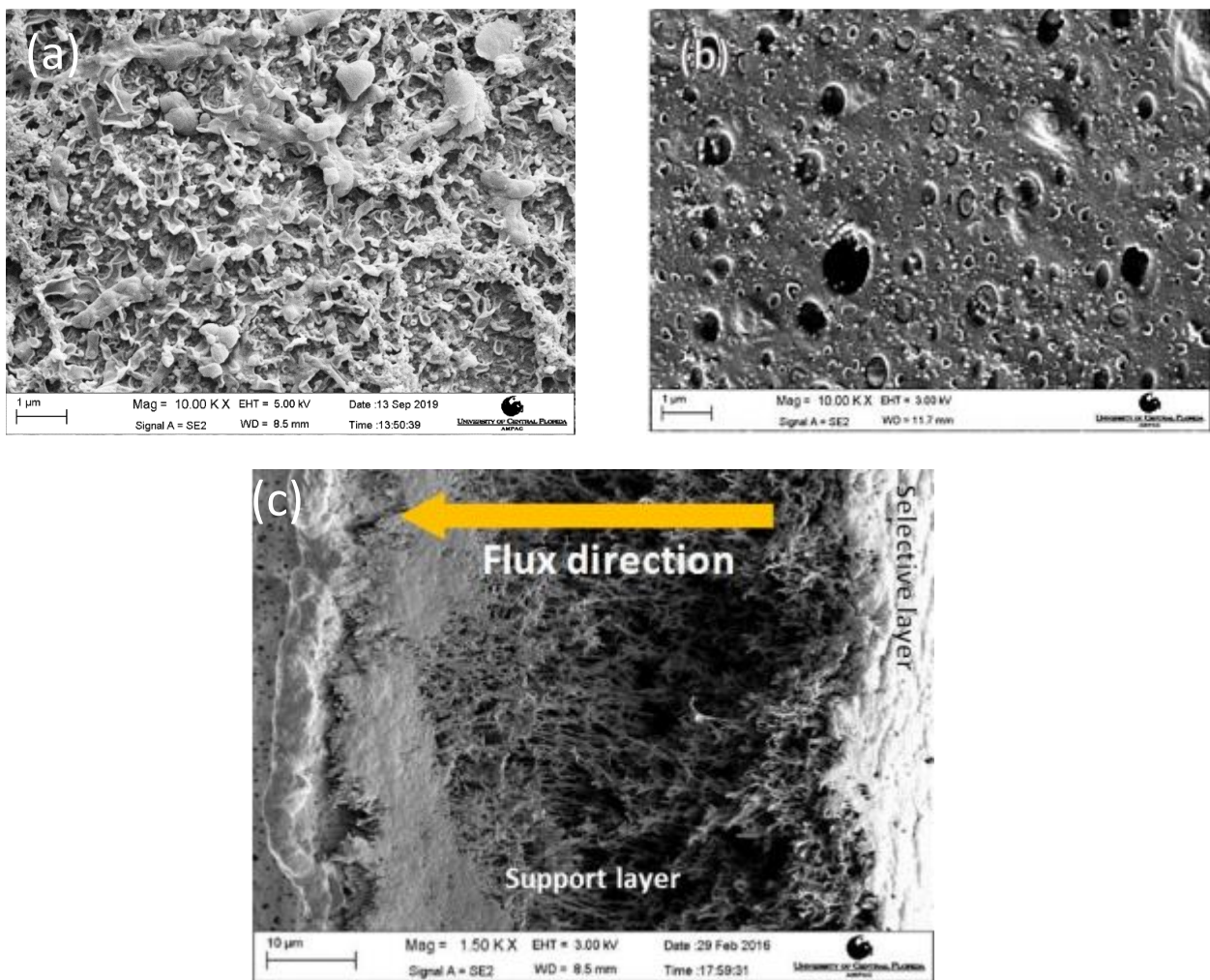further experiments involving flux analyses were operated under FO mode.

Figure 4-2: SEM images of the aquaporin membrane demonstrating (a) colloidal fouling resulting from a 14-hr run-time using 100,000 ppm mineral oil/SDS as the FS, (b) the fresh membrane active surface before any operation and (c) a cross-sectional image of the membrane clearly showing the differences in the selective and support layers [12].

4.2 Performance of FO System using Mineral Oil Emulsions

In this study, mineral oil was used as a model control oil due to the similarity in densities with SBM (~ 0.87 g/mL) [6]. Here, the effects of the various mineral oil/surfactant solution concentrations on flux are demonstrated. Two high concentration solutions were tested, 10,000 and 100,000 ppm using an oil/surfactant ratio of 9:1 (w:w), respectively.
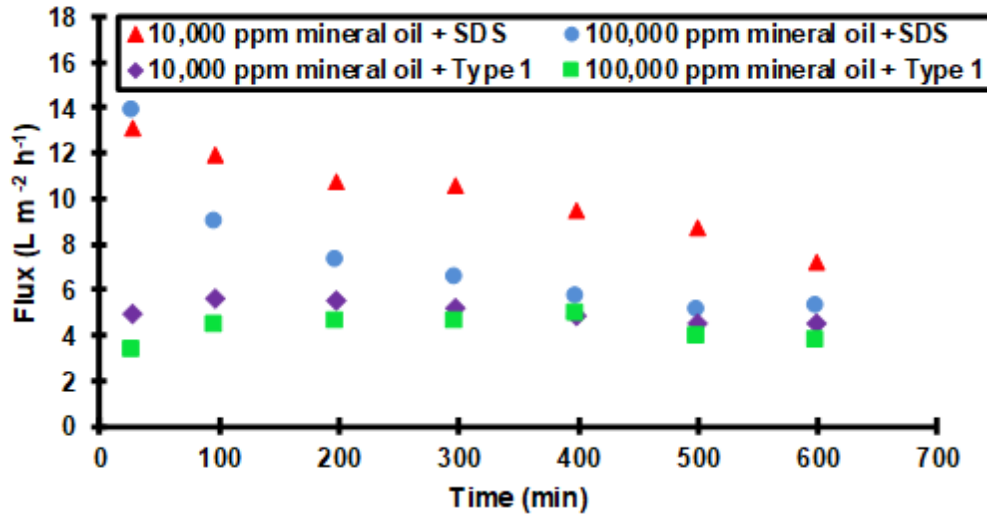

Figure 4-3: Average water fluxes for all FS containing mineral oil over a 600 minute run-time. The DS consisted of 2 M NaCl and CFV remained at 5 cm s^{-1}.

