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Yin, Wenqiang

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**MEMBRANE FOULING IN SEAWATER REVERSE
OSMOSIS (SWRO) DESALINATION PROCESS**

**YIN WENQIANG
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
2019**

MEMBRANE FOULING IN SEAWATER REVERSE OSMOSIS (SWRO) DESALINATION PROCESS

YIN WENQIANG

School of Civil and Environmental Engineering

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

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.

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Authorship Attribution Statement

This thesis contains material from 2 paper(s) published in the following peer-reviewed journal(s) in which I am listed as an author.

Chapter 4 is published as Yin, W., Li, X., Suwarno, S. R., Cornelissen, E. R., & Chong, T. H. Fouling behavior of isolated dissolved organic fractions from seawater in reverse osmosis (RO) desalination process. *Water Research* **159**: 385-396 (2019). DOI: 10.1016/j.watres.2019.05.038.

The contributions of the co-authors are as follows:

- Prof. Chong and Dr. Suwarno provided the initial project direction.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Li and Prof. Cornelissen.
- Prof. Chong edited the final manuscript drafts.
- Dr. Suwarno provided guidance of fractionation process.
- I completed the fractionation process and organic fouling study with the analysis of membrane autopsy.
- FYP student Ang Wee Heng John and FYP student Tan Man Ping Joanne provided help in the experiment.
- All experiments and data analysis were conducted by me in the Singapore Membrane Technology Centre (SMTC).

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- Prof. Chong provided the initial project direction.
- Prof. Chong edited the final manuscript drafts.

- I prepared the manuscript drafts. The manuscript was revised by Dr. Ho and Prof. Cornelissen.
- I completed the fractionation process and biofouling study with analysis of the membrane autopsy.
- Ms. Tan Hwee Sin provided help in the experiment of AOC measurement.
- All experiments and data analysis were conducted by me in the Singapore Membrane Technology Centre (SMTC).

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LIST OF SYMBOLS

A	Membrane area
CP	Concentration polarization
C_b	Salt concentration in bulk
C_p	Salt concentration in permeate
C_m	Salt concentration near membrane surface
e	Electron charge
I	Membrane fouling potential
J_v	Permeate flux
k	Boltzmann's constant
k_m	Mass-transfer coefficient
$N_{initial}$	Initial cell count
N_{final}	Final cell count
$N_{negative}$	Cell count in negative control
n_i	The number of ions
R_m	Membrane resistance
R_f	Foulant hydraulic resistance
t	Filtration time
T	Absolute temperature
V	Permeate volume
z_i	The valence of ions
μ	Viscosity
θ	Contact angle
γ^{LW}	Lifshitz-van der Waals component
γ^+	Electron acceptor
γ^-	Electron donor
$\mathcal{E}_0$	Dielectric permittivity of the fluid
$\mathcal{E}_r$	Dielectric permittivity of the water
ζ_m	Surface potential of membrane
ζ_c	Surface potential of colloids

List of symbols

κ	Inverse Debye screening length
$\Delta\pi_m$	Osmosis pressure difference between feed and permeate
ΔP	Pressure drop
ΔG^{TOT}	Total interaction energy
ΔG^{LW}	Lifshitz-van der Waals interaction
ΔG^{EL}	Electrostatic double layer interaction
ΔG^{AB}	Lewis acid-base interaction

LIST OF ABBREVIATIONS

AB	Acid-base
AFM	Atomic Force Microscopy
AOC	Assimilable Organic Carbon
AOM	Algal Organic Matter
BP	Biopolymers
BSA	Bovine Serum Albumin
BOM	Biodegradable Organic Matters
BDOC	Biodegradable Dissolved Organic Carbon
BECP	Biofilm-enhance Concentration Polarization
CP	Concentration Polarization
CEOP	Cake Enhance Osmotic Pressure
DI	Deionized
DBP	Disinfection By-product
DLVO	Derjaguin-Landau-Verwey-Overbeek
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
ED	Electrodialysis
EDL	Electrical Double Layer
EPS	Extracellular Polymeric Substances
FA	Fulvic Acids
F.BP	Fraction of Biopolymers
F.HS&BB	Fraction of Humic Substances and Building Blocks
F.LMW	Fraction of Low Molecular Weight
FEEM	Fluorescence Excitation Emission Matrix
HA	Humic acids
HS&BB	Humic Substances and Building Blocks
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
LC-OCD	Liquid Chromatography with Organic Carbon Detection
LMW	Low Molecular Weight
LW	Lifshitz-van der Waals

List of abbreviations

MD	Membrane Distillation
MF	Microfiltration
MFI	Modified Fouling Index
MW	Molecular Weight
MWCO	Molecular Weight Cut Off
NF	Nanofiltration
NOM	Natural Organic Matters
PA	Polyamides
POM	Particulate Organic Matter
RO	Reverse Osmosis
SA	Sodium Alginate
SMP	soluble microbial products
SPE	Solid-Phase Extraction
SWRO	Seawater Reverse Osmosis
TDS	Total Dissolved Solid
TEP	Transparent Exopolymers
TOC	Total Organic Carbon
TMP	Trans-membrane Pressure
UF	Ultrafiltration
VDW	Van Der Waals
XDLVO	Extended Derjaguin-Landau-Verwey-Overbeek

SUMMARY

Seawater reverse osmosis (SWRO) desalination technology is an important technology for providing potable water for industries and human daily life due to its lower-energy consumption compared to thermal based desalination technology. However, membrane fouling is still a persistent problem in SWRO desalination plants. Organic fouling and biofouling, in particular the interplay between them, are the challenges that require attention.

In the first part of my study, the focus was on organic fouling in SWRO desalination process. Classifying organics in seawater will provide an in-depth understanding of the important fraction on SWRO organic fouling. The dissolved organic matter (DOM) in seawater was fractionated and concentrated by a membrane-based technique into three major fractions according to their molecular weight (MW) as defined in the liquid chromatography with organic carbon detection (LC-OCD) method, namely the fraction of biopolymer (F.BP, MW > 1000 Da), fraction of humic substance with building block (F.HS&BB, MW 350 – 1000 Da), and fraction of low molecular weight compounds (F.LMW, MW < 350 Da). An overall recovery of >80% of the organics in seawater was attained. Compared with model foulants such as sodium alginate (SA), bovine serum albumin (BSA), and humic acid (HA), all isolated organic fractions showed lower fluorescence intensities, and had lower fouling potentials than common model foulants used in SWRO fouling studies, thus the model foulants were not good representatives of the natural organics in seawater. In addition, results from atomic force microscopy (AFM) and extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory showed that initial fouling (i.e., foulant-membrane interaction) was the main driver in SWRO organic fouling with F.BP as the major contributor followed by F.LMW. In addition, divalent ions were found to enhance the RO fouling by increasing the adhesion and cohesion forces between foulant-membrane and foulant-foulant.

In second part of my study, the focus was on biofouling and the interplay between organic fouling and biofouling in SWRO desalination process by using the isolated

Summary

dissolved organic fractions. From the assimilable organic carbon (AOC) results, the AOC/DOC ratio was in the order of F.LMW (~35%) > F.BP (~19%) > F.HS&BB (~8%); AOC/DOC of seawater was ~20%; organic compositions of seawater were BP ~6%, HS&BB ~52% and LMW ~42%; thus LMW accounted for >70% of AOC in seawater. Their impact on SWRO biofouling in term of flux decline rate was in the order of F.LMW (~30%) > F.BP (~20%) > F.HS&BB (<10%). Despite being the major organic compound in seawater, HS&BB showed marginal effect on biofouling. The role of indigenous BP was less critical owing to its relatively low concentration. LMW, which was the major AOC contributor, played a significant role in biofouling by promoting microbial growth that contributed to the build-up of soluble microbial products and exopolymeric substances (i.e., in particular BP). Therefore, seawater pretreatment shall focus on the removal of AOC (i.e., LMW) rather than the removal of biopolymer.

In third part of my study, the focus was on the LMW removal by using low-pressure NF pretreatment process and the subsequent impact on SWRO fouling. Three different membranes were evaluated: NF270 was a commercial membrane based on polyamide thin film composite with negatively charged surface, NF1 and NF2 were glutaraldehyde cross-linked layer-by-layer polyelectrolyte membranes with positively charged surface (i.e., NF2 contained more polyelectrolyte layers than NF1). The organic/inorganic rejection of NF membranes followed the order of NF2 > NF1 > NF270 while pure water permeability (PWP) was in the order of NF1 > NF270 > NF2. Meanwhile the degree of RO fouling in term of flux decline and foulant amount was in the order of NF270 > NF1 > NF2. In addition, the results suggested that NF membrane can be optimized to achieve excellent removal of LMW, but a balance between permeability, rejection and fouling shall be considered when selecting the membrane for seawater pretreatment. For instance, NF2 membrane with the lowest permeability (~1.9 LMH/bar) was less competitive even though it showed the lowest SWRO fouling (i.e., flux decline ~3%) as compared to NF 1 (permeability of 4.0 LMH/bar, flux decline ~10%).

CHAPTER 1 Introduction

1.1 Background

Water scarcity is one of the main challenges facing many countries around the world. The demand of fresh water is increasing at an accelerating rate with the increase in population and expansion of industrial and agricultural activities. To date, fresh water sources such as surface water and groundwater are over-exploited. To overcome the water scarcity, seawater desalination by reverse osmosis (RO) technology is regarded as the most widely used technique to convert seawater to high quality potable water. For example, more than 60% desalination capacity in the world is based on membrane technology (Abdelkareem, Assad et al. 2018).

RO membrane-based desalination technology is popular as compared to thermal-based desalination technology due to its lower energy consumption of about $\sim 3 - 4 \text{ kWh/m}^3$ (Amy, Ghaffour et al. 2017), which is 8 times lower than thermal-based method (i.e., $\sim 35 \text{ kWh/m}^3$) (Fritzmman, Löwenberg et al. 2007, Amy, Ghaffour et al. 2017). About 85% of total energy consumed by SWRO desalination process is associated with the RO process while other units such as intake, pre-treatment, and post-treatment etc. consume about 15% of total energy. However, membrane fouling is still the bottleneck of RO technology that results in a decrease in productivity and quality, an increase in energy demand and chemical usage for membrane cleaning, thus an increase in the operation & maintenance cost. Therefore, an understanding of the mechanisms of RO fouling is critical to mitigate fouling process in order to prolong the membrane lifetime and reduce the energy demand and chemical usage.

1.2 Problem statement

Organic fouling caused by dissolved organic matter (DOM) in seawater can significantly increase the operational costs and energy consumption during SWRO, but organic fouling in SWRO process has not been fully understood (Ang, Tiraferri et al. 2011). Based on operational definition, for example retention by a filter (i.e. 0.45 μm), the retained organic matters are referred to as particulate organic matter (POM) while the fraction that passed through the filter are referred to as DOM. Typically, the pretreatment process in SWRO demonstrated high efficiency in the removal of POM but not DOM (Jamaly, Darwish et al. 2014), thus the focus of this study is on the impacts of DOM on RO fouling.