When the SDS surfactant was used as the emulsifier, the initial water fluxes (average fluxes over the first 30 minutes) were similar for both concentrations at 13.1 and 13.8 LMH for the 10,000 and 100,000 ppm solutions, respectively (Figure 4-3). The 10,000 ppm solution demonstrates a relatively small decline to 11.9 LMH in the first 100 minutes, and flux remains relatively constant until another decline is observed at 400 minutes, where the flux trend can then be seen steadily decreasing thereafter. A major decline in flux, from 13.8 to 8.1 LMH can be observed for the 100,000 ppm solution in the same 100-minute time frame and declines steadily over the rest of the operational period, though the decrease becomes less drastic with time. This

phenomenon has been observed in other studies [11] and is often attributed to the formation of a fouling layer that leads to cake-enhanced concentration polarization (CECP). CECP is caused by a subsequent decrease in osmotic pressure along with the accumulation of NaCl ions caused by a fouling layer at the membrane interface, which can also lead to a decline in transfer of NaCl ions to the bulk feed solution due to impediment by this fouling layer. A graphical depiction of this phenomenon in Lee et al. (2010) [35] demonstrates a buildup of NaCl ions caused by reverse diffusion in the internal support layer as well as beneath the organic foulant layer, thereby resulting in a decreased osmotic pressure gradient. The evidence of CECP in this study is demonstrated by the flux declines observed for oil-containing feed solutions over the initial hours of operation as well as the decrease in RSF compared to that of DI water (Figure 4-4, Table 2).

Emulsion solutions containing Type 1 and mineral oil demonstrate stable, but much lower water permeation rates compared to the SDS solutions over the entire 600-minute operational period (Figure 4-3). Additionally, in contrast to the SDS solutions, Type 1 solutions do not demonstrate a difference in flux that relates to concentration. Instead, both of these solutions sustain a relatively constant water flux rate of ~ 5.0 LMH. However, both the 10,000 ppm and the 100,000 ppm solutions demonstrate lower RSF rates than both DI water and the SDS emulsion solutions of the same respective concentrations, which may be a result of CECP caused by the rapid formation of an oil foulant layer (Table 4-1).

Table 4-1: Summary of water flux, reverse salt flux and oil rejection for all mineral oil solutions under FO mode.

Feed solution (FS)	Water Flux ($L\ m^{-2}\ h^{-1}$)	Reverse Salt Flux ($g\ m^{-2}\ h^{-1}$)	J_s/J_w (g/L)	Organics rejection (%)	Mode
DI water	12.68	7.35	0.58	-	FO
10,000ppm Mineral oil + SDS	12.66	3.08	0.24	>99.99	FO
100,000ppm Mineral oil + SDS	12.91	4.65	0.36	>99.99	FO
10,000ppm Mineral oil + Type 1	6.05	2.91	0.48	>99.99	FO
100,000ppm Mineral oil + Type 1	4.97	3.64	0.74	>99.99	FO

*Note: Water fluxes and RSF presented are taken as an average of initial fluxes for the first one hour of running time.

4.3 Long-term Operational Performance

The effects of long-term operational time (24 hours) on membrane performance were assessed and will be addressed in this section. Figure 4-4 demonstrates the water flux of all four different mineral oil/surfactant mixtures compared to a DI water only (as a control) over a 24-hour operational duration. As discussed in the preceding section, both mineral oil/SDS solutions demonstrated somewhat gradual declines in water permeation rates over the course of the 600-minute (10 hr) operational time. This is a similar trend to that which was observed during the longer duration tests. A decrease in flux for the 100,000 ppm mineral oil/SDS emulsion FS can be observed for the first nine hours before it reaches a steady flux averaging ~5.5 LMH for the rest of the 24-hr run-time. The decreasing flux trend for the 10,000 ppm solution differed in that it continued for 22 hours, where it then reached a similar flux rate to that of the 100,000 ppm solution and remained relatively constant thereafter. This lag time is not observed for Type 1 emulsion solutions before declines in water flux are observed, and instead they produce a stable, low water flux over the entire operational period. The charge-charge interactions between the

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surfactant portion of the micelles and the membrane are thought to be the main cause of this observation due to membrane fouling [37].
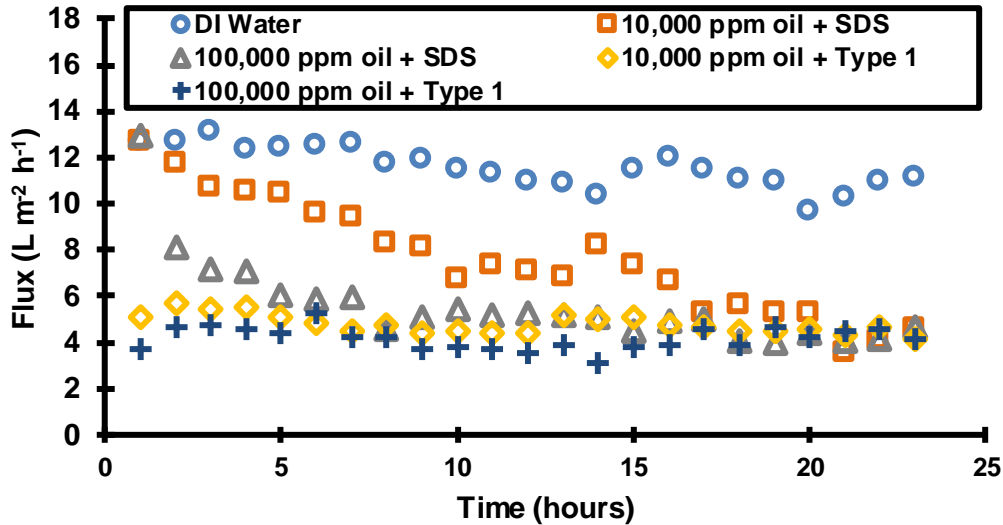

Figure 4-4: Water flux rates of all four mineral oil solutions compared to DI water when run over a 24-hour operational period.

The aquaporin-based PES membrane that was used in this study demonstrates a negative zeta potential on the active surface (-55 mV) similar to that of the anionic SDS surfactant (-60 mV) [38]. Type 1 is a nonionic surfactant that possesses a zeta potential of -28 mV. It is thought that the electrostatic repulsive forces acting on the anionic SDS emulsions were enough to reduce membrane fouling initially, though were not enough to compensate for these high concentrations when operated over a long term [39]. Furthermore, the absence of a lag time for water flux declines for Type 1 solutions is most likely explained by this as well, as there would be little to no repulsive interaction between the micelle surface and surface of the membrane, resulting in rapid formation of a fouling layer and an invariable flux.