The DOM in seawater is a complex mixture of polysaccharides, proteins, amino acids, carbohydrates, and humics with wide ranges of molecular weights (MWs), functional groups, structural features, and in complex matrix. Most oceanic DOM is of marine origin, where the DOM accumulation at surface ocean (<1000 m) is closely associated with biological production from biotic and abiotic removal processes while the DOM at the deep ocean (>1000 m) is refractory (Ogawa and Tanoue 2003, Carlson and Hansell 2015). In comparison to surface water and wastewater, the DOM concentration in seawater is relatively low (typically < 5 mg-C/L), but severe RO fouling can still be easily triggered by these organics. In general, the studies on RO organic fouling by natural seawater have focused more on the assessment of the pretreatment process and the overall RO membrane performance, the fundamentals of fouling are less discussed (Jeong, Naidu et al. 2016). In other studies, various model foulants such as alginic acid or sodium alginate (SA), bovine serum albumin (BSA), and humic acid (HA) have been employed as the surrogates of DOM to understand their effects on RO membrane fouling (Ham, Kim et al. 2013, Park, Jeong et al. 2019). The relevant investigations clearly demonstrate different fouling tendencies with different groups of organic

components in membrane process (Miyoshi, Hayashi et al. 2016, Ding, Yamamura et al. 2018), e.g., fouling rate has strong correlation ($R = 0.74$) with TEP concentration but neglectable correlation ($R = -0.09$) with TOC concentration in Miyoshi's study. The fouling layers formed on the membrane surface appear to lead to different resistances from the complex organic solutions (Ao, Liu et al. 2016), e.g., the irreversible fouling resistance of organic solution with high turbidity is 5 times higher than that with low turbidity. In addition, the co-existence of various types of model foulants also resulted in a synergistic fouling effect on membranes (Li and Elimelech 2006, Ang and Elimelech 2007), e.g., flux decline caused by the combined fouling (i.e., alginate + BSA) was increased ~20% compared with single organic fouling (i.e., BSA) without divalent ions in Ang's study. However, the straightforward analysis with model foulants in RO fouling seems insufficient to represent the actual fouling phenomena in SWRO, which may lead to missing or inaccurate results. The extraction of natural organics from real seawater sources becomes the main challenge for the investigation of RO fouling using real seawater.

In addition to organic fouling, the biofilm formation on RO membrane is closely associated with the organics in RO feed water. For instance, bacteria consume feed organics to proliferate; extracellular polymeric substances (EPS) are secreted by bacteria cells; soluble microbial products (SMP) are released from metabolism of feed organics (i.e., utilization associated products, UAP) as well as during cell lysis and hydrolysis of EPS (i.e., biomass associated products, BAP); a portion of the SMP could be easily utilized by bacteria (Kunacheva and Stuckey 2014). In general, DOM can be further categorized into biopolymer (BP, molecular weight, MW >1000 Da), humic substances and building blocks (HS&BB, MW 350 – 1000 Da), and low molecular weight compounds (LMW, MW < 350 Da) by liquid chromatography-organic carbon detection (LC-OCD) analysis (Huber, Balz et al. 2011). Biodegradable organic matter

or biodegradable organic carbon (BOM or BDOC) is defined as the DOM that can be mineralized by heterotrophic microorganisms; while assimilable organic carbon (AOC) is that portion of BDOC that can be readily utilized to support microbial growth (Wang, Tao et al. 2014). Over the years, AOC measurement has been widely applied as a surrogate to predict the biofouling potential of various types of water in various water treatment processes (Water and Solutions 2005, Weinrich, LeChevallier et al. 2016, Terry and Summers 2018) including seawater applications (Water and Solutions 2005, Jeong et al. 2013b, Jeong et al. 2016, Weinrich et al. 2016). The AOC measurement method based on colony forming units was first proposed by van der Kooij (van der Kooij et al. 1982), and later improved by other researchers to enhance its accuracy and efficiency (van der Kooij, Visser et al. 1982, Kaplan, Bott et al. 1993, LeChevallier, Shaw et al. 1993). In addition, flow cytometry instrument has been used to measure the AOC rapidly by counting the true volumetric cells in the solution (Hammes and Egli 2005, Elhadidy, Van Dyke et al. 2016). Assessing the AOC concentration in SWRO process is critical as it has been reported that after pretreatment processes of raw seawater, the RO feed water still have high biofouling potential as surviving cells can proliferate by consuming the residual biodegradable substances (Matin, Khan et al. 2011). For example, organic molecules (MW < 1000 Da) leaking from coagulation or ultrafiltration (UF) membrane showed a strong relationship with AOC content (Hem and Efraimson 2001). In addition, it was reported that an increase in AOC level was associated with excessive chemical dosing (i.e., chlorination and then de-chlorination with sodium bisulfite), fluctuation of water quality (i.e., algal blooms) and organic oxidation (Weinrich, LeChevallier et al. 2016). Furthermore, study also showed that NF permeate with very low DOM amount could still be preferentially consumed by the bacteria (Meylan, Hammes et al. 2007).

Despite large amount of research work on organic fouling and biofouling in RO process, the role of organic compositions in seawater on SWRO biofouling remains unclear, more importantly the interplay between them. Most of previous studies used nutrient broth or acetate as the nutrient source to simulate biofouling (Chong, Wong et al. 2008, Siddiqui, Rzechowicz et al. 2015, Harlev, Bogler et al. 2019), which was not good representative of organics in seawater and might not capture the actual mechanism in SWRO biofouling. Since biopolymers and humic substances were identified as the major organic foulant on RO membrane, it was recommended to reduce the high molecular weight organic content in RO feed to reduce the flux decline (Deng, Ngo et al. 2019). On the other hand, it was established that the removal of AOC, i.e., reduction in biofouling potential, was accompanied by the removal of LMW in seawater pretreated with biofilter and MBR (Naidu, Jeong et al. 2013, Jeong, Rice et al. 2014), nevertheless the studies did not perform SWRO biofouling test to confirm its actual impact. Therefore, this warrants further investigation on the effect of different dissolved organic compounds on biofouling in SWRO process in order to formulate an effective pretreatment that target at the culprit for fouling mitigation.