4.4 Oil Droplet Analysis

Emulsified oil particles are those that have a diameter less than 20 µm, therefore, an oil droplet size analysis was performed for all four mineral oil solutions to ensure capability of this membrane for emulsion particle separation. The particle size distribution data show reputable emulsification for all four solutions, with all of them indicating a major peak particle diameter around 10 µm (Figure 4-5 (a) and (b)). The Type 1 solutions demonstrate a narrow particle size distribution with one major peak at 9.6 and 10.0 µm for the 10,000 ppm and 100,000 ppm concentrations, respectively. The 100,000 ppm solution also demonstrates a smaller peak at 14.0 µm, whereas the 10,000 ppm solution reveals a broader minor peak distribution in the range of 13.8 to 16.6 µm. Solutions where SDS was used as the emulsifier demonstrate an overall larger particle size distribution as compared to Type 1 solutions; a narrow peak can be observed at 10.1 µm and two smaller peaks at 14.0 and 17.0 µm thereafter for the 10,000 ppm concentration. Furthermore, the 100,000 ppm mineral oil/SDS solution displays a very wide major peak at 10.0 µm and another minor peak at 14.9 µm. The larger mean particle sizes of SDS solutions compared to nonionic surfactants has been previously reported , and is most likely attributed to the chemical composition of the surfactants [7]. Furthermore, the relatively wider distribution range of the SDS solutions is presumably a result of the inability of SDS to form an adequate interfacial skin layer on the oil particle surface at these high concentrations, thereby leading to a phase separation in droplets whereby they agglomerate and form slightly larger particles that have a tendency towards coalescence [31, 40, 41]. Further studies may incorporate a different oil/surfactant ratio that results in higher SDS concentrations in these types of solutions in order to determine if this is the case. Though, overall the Type 1 solutions do show to form more stable emulsions, as demonstrated by the narrow size distribution of both concentrations.
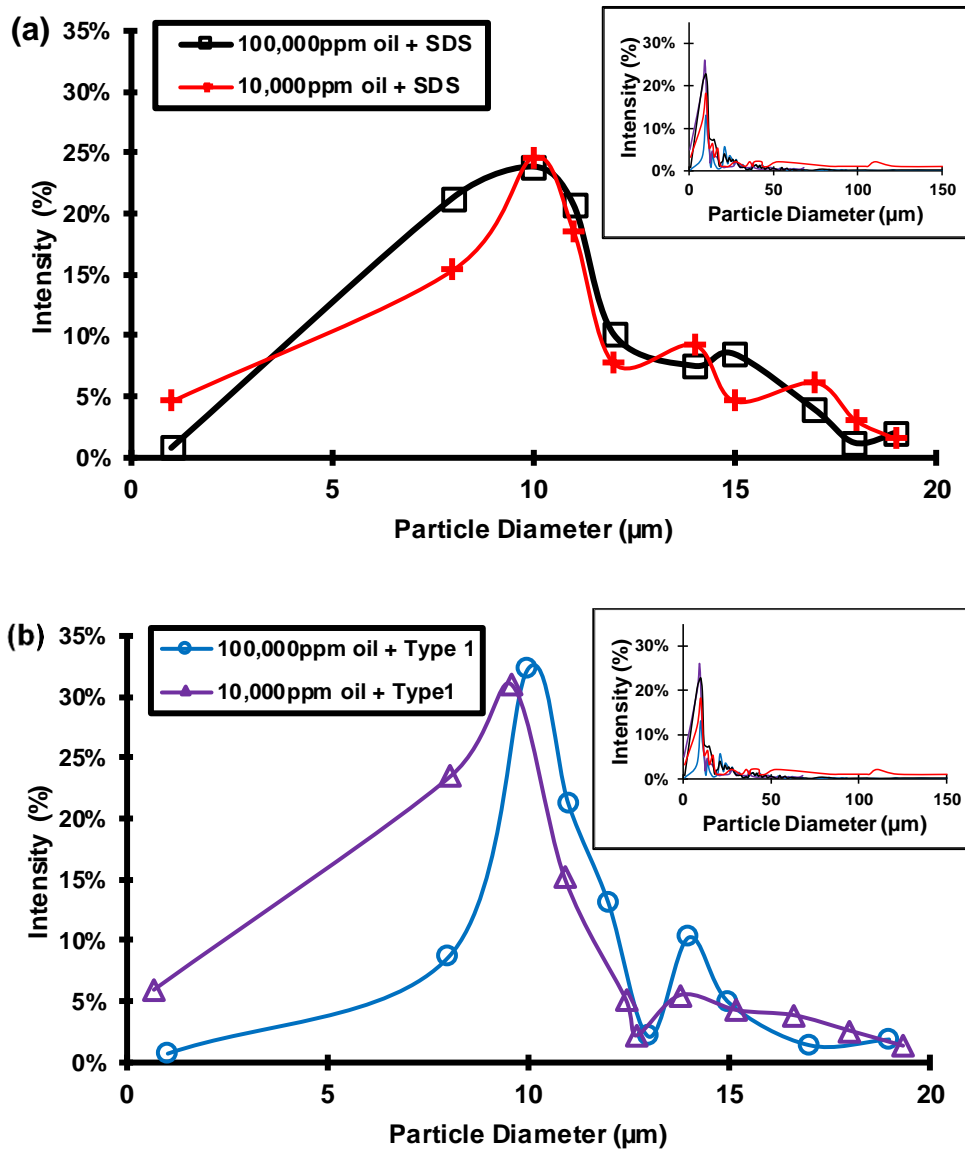
Figure 4-5: Particle size distributions of emulsified oil particles (below 20 µm) of 10,000 and 100,000 ppm mineral oil solutions stabilized by (a) SDS and, (b) Type 1. Insert: Generalized particle size distributions of these same solutions.

Additional CLSM analysis was performed for the 10,000 and 100,000 ppm mineral oil/SDS solutions to clearly demonstrate the structure and formation of the micelles. For the purpose of graphical depiction, a relatively larger oil particle size (~50µm) from the 10,000 ppm solution was chosen for ease of observation of the microstructure (Figure 4-6). As shown in

Figure 4-6, the surfactant (SDS) adsorbs to the oil particle surface, creating an interfacial skin

layer that is difficult to break down, thus contributing to emulsion stability. While particle size

and stability of emulsions is directly related to chemical composition and concentration of

surfactants and other molecules in the water, they all possess this same general structure whereby