1.3 Objectives and scope

The objectives and scope of this study are shown and summarized as follow:

Chapter 1

- 1) Literature review on fouling in seawater reverse osmosis (SWRO) desalination process (**Chapter 2**).
- 2) Materials and methods (**Chapter 3**).
- 3) Investigate the SWRO organic fouling mechanism by using isolated organic fractions from seawater. First, DOM in seawater was fractionated into different fractions based on their MWs, i.e., biopolymer (BP, molecular weight, MW >1000 Da), humic substances and building blocks (HS&BB, MW 350 – 1000 Da), and low molecular weight compounds (LMW, MW < 350 Da), using a membrane-based technique, i.e., a combination of ultrafiltration (UF) and nanofiltration (NF) membranes. Then, the isolated organic fractions and their corresponding model foulants were characterized by size exclusion liquid chromatography and fluorescence spectroscopy, and were compared in term of their fouling potentials. In addition, SWRO fouling of the isolated organic

fractions were performed. The interaction force and interfacial energy were examined by AFM force-distance measurement and XDLVO theory (**Chapter 4**).

- 4) Investigate the biofouling potential of the isolated organic fractions from seawater and to evaluate their impacts on membrane biofouling in SWRO desalination process. First, three major dissolved organic fractions were isolated from seawater by the fractionation method developed in Chapter 4. Second, the biofouling potential of the isolated dissolved organic fractions was characterized by the assimilable organic carbon (AOC) measurement. Third, the organic transformation that occurred during the bacteria growth was examined. Fourth, the bacteria-clean/fouled membrane interactions were characterized by atomic force microscopy (AFM) analysis. Last, the impact of isolated dissolved organic fractions on SWRO biofouling was investigated using a laboratory cross-flow RO setup (**Chapter 5**).
- 5) Investigate the fouling mitigation in SWRO process by removing LMW compounds in seawater using low-pressure nanofiltration (NF) membrane. First, three NF membranes were characterized in terms of permeability and molecular weight cut off (MWCO): NF270, which was a commercial membrane based on polyamide thin film composite membrane; NF1 and NF2, which were glutaraldehyde cross-linked layer-by-layer polyelectrolyte membranes (i.e., NF2 contained more polyelectrolyte layers than NF1). The organic/inorganic rejection properties of membranes were determined from LC-OCD, ICP-OES and IC measurements. The key water quality parameters of NF permeate were monitored by LC-OCD (i.e., LMW) and AOC measurements. The impact of LMW and AOC concentrations on SWRO fouling was critically assessed (**Chapter 6**).

CHAPTER 2 Literature Review

2.1 Pressure-Driven Membrane Processes

2.1.1 Fundamentals

Membrane acts as a selective barrier that retains certain components while allows other components to pass through (Mulder 2012). The most common type of membrane used in water-related process is the pressure-driven membrane. In general, there are 4 categories of pressure-driven membrane: microfiltration (MF, pore size $\sim 0.1 - 10 \mu\text{m}$), ultrafiltration (UF, pore size $\sim 0.001 - 0.1 \mu\text{m}$), nanofiltration (NF, MWCO 200 – 1000 Da) and reverse osmosis (RO, non-porous, MWCO < 200 Da). Recent years, reverse osmosis (RO) technology becomes popular for potable water production include seawater desalination, due to its excellent salt rejection properties and lower energy consumption as compared thermal-based desalination process (Clever, Jordt et al. 2000).

In natural osmosis process, solvent (i.e., water) permeates across the semipermeable membrane from low concentration (i.e., low osmotic pressure) solution to high concentration (i.e., high osmotic pressure) solution. In RO process, hydraulic pressure difference higher than the osmotic pressure difference across the membrane need to be applied to reverse the water flow direction (**Figure 2.1**). The permeate flux of RO, J_v , defined as the volumetric flow of permeate per unit membrane area is given by the osmotic pressure-resistance model:

$$J_v = \frac{Q_p}{A_m} = \frac{\text{TMP} - \Delta\pi_m}{\mu R_m} \quad \text{Equation (2-1)}$$

Where TMP is trans-membrane pressure, and $\Delta\pi_m$ is the effective osmotic pressure difference across the membrane, and μ is the permeate (i.e., water) viscosity, and R_m is the membrane hydraulic resistance.

Figure 2.1 Illustration of reverse osmosis process

2.1.2 RO Membrane, Modules and Operation Mode

Most of current commercial RO membranes are thin film composite membranes based on polyamides (PA). The spiral wound module (SWM) (**Figure 2.2**) is the most common configuration for RO as it can be operated at high pressure (typically up to 69 bar) and has moderate packing density. The SWM consists of multilayers of feed channel spacer-RO membrane-permeate spacer sandwiched together and rolled up like a ‘Swiss roll’. The function of the feed channel spacer is to improve the hydrodynamics (i.e., mass transfer) in order to reduce concentration polarization (CP) and membrane fouling.

SWM is the most common configuration for SWRO with market share of > 90% (Karabelas, Kostoglou et al. 2015), other configurations such as hollow fiber and flat-sheet plate & frame are less common due to the following reasons:

- (a) The hollow fiber RO membrane is based on cellulose acetate which is prone to microbial attack and has limited pH range of 7 – 10 as compared to TFC polyamide RO with pH range of 2 – 11, which can be cleaned by acid and base.

(b) The flat-sheet plate & frame configuration has low packing density as compared to SWM, thus increases the footprint.

Figure 2.2 Spiral wound membrane module for desalination (Karabelas, Kostoglou et al. 2015).

The membrane system can be operated in crossflow or dead end mode (**Figure 2.3**). In dead end operation, there is no retentate stream, so 100% recovery can be obtained. In crossflow operation, the surface shear can improve the hydrodynamics which reduces the CP, but only a fraction of feed is passed through the membrane, hence recovery is <100%. For practical operation, the RO is typically operated in crossflow mode.

Figure 2.3 Membrane operation in (a) cross flow mode, and (b) dead end mode.

2.1.3 Concentration Polarization (CP)

CP is a common phenomenon in membrane process (Song and Elimelech 1995, Song and Yu 1999). CP arisen due to the accumulation of rejected solutes (i.e., ions) on the membrane surface, which generates a solute flow back to bulk solution due to concentration gradient. At steady state, the convective solute flow to membrane will be balanced by solute flow through membrane plus back-transport flow from membrane surface as shown in **Figure 2.4**. The magnitude of CP is an exponential function of flux/mass transfer ratio:

$$CP = \frac{C_m - C_p}{C_o - C_p} = \exp\left(\frac{J_v}{k_m}\right) \quad \text{Equation (2-2)}$$

Where C_m is the salt concentration at membrane surface, C_o is the salt concentration in bulk solution, and C_p is the salt concentration in permeate. k_m is the mass-transfer coefficient. Thus, reduce the operating flux and improve the mass transfer (i.e., using feed channel spacer) can reduce CP (Matthiasson and Sivik 1980).

Figure 2.4 Concentration polarization schematic description.

CP is not desired as it increases the concentration thus osmotic pressure at the membrane surface. CP is also linked to membrane fouling since the fouling species accumulate on the membrane surface under the effect of CP.

In RO operation, as the foulant accumulated on the membrane surface, it could easily form a cake layer on the top of the membrane, which enhances the CP phenomenon. This phenomenon is known as cake enhanced osmotic pressure (CEOP) (**Figure 2.5**), where the back diffusion of colloids and ions is hindered by the ‘un-stirred’ cake or fouling layer (Chong, Wong et al. 2007).

Figure 2.5 Concentration polarization(a) before fouling and (b)after fouling (Tang, Chong et al. 2011).

Mathematically, RO membrane fouling can be described as following (Tang, Chong et al. 2011):

$$J_v(t) = \frac{\text{TMP} - \text{CP}(t)\Delta\pi}{\mu(R_m + R_f)} \quad \text{Equation (2-3)}$$

Where TMP is trans-membrane pressure, CP is concentration polarization modulus, $\Delta\pi$ is osmotic pressure difference across the membrane, μ is water viscosity, R_m is the membrane hydraulic resistance, and R_f is the fouling resistance. The fouling resistance

is the sum of reversible, irreversible and irremovable fouling resistances; while the CEOP effect is reflected by changes in CP as a function of time.

2.1.4 Seawater Reverse Osmosis (SWRO) Desalination Process

In general, seawater contains ~96% water and ~4% of total dissolved solid (TDS), which composes of large amount of salts, in particular sodium and chloride ions (Kaya, Sert et al. 2015). The TDS in seawater varies with location based on evaporation rate and temperature (Wright 1995, Dalvi, Al-Rasheed et al. 2000). The high TDS gives rise to high osmotic pressure, thus SWRO desalination process typically requires pressure of > 50 bar, which means high energy demand of > 2.5 kWh/m³ water produced.

A full scale SWRO desalination plant consists of the following items as shown in **Figure 2.6** (Voutchkov and Semiat 2008): (i) seawater intake, which is to obtain the seawater source; (ii) intake screens, which removes large particles and debris from seawater; (iii) pretreatment, which removes small particles, colloids, microorganisms and large molecular weight organic matters; (iv) RO process, which rejects all the contaminants and salts to get pure water; and (v) post-treatment, which consists of disinfection and remineralization to meet the standards of potable water.

Figure 2.6 Schematic diagram of seawater reverse osmosis (SWRO) desalination process.

SWRO desalination process has been successfully applied in many countries such as Israel and Singapore. By 2020, the total capacity in Israel is expected to rise to 650 million m^3/year , which occupies 30% of the total potable water supply (Dreizin, Tenne et al. 2008). In Singapore, due to limited natural water resources and catchment areas, desalinated water by RO technology becomes an important source of water, i.e., 4th National Tap (Chua, Hawlader et al. 2003); the current total capacity is 1.6 million m^3/d , which by 2060 it is expected to meet up to 30% of Singapore's water needs.

2.1.5 Membrane Fouling

Membrane fouling is the deposition of unwanted materials on a membrane surface or in the membrane pores (Potts, Ahlert et al. 1981). For non-porous RO membrane, the foulants can adsorb, deposit and accumulate on the membrane surface. As a consequence of membrane fouling, flux decline for constant pressure operation or increase in TMP for constant flux operation (**Figure 2.7**).

Figure 2.7 Operation conditions of (a) constant pressure, and (b) constant flux.

In general, membrane fouling can be divided into reversible, irreversible and irremovable fouling. Reversible fouling refers to the foulants that can be easily removed from the membrane by physical cleaning. Irreversible fouling refers to the foulants that

can only be removed by chemical cleaning while irremovable fouling refers to foulants that stay permanently on the membrane surface, i.e., permanent loss of membrane permeability (Fan, Harris et al. 2001).

Fouling in RO process can be generally classified into scaling, colloidal fouling, organic fouling and biofouling (Chian, Chen et al. 2007). Scaling refers to the crystallization/precipitation of inorganic salt when the concentration of sparingly soluble salt, i.e., calcium carbonate, calcium sulfate, etc., exceeds the saturation level at the RO membrane surface. Scaling in RO can be easily prevented by avoiding high recovery operation to maintain the system below the solubility limit of salts or adding scale inhibitors (Jiang, Li et al. 2017). Colloidal fouling refers to the deposition of colloids, i.e., rigid inorganic colloids such as silica, aluminium silicate, iron hydroxide etc. and organic macromolecules, typically in the size range of 1-1000 nm, and formation of a cake layer on the RO membrane surface (Tang, Chong et al. 2011). Colloidal fouling by organic compounds is also known as organic fouling. Colloidal fouling can be mitigated by seawater pretreatment such as coagulation-flocculation or microfiltration-ultrafiltration and combination of processes, in which the effectiveness depends strongly on the size and nature of colloids. Biofouling is related to biofilm formation on membrane surface, which is recognized as the most challenging problem for many SWRO desalination plants (Nejati, Mirbagheri et al. 2019). This is because even with 99.9% removal of microorganisms in RO feed water, severe biofouling can still occur (Matin, Khan et al. 2011). The focus of this work is on organic fouling and biofouling which are elaborated in the following sections.