the surfactant can be seen tightly bound on the outer surface of the oil droplet, generating the
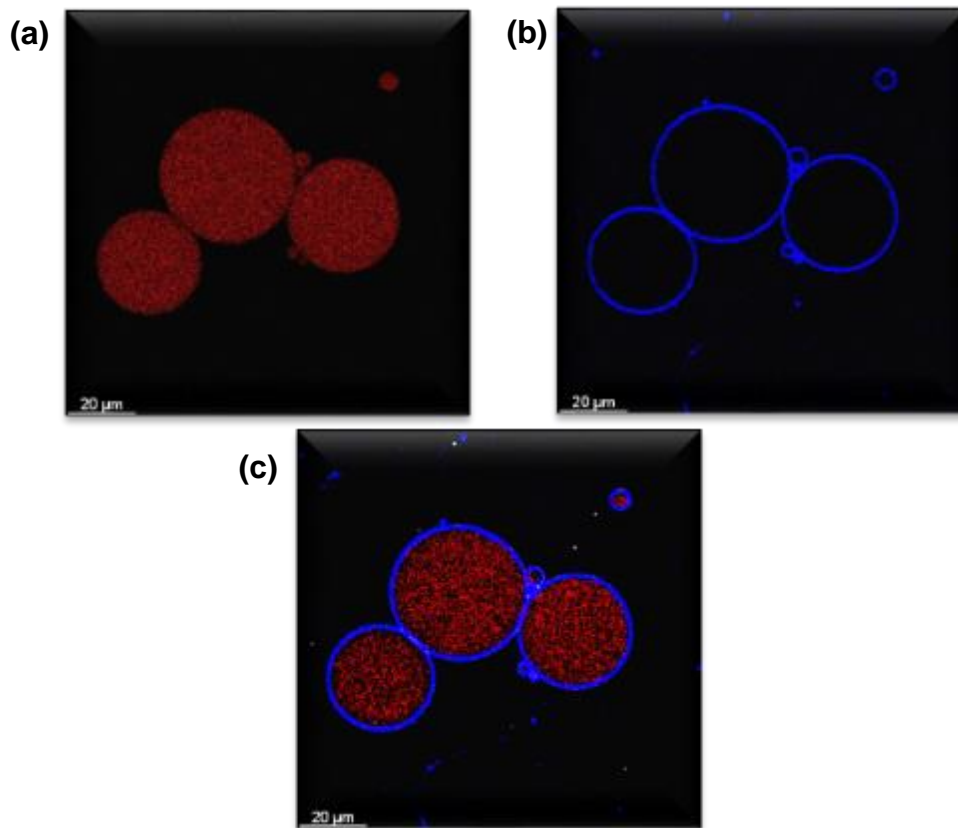
stable micelle structure shown.

Figure 4-6: Confocal fluorescence image of the 10,000 ppm mineral oil/SDS sample depicting (a) mineral oil dyed with Nile Red (b) SDS dyed with Methylene Blue and (c) the stable micelle produced by the interaction between the surfactant on the oil droplet surface.

4.5 Performance of FO System using SBM Emulsions

Table 4-2: Summary of water flux, reverse salt flux and oil rejection for all SBM solutions under FO mode.

Feed Solution (FS)	Water Flux $(L\ m^{-2}\ h^{-1})$	Reverse Salt Flux $(g\ m^{-2}\ h^{-1})$	J_s/J_w (g/L)	Organics rejection (%)	Mode
DI water	12.68	7.35	0.58	-	FO
10,000ppm SBM + SDS	10.11	6.48	0.64	>99.99	FO
100,000ppm SBM + SDS	9.01	4.02	0.45	>99.99	FO
10,000ppm SBM + Type 1	3.65	2.34	0.64	>99.99	FO
100,000ppm SBM + Type 1	3.90	5.59	1.43	>99.99	FO

*Note: Water and RSF presented are initial fluxes for the first one hour of running time.

As government regulations regarding acceptable oil discharge concentrations from ships have become more stringent, a low-cost, low energy and efficient separation method to treat this wastewater is required. Therefore, performance of the custom FO system utilizing the aquaporin-based membrane for oil separation using an oil composition more comparable to that which would be found in bilgewater, SBM, was analyzed. The same FS concentrations of oil/surfactant as in the mineral oil experiments were used, as well as the DS of 2 M NaCl and CFV of 5 cm s^{-1} (Table 3-1). Although these solutions were only run over a 400-minute operational period, as the difference in flux values is apparent very early on during operation (Figure 4-7).
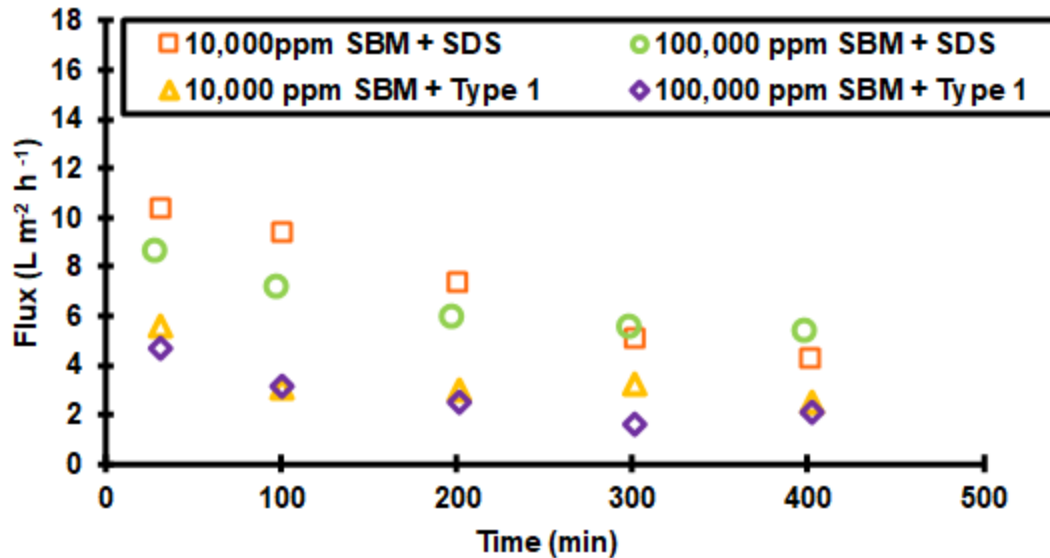
Figure 4-7: Average water fluxes for all FS containing SBM over a 400 minute run-time. The DS consisted of 2 M NaCl and CFV remained at 5 cm s^{-1}.

When surfactants are compared for the SBM solutions, lower water fluxes resulting from Type 1 emulsions compared to SDS emulsions are still noted, and remain similar with concentration. This further proves the hypothesis that the Type 1 emulsifier results in a quick-forming oil foulant layer composed of more stable emulsion particles, thus declining water permeation rates. Though, overall the membrane system demonstrated lower water flux rates for all SBM solutions compared to those containing mineral oil, leading to the conclusion that SBM alone may also hinder water permeation across the membrane (Figure 4-8). SBM has previously shown to produce stable emulsions without the addition of surfactants, while also demonstrating increased stability upon the addition of surfactants [6]. The increased stability of the emulsions, along with the high concentrations tested may be the cause of the low water permeation for these solutions, as it becomes more difficult to draw water through the small channels created by tightly packed particles in solution.
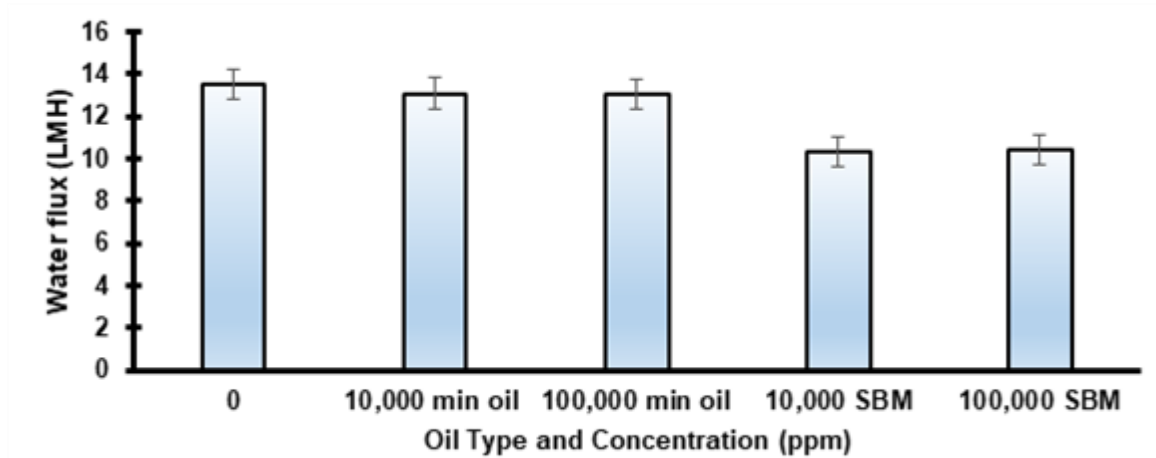
Figure 4-8: Initial water flux comparisons of SDS feed solutions containing mineral oil vs. SBM using a 2 M NaCl draw solution. Initial water flux refers to the first one hour of running time.

Though a trend is not observed for the RSF rates for the SBM emulsions, the J_s/J_w values of three out of four of the solutions are higher than that of pure DI water, denoting a higher transfer of NaCl ions across the membrane and into the bulk feed solution per volume of water permeated through the membrane (Table 4-2). The reason for this increased salt diffusivity is not known, though is most likely related to particle stabilization at the membrane surface. The surfactant portion of the micelles on the droplet surface create an impermeable layer that stops the particles from agglomerating, thus creating channels between the particles when placed in tightly-packed spaces [40]. This porosity of the foulant layer resulting from these interactions between particles provides the pathways by which salt ions can travel.

4.6 The Effect of NaCl in FS on FO Performance

The stability of the Type 1 emulsion particles contributed to a low water flux for all tested solutions, thereby necessitating destabilization of these emulsions to enhance flux. The addition of NaCl to oil emulsion solutions has demonstrated a demulsification effect which has been previously reported [6, 42]. Therefore, the effects of NaCl addition in the 100,000 ppm Type 1/SBM emulsion on water permeation over a 13-hour run time were tested. As the addition of salt into the FS would cause a reduction in the osmotic pressure gradient across the membrane, two different DS concentrations were used: both the original concentration of 2 M as well as a 5 M NaCl DS to restore this gradient and demonstrate more comparable flux results. As depicted in Figure 4-9 the flux rate using the 2 M DS demonstrates a similar trend to the SDS/mineral oil emulsions in the previous section, whereby they produce a rapid decline in the first few hours and a more stable, but much lower flux thereafter. In this case, this trend is most likely a result of a decreased osmotic pressure gradient due to RSF as opposed to CECP. Increasing the concentration of NaCl in the DS to 5 M resulted in a relatively high initial flux of 6.8 LMH over the first hour. However, a flux decrease to 4.9 LMH resulted after two hours and continued to decrease steadily thereafter, though still remaining above the 2 M DS curve over the entire operational period. Additionally, when compared to the water permeation rates of the same FS void of NaCl addition, the resulting water permeation rates are higher for the first 7 hours of operation time and remain almost equivalent thereafter. The given results demonstrate the potential for destabilization of oil emulsions in the presence of NaCl, thus resulting in higher water fluxes when the osmotic gradient is restored.
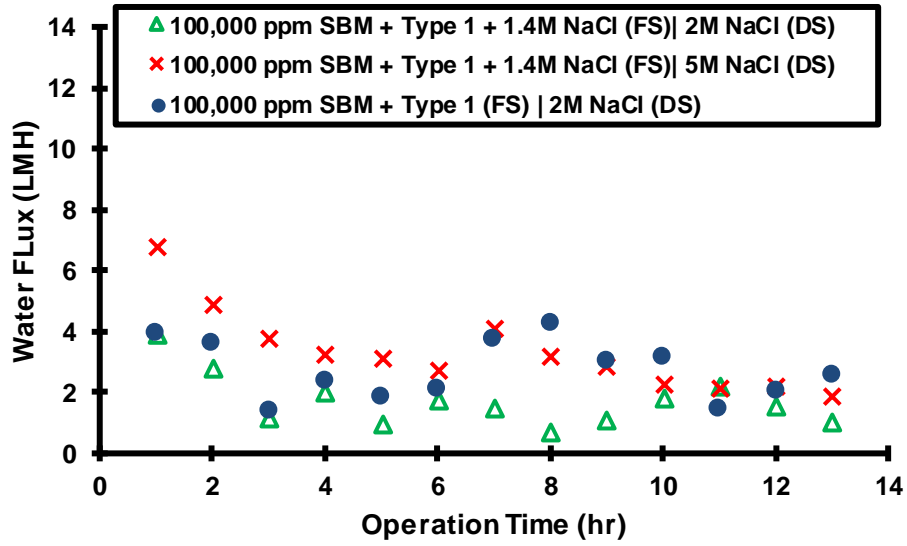
Figure 4-9: Water flux comparison of a FS containing 100,000 ppm SBM + Type1 + 1.4 M NaCl against a (△) 2 M and (✖) 5 M NaCl DS over a 13-hr run-time. (●) denotes the water flux of a 100,000 ppm SBM + Type 1 FS against a 2 M DS for comparison.

**CHAPTER FIVE : CONCLUSION AND PRACTICAL APPLICATION**

Increasing populations and industrialization result in large amounts of oily wastewater around the globe. While conventional removal techniques such as skimming, dissolved air flotation (DAF) and flocculation are efficient at removing free oil particles from these wastewaters, they have no effect on emulsified oil (i.e., O/W emulsions) [2]. As a result, these waters are being injected deep into the earth via deep well injections and are therefore permanently removed from the water cycle. However, the long-term impacts of these deep well injections are not yet known, which further warrants the search for an advanced technology to recycle these waters containing stable emulsified oil particles. Conventional water treatment technologies such as reverse osmosis (RO) and nanofiltration (NF) have high associated operational costs and have shown to have fouling problems resulting in inefficiency of the systems. Conversely, FO systems do not require high operating costs and have proven to be efficient at separating emulsified oil particles up to 99.99%. Additionally, fouling on these membranes is reversible, thereby saving on maintenance costs for membrane cleaning. There is still much research to be done before this system can be implemented on a large scale, though it shows great promise as an environmentally friendly and cost-effective means of water reclamation from emulsified oily wastewater.