2.2 Organic Fouling

Despite the organic concentration in seawater is lower compared to the inorganic parts, organic fouling is still the Achilles heel of SWRO desalination process since organic

fouling layer can support bacteria growth that causes subsequent biofilm formation (Shon, Kim et al. 2009).

2.2.1 Characteristics of Seawater Organic Matters

Natural organic matters (NOM) in seawater are generally divided into two parts, i.e., particulate organic matters (POM) and dissolved organic matters (DOM). POM is commonly defined as the organic matters with particle size larger than 0.45 μm , while DOM is defined as the organic matters with particles size less than 0.45 μm . In seawater, POM occupies very small portion of the total organic matters (Thurman 1985). Typically, the pretreatment process in SWRO demonstrated high efficiency in the removal of POM but not DOM (Jamaly, Darwish et al. 2014).

DOM in seawater consists of various organic matters with a wide range of molecular weight (MW) distribution (Matilainen, Gjessing et al. 2011). The main components of DOM in seawater consist of polysaccharides, proteins, humic acids, carbohydrates, amino sugars and low molecular weight compounds (Thurman 1985, Ogawa and Tanoue 2003). The relevant analytical techniques for organic matters are summarized in

Table 2.1. Traditionally, the concentration of organics in seawater is quantified in term of total organic carbon (TOC). However, detailed characteristics of the organics cannot be well presented (Rodriguez 2011, Miyoshi, Hayashi et al. 2016). UV absorbance was popular to characterize specific organics which absorb UV light at wavelength of 254 nm. The drawback is that part of the residual organics cannot be captured by UV detection. Fluorescence-excitation emission matrix (F-EEM), and the attenuated total reflectance-fourier transform infrared spectrometry (ATR-FTIR) are also powerful tools to characterize the organics, and the disadvantages are listed in **Table 2.1.**

Recent years, liquid chromatography-organic carbon detection (LC-OCD) has been widely used to characterize the organics in seawater based on their MW, where DOM can be separated into biopolymers (BP, MW > 1 kDa), humic substances with building blocks (HS&BB, MW 350 – 1000 Da), and low molecular weight compounds (LMW, MW < 350 Da) (Huber, Balz et al. 2011). From LC-OCD analysis, seawater mainly consists of HS&BB and LMW compounds, occupying ~40-70% of the total DOC (Penru, Simon et al. 2013, Simon, Penru et al. 2013). Humic substances are the major portion in natural water (Fan, Harris et al. 2001), which consist of complex mixtures such as aromatic and aliphatic components with mainly carboxylic and phenolic functional groups (Thurman 1985). Reported MW of humic substances is about 1000 Da by using the LC-OCD analysis (Alizadeh Tabatabai, Schippers et al. 2014). In addition, it was reported that BP, although occupies the least percentage of seawater organics, seems to trigger severe RO fouling (Miyoshi, Hayashi et al. 2016).

Table 2.1 Common analytical techniques for characterization of DOM in seawater.

	Applications	Advantages	Disadvantages	Typical range
TOC	Measure the total concentration of organic carbon	-Timesaving -Detect low concentration (ppb level)	No detail of organic MW	Organic concentration: 0-100 ppm
UV254	-Identify aromatic constituents	Timesaving	Missing non-UV absorbed organics	Wavelength: 254 nm
LC-OCD	Measure organic carbon based on MW	-MW distribution -Concentration of different fractions based on MW -Detect low concentration (ppb level)	Time-consuming	MW range: <0.45 μm
F-EEM	Detect protein-like, tryptophan-like, tyrosine-like, humic-like, and fulvic-like materials	-Timesaving -Detect low concentration (ppb level)	Missing non-fluorescent organics	Wavelength: 200-800 nm
ATR-FTIR	Provide the functional groups of organics	-Timesaving -Suitable for solid and liquid samples	Less detail of organic species	Wavelength: 400-5000 cm^{-1}

2.2.2 Fouling Evaluation with Model Organic Foulants

In order to study the organic fouling in RO process, various model foulants with uniform structure and well-known feature such as alginic acid or sodium alginate (SA),

bovine serum albumin (BSA), humic acid (HA) and fulvic acid (FA) have been employed as the surrogates of DOM (Zularisam, Ismail et al. 2006, Ham, Kim et al. 2013).

SA is regarded as high MW organics (i.e., MW > 200 kDa) (Shon, Vigneswaran et al. 2008). As shown in **Figure 2.8**, the abundant carboxylic functional groups in SA structure may result in severe membrane fouling, especially at condition of low pH and high ionic strength (e.g., 100 mM) due to the reduction of electrostatic repulsive force (Lee, Kim et al. 2007). In the presence of multivalent ions, the fibrillar-like or rod-like structures of SA can readily form a three-dimensional cross-linked structure (Tang, Chong et al. 2011). Taking Ca^{2+} as an example, Ca^{2+} shows strong interaction with carboxylic functional group, and each Ca^{2+} can bind to two macromolecules to form an egg-box structure (**Figure 2.9**) (Katsoufidou, Yiantsios et al. 2007).

Figure 2.8 Chemical structure of sodium alginate (SA) (Katsoufidou, Yiantsios et al. 2007).

Figure 2.9 Schematic illustration of alginate reaction with Ca^{2+} (Li, Xu et al. 2007).

BSA, as a common representative of protein, has a spherical structure and the MW is well defined (MW ~67 kDa). BSA has been frequently selected as the model foulant to study protein fouling in membrane processes (Li, Xu et al. 2007, Mo, Tay et al. 2008). Similar to the SA, significant fouling can be observed under the condition of high ionic strength and Ca^{2+} (Mo, Tay et al. 2008). In addition, BSA is sensitive to the pH of solution because of the presence of carboxylic and amine functional groups (Tang, Chong et al. 2011), where negative charge can be observed when pH value is higher than its isoelectric point (pH = 4.7). It has been reported that most severe membrane fouling occurred when pH reached the isoelectric point, where the repulsion force between membrane and protein is the weakest (Mo, Tay et al. 2008).