This study carefully investigated the efficiency of a novel and commercially available FO membrane on high concentration, stabilized oil emulsion separation performance by water flux, reverse salt flux (RSF), and fouling propensity analyses. Utilizing feed solutions (FS) containing mineral oil and a standard bilge mix at high total organic concentrations, water fluxes as high as 13.8 and 10.1 LMH, respectively, were observed when operated under the FO mode. In addition, a flux recovery of 98 % was demonstrated as a result of undergoing a cleaning protocol for feed

solutions containing 10,000 ppm mineral oil/SDS, thus demonstrating a reversible fouling component associated with the membrane and operational parameters. Furthermore, oil/surfactant rejection was greater than 99.99% for all tests, demonstrating that this membrane is proficient in oil separation at concentrations up to 100,000 ppm. Though, further studies aimed at decreasing the effects of membrane fouling and internal/external concentration polarization on water permeation by means of membrane enhancement are still needed in order to optimize this process as a proposed pier-side treatment option for ship bilgewater using concentrated seawater as the DS.

Future work should focus on membrane enhancements and system operations in order to reduce fouling of the membrane. For example, increasing CFV has shown to decrease membrane fouling in FO systems, although this may result in erosion of the aquaporin-based active layer in this system. Furthermore, literature has demonstrated a low fouling propensity of FO membranes by the addition of an additional selective layer on the DS side that reduces salt transport and ICP as a direct result [32]. With further research efforts focused on these types of operational enhancements, FO systems have the potential to be implemented for oily wastewater treatment worldwide.
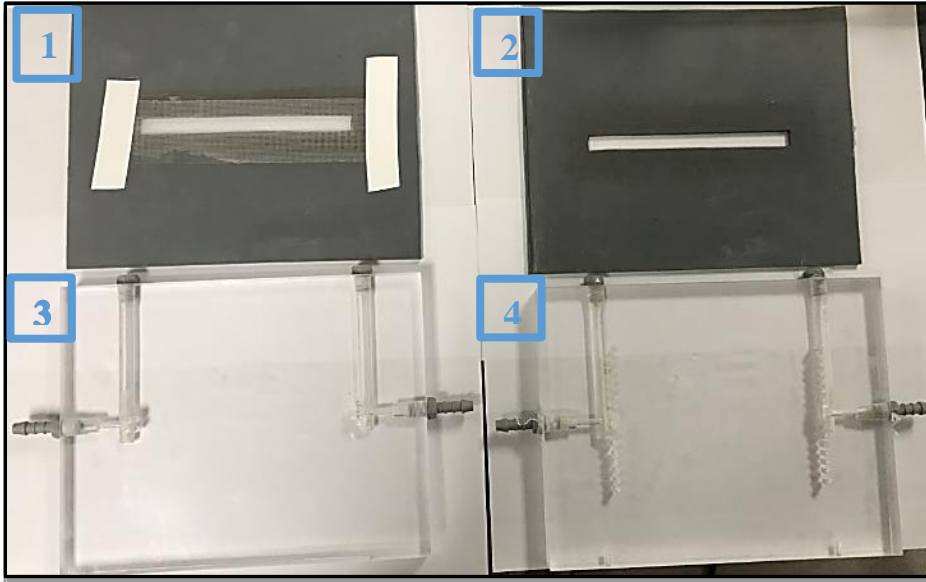
Materials needed to construct the FO cell

1-2. 5-mm thick rubber gaskets

3-4. Pre-cut plexiglass with custom flow channels
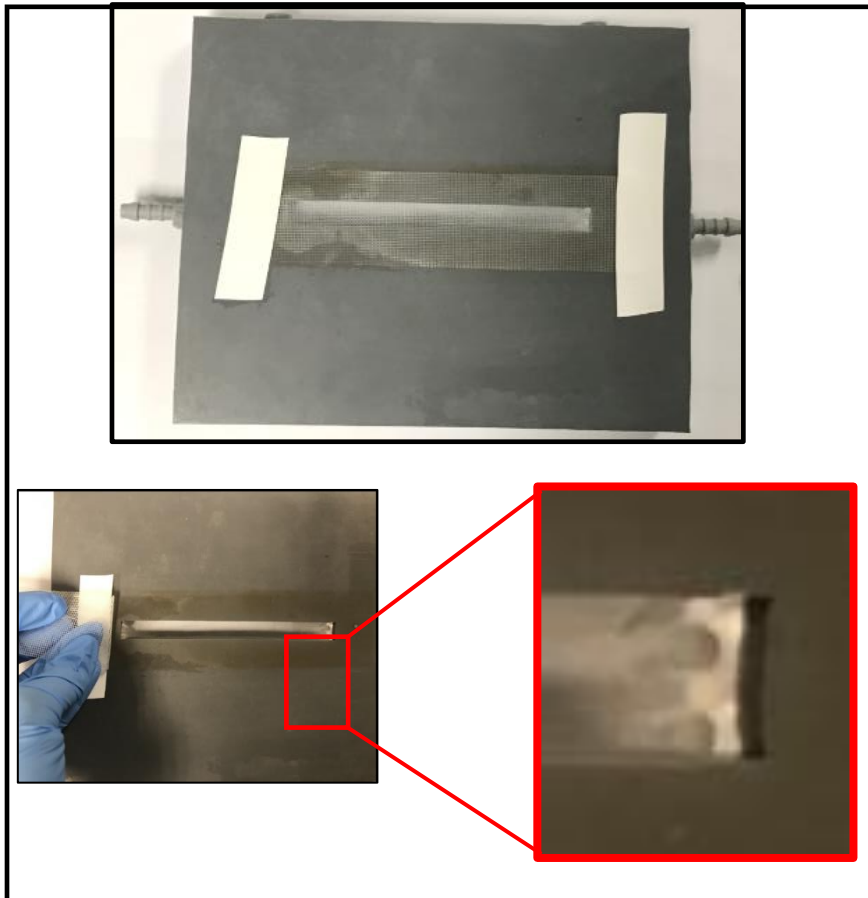

Step 1: Place the rubber gasket with the permeable mesh (**1**) on one of the pieces of plexiglass (**3** is shown).

Step 2: Lift the permeable mesh to ensure that the gasket is not obstructing the flow input and output channels. After ensuring that there is no obstruction, place the mesh back over the flow channel and confirm that it is secured to the gasket with waterproof tape.

Step 3: Place the remaining rubber gasket (**2**) on top, as shown. Confirm that the incisions in the rubber gaskets are aligned in order to ensure that they will not obstruct flow through the channels.
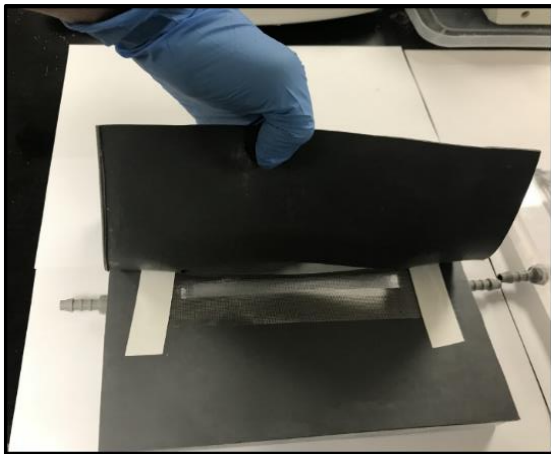
Step 4: While holding the top rubber gasket in place (**2**), carefully lift it on one side to create an opening wide enough to place the membrane inside (between gaskets **1** and **2** gaskets). It is important that the top rubber gasket does not move during this step in order to ensure that the flow channels will not be obstructed.

**Step 4:** While holding the top rubber gasket in place (**2**),
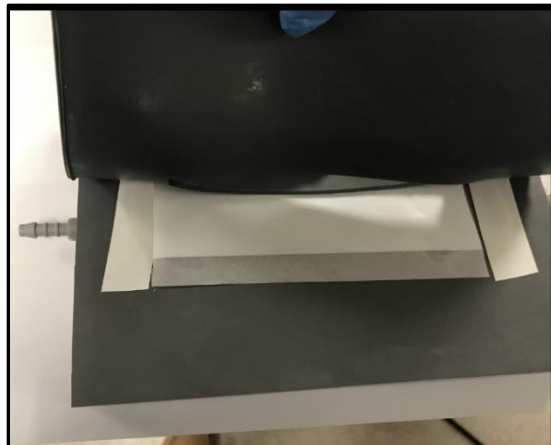
Step 5: Place membrane in between the two rubber gaskets, as shown. Make sure the active surface is facing the FS if the test is to be run under FO mode, and the DS if it is under PRO mode.
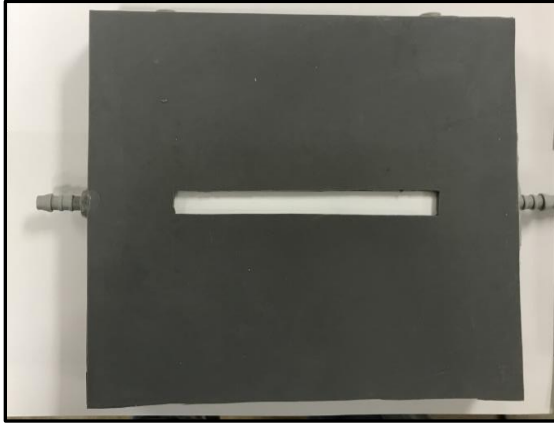
Step 6: Ensure that the membrane is covering the entire incision and that no gaps in coverage can be seen. If there is a section that the membrane is not covering, repeat step 5 until no openings can be seen.
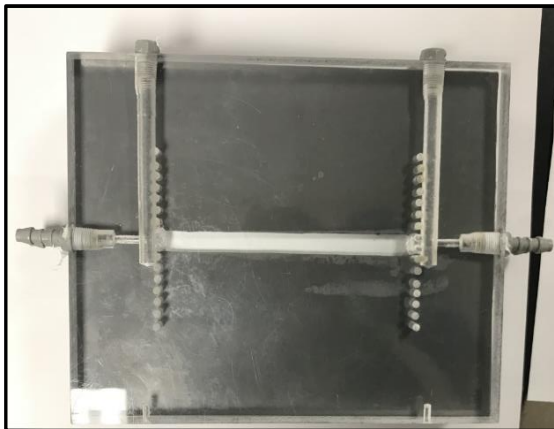
Step 7: Place the remaining piece of plexiglass (4) on top, making sure that the flow channel openings are pointed down and placed inside the incision of the rubber gasket. Again, it is important to ensure that the flow channel openings are not obstructed by the gasket.
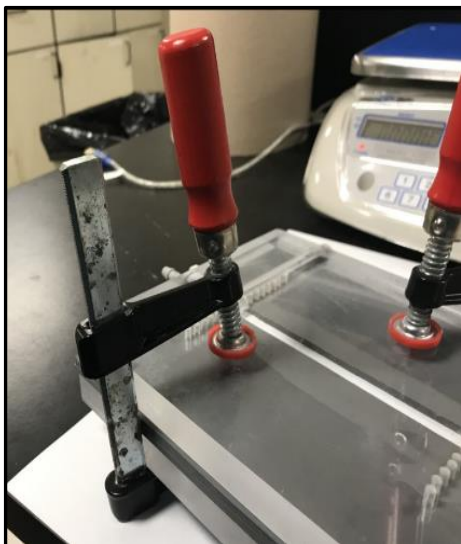
Step 8: Carefully place clamps around the constructed FO cell. Strategically place and tighten clamps ensuring that nothing moves during tightening. Tighten clamps as much as possible to ensure that water cannot escape the system. Usually ~ six clamps are needed for one FO cell.
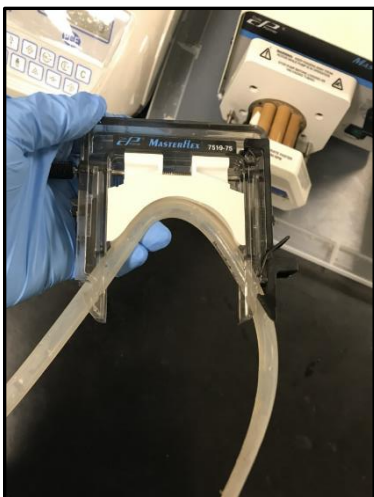
**Step 9:** Place FS tubing in the holder exactly as shown in the figure. If the tubing is not placed like this, it will not fit correctly into the pump and the flow will be compromised.
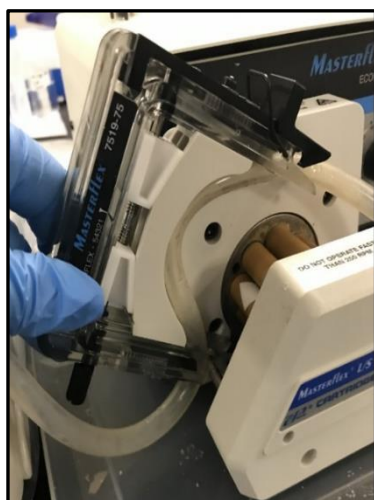
Step 10: The holder has two plastic hooks on the end that latch onto the pump. Place the holder onto the pump and ensure that the hooks are latched on. Push down in the small black tab on the right of the holder to clamp down.
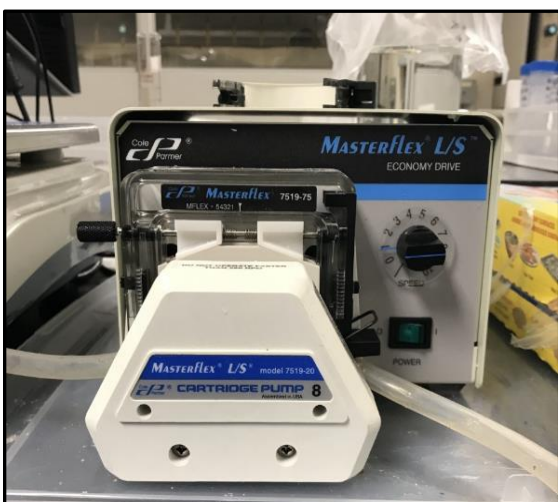
Step 11: This is how the tubing should look when attached to the pump. The small black tab should be on the right-hand-side as shown. Repeat steps 9 and 10 for the DS tubing. This time, place the holder directly in front of the one holding the FS (2 holders will fit in one pump). This is how identical CFVs are achieved.
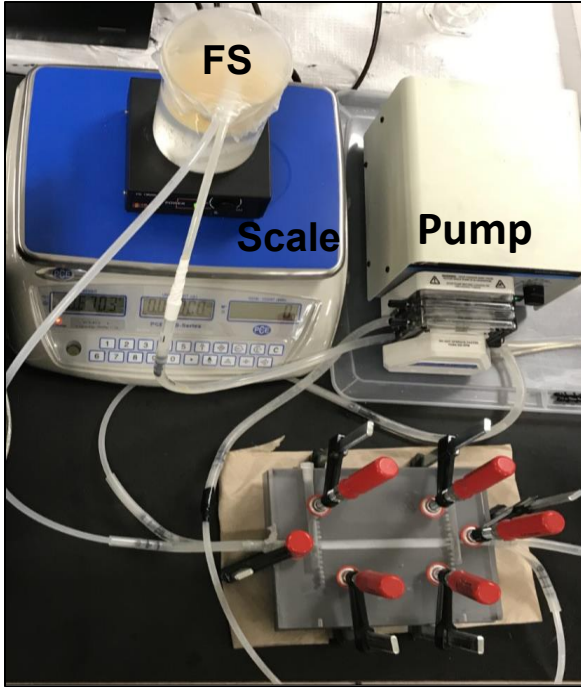
Step 12: This is an image of the completed FO setup. Before beginning any experiment, place a paper towel underneath the cell. This makes it easier to see any leakage in the system.