HA and FA has been widely utilized to analyze the organic fouling in membrane filtration processes (Hong and Elimelech 1997, Yuan and Zydney 1999, Mänttari, Puro et al. 2000). As illustrated in **Figure 2.10**, HA and FA are anionic polyelectrolytes with negatively charged carboxylic acid (COOH^-), methoxyl carbonyls (C=O) and phenolic (OH^-) functional groups. HA and FA have different solubility in water; FA is more soluble than the HA at any pH level, and HA shows a high solubility at higher pH (pH $\approx$ 10) (Leenheer 1994). Their structure can be easily affected by the pH and ionic strength in solution (i.e., long linear chains at high pH and low ionic strength, and coiled, spherical molecules at low pH and high ionic strength). Inorganic ions such as Ca^{2+} can neutralize the surface charge of the foulant, enhancing aggregation and consequently causing severe fouling (Schäfer, Schwicker et al. 2000). Moreover, it was found that HA can cause more severe fouling than FA because it is hydrophobic material with more aromatic functional groups, and larger MW (Zularisam, Ismail et al. 2006).

Figure 2.10 Chemical structure of marine (a) humic acid, and (b) fulvic acid (Harvey, Boran et al. 1983).

In reality, natural water consists of more than one type of potential organic foulants that come in various sizes or molecular weights, as well as different functional groups and chemical structures. The different membrane fouling tendencies of single and mixed organic compounds were demonstrated, where fouling of mixed species could not be simply described by the fouling of single species (Miyoshi, Hayashi et al. 2016, Ding, Yamamura et al. 2018). For example, more severe fouling was observed in SA and BSA mixed solution than in individual solution due to the greater foulant-foulant adhesion force, and “egg-box” formed by SA and Ca^{2+} was crosslinked with BSA molecules (Ang and Elimelech 2007).

2.2.3 Fouling Evaluation with Natural Organic Matters (NOM)

In an extensive review article, it was highlighted that membrane fouling by NOM is rather complex as it is highly affected by the NOM properties such as organic concentration, specific organic portions, molecular size, chemical structures and charge density (Jiang, Li et al. 2017).

Size distribution of NOM is one of the main factors in affecting membrane fouling. Organics with large MW such as proteins and polysaccharides tend to foul the membrane by adsorption (Ridgway, Orbell et al. 2017). Hydrophobicity of the NOM is another factor that influences the fouling behavior in membrane process. XAD resin

was used to fractionate the NOM in surface water according to the degree of hydrophobicity, where major three fraction can be obtained, i.e., hydrophilic fraction, hydrophobic fraction, and transphilic fraction (Fan, Harris et al. 2001, Penru, Simon et al. 2013). In terms of their fouling phenomenon, study demonstrated that hydrophobic NOM fractions caused more severe fouling than hydrophilic fractions in the following order: hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged (Nilson and DiGiano 1996). This also implicates that the charge of the organics also a factor that lead to various level of fouling because foulant and membrane could have electrostatic attraction or electrostatic repulsion according to the surface charge of two materials (Mo, Tay et al. 2008).

In seawater reverse osmosis (SWRO) desalination plant, due to the low concentration of NOM as compared with other water sources, organic fouling still occurs. From SWRO membrane autopsies, it has been identified that the major organic foulants consist of high molecular weight compounds include biopolymers such as polysaccharides and proteins (Jeong, Kim et al. 2013, Miyoshi, Hayashi et al. 2016). Transparent exopolymer particles (TEP) and extracellular polymeric substances (EPS) are also detected on the RO membrane surface, the detailed characteristic and fouling behavior will be discussed in the **Section 2.3**. In addition, recent study also suggested that low molecular weight compounds were observed on fouled RO membrane (Jeong, Naidu et al. 2016).

2.2.4 Interfacial Force Investigation in Organic Fouling

Generally, the fouling mechanism can be divided into two steps; organics first interact with clean membrane, followed by the subsequent interaction with the organic-fouled membrane. The interaction between foulant and membrane includes chemical and physical interaction. Chemical interaction normally causes irreversible fouling due to

high strength of adsorption, while physical interaction with weak adsorption results in reversible fouling.

2.2.4.1 Extend Derjaguin-Landau-Verwey-Overbeek (XDLVO) Theory

Organic foulants are attracted to the membrane surface under physical factor such as permeation drag and/or the chemical interaction, where the constituents could bind with the functional groups of membrane (Brant and Childress 2002). In order to analyze the interactions between foulant-membrane and foulant-foulant, classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has been used, where the total interaction energy is the sum of the van der Waals (VDW) interaction and the electrical double layer (EDL) interaction (Brant and Childress 2002). The VDW interaction is not affected by the solution chemistry, while the EDL interaction can be strongly affected by the solution chemistry. This explained why the diameter of the organic compounds becomes larger in the presence of Ca^{2+} and Mg^{2+} (Jin, Huang et al. 2009). Organic aggregation easily happens when the absolute value of VDW force is higher than that of EDL force. However, DLVO theory did not provide satisfactory description of the fouling behavior. For example, the chemical and morphological heterogeneity of the membrane surface may lead to different energy distributions on surface. In addition, surface tension was excluded in classical DLVO theory (Bhattacharjee, Sharma et al. 1996, Meagher, Klauber et al. 1996, Brant and Childress 2002). Therefore, an extended DLVO (XDLVO) theory was developed by van Oss (van Oss 1993), which included an additional interaction energy named Lewis short-ranged acid-base (AB) interaction between two surfaces immersed in a polar solvent (water). AB interaction can be simply affected by the hydrophobicity of immersed colloids. For example, hydrophobic colloids in water can aggregate faster because of evacuation of water from each colloid. Many studies have demonstrated that XDLVO theory was more reasonable to describe the interactions between foulant and membrane (Brant and Childress 2002, Lin, Lu et

al. 2014). For example, AB interaction was identified as the key factor that governed the organic fouling in seawater condition; it was concluded that initial fouling rate, i.e., flux decline, was controlled by the alginate-membrane adhesive free energy while lateral fouling rate was governed by the alginate-alginate adhesive free energy after the RO membrane surface was covered by alginate foulant (Jin, Huang et al. 2009). In another study, it was highlighted that BSA fouling was more severe due to BSA-BSA interaction rather than BSA-membrane interaction (Mo, Tay et al. 2008).

In XDLVO theory, the total interaction energy ΔG^{TOT} between solid materials can be determined by including the Lifshitz-van der Waals (LW) interaction ΔG^{LW} , electrostatic double layer (EDL) interaction ΔG^{EL} , and Lewis acid-base (AB) interaction ΔG^{AB} , which can be expressed as follow (van Oss 1993, Van Oss 2006):

$$\Delta G^{\text{TOT}} = \Delta G^{\text{LW}} + \Delta G^{\text{EL}} + \Delta G^{\text{AB}} \quad \text{Equation (2-4)}$$

To obtain the surface tension parameters of the solid materials, contact angle measurements were carried out. The extended Young's equation was used to calculate the γ_s^{LW} , γ_s^+ and γ_s^- for the solid materials, which can be written as follow:

$$(1 + \cos\theta)\gamma_l^{\text{TOT}} = 2 \left[\sqrt{\gamma_s^{\text{LW}}\gamma_l^{\text{LW}}} + \sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_s^-\gamma_l^+} \right] \quad \text{Equation (2-5)}$$

Where θ is the contact angle, γ_s^{LW} , γ_s^+ , and γ_s^- are the Liftshitz-van der Waals component, electron acceptor and electron donor, respectively. The subscript of s and l represents solid materials and probe liquids.

Cohesion energy is the energy between two same solid surfaces, such as foulant-foulant interaction, while adhesion energy is the energy between two different solid surfaces,

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i.e., such as foulant-membrane interaction. When the gap between two solid surfaces is close to the minimum equilibrium cut-off distance (i.e., the value reaches to 0.158 nm), the cohesion and adhesion energy can be expressed as (Meinders, Van der Mei et al. 1995, Van Oss, Docoslis et al. 1999):

$$\Delta G_{y0}^{LW} = 2 \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_m^{LW}} \right) \left(\sqrt{\gamma_c^{LW}} - \sqrt{\gamma_1^{LW}} \right) \quad \text{Equation (2-6)}$$

$$\Delta G_{y0}^{AB} = 2\sqrt{\gamma_1^+}(\sqrt{\gamma_m^-} + \sqrt{\gamma_c^-} - \sqrt{\gamma_1^-}) + 2\sqrt{\gamma_1^-}(\sqrt{\gamma_m^+} + \sqrt{\gamma_c^+} - \sqrt{\gamma_1^+}) - 2(\sqrt{\gamma_m^+ \gamma_c^-} + \sqrt{\gamma_m^- \gamma_c^+}) \quad \text{Equation (2-7)}$$

Where the subscript of m and c correspond to membrane and organic foulant, respectively.

The EL interaction energy can be calculated by the following equation:

$$\Delta G_{y0}^{EL} = \frac{\epsilon_0 \epsilon_r \kappa}{2} (\zeta_m^2 + \zeta_c^2) \times \left(1 - \coth(\kappa y) + \frac{2\zeta_m \zeta_c}{\zeta_m^2 + \zeta_c^2} \operatorname{csch}(\kappa y) \right) \quad \text{Equation (2-8)}$$

Where $\epsilon_0 \epsilon_r$ is the dielectric permittivity of the fluid (i.e. $\epsilon_0 = 8.85419 \times 10^{-12}$, $\epsilon_r = 78$, respectively), ζ_m and ζ_c are the surface potentials of the membrane and organic foulant which were determined by zeta potential measurements, respectively. κ is the inverse Debye screening length which was determined using following equation:

$$\kappa = \sqrt{\frac{e^2 \sum n_i z_i^2}{\epsilon_0 \epsilon_r k T}} \quad \text{Equation (2-9)}$$

Where e is the electron charge, n_i is the number of ions, z_i is the valence of ions, k is the Boltzmann's constant and T is the absolute temperature.

Overall, quantification of interaction energy between membrane-foulant and foulant-foulant could provide good interpretation in terms of membrane fouling mechanism, and further propose a suitable way for fouling control. However, the XDLVO model does not consider the membrane surface roughness effect, where some studies overcame the drawback by including the roughness parameter in the calculation (Chen, Tian et al. 2012, Zhao, Shen et al. 2015).

2.2.4.2 Atomic Force Microscope (AFM)

Atomic force microscope (AFM) has been widely used to study the membrane fouling mechanism (Tang, Kwon et al. 2009, Miao, Wang et al. 2017, Miao, Wang et al. 2017). AFM as a tool for investigating membrane surface properties, can provide high resolution images of membrane morphology (Bowen, Hilal et al. 1996). More importantly, AFM can quantify the interaction force between two solid materials such as cantilever and membrane surface, which allows the examination of fouling mechanism at atomic level. In AFM measurement, the cantilever approaches, contacts and withdraws from the sample surface. Based on the deflection of cantilever and calibration of spring constant and deflection sensitivity, the force-distance curve (**Figure 2.11**) can be obtained. Information such as adhesion, electrical effect, elasticity and harness can be obtained. Furthermore, in order to achieve more practical measurement, model foulants of organic compounds, bacteria, and materials with important functional groups were coated onto the cantilever tip to study the interaction force between foulants and membranes (Ang and Elimelech 2007, Tang, Kwon et al. 2009, Thwala, Li et al. 2013, Boo, Hong et al. 2018). As shown in **Figure 2.12**, the cantilever tip was coated with foulant molecules. When it approaches to the clean membrane or fouled membrane, the interaction force between two materials (foulant