Figure A-1: Step-by-step instructions for how to set up the custom lab-scale FO system.
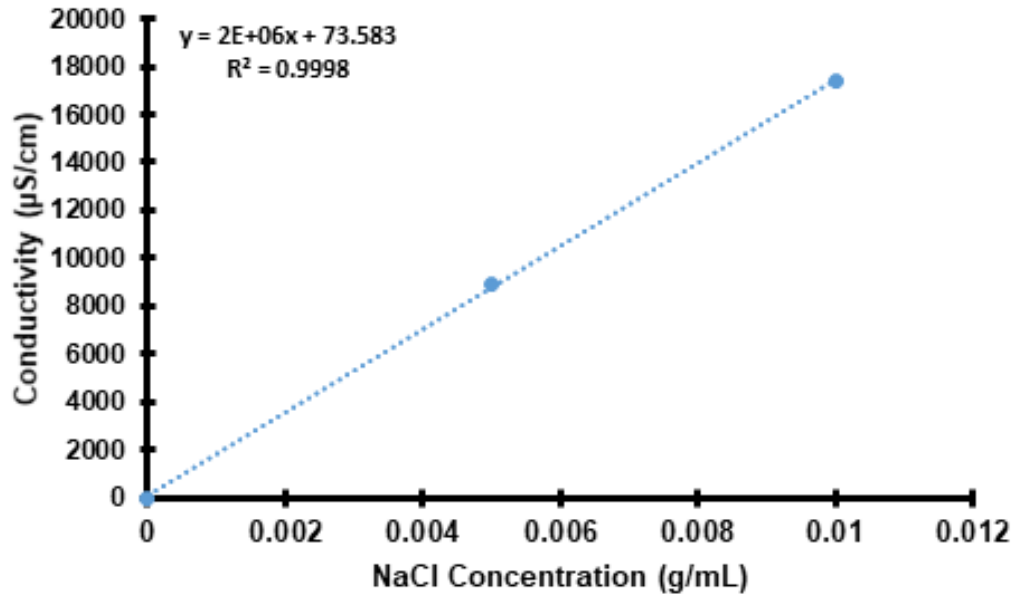
Figure A-2: **Calibration curve of conductivity vs. NaCl concentration used to determine J$_S$ values.**
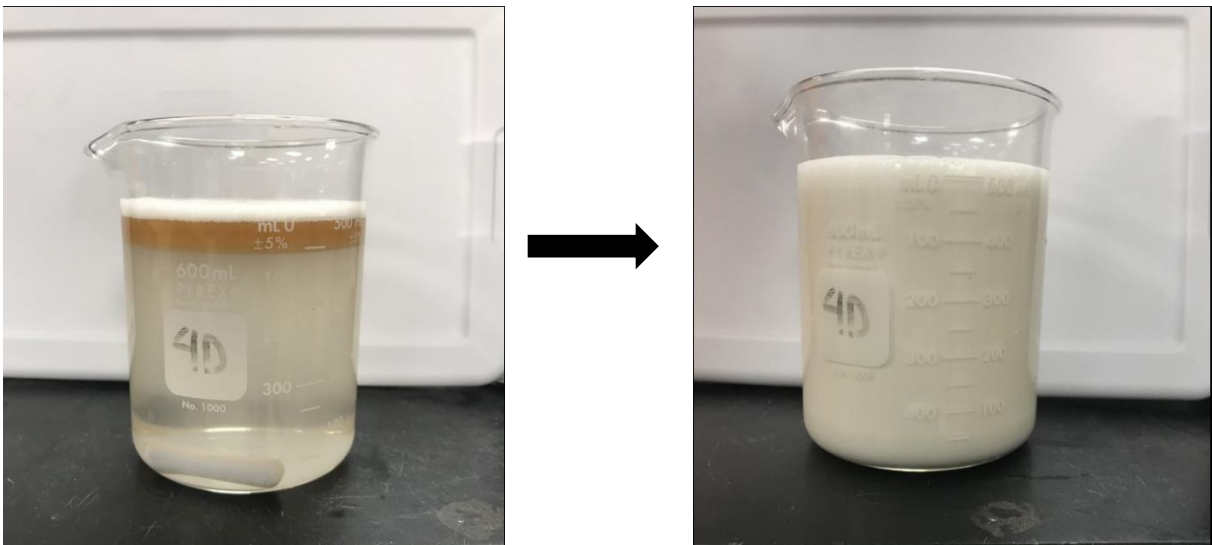

Figure A-3: FS containing 100,000 ppm Type 1 + SBM before (Left) and after homogenization (Right).

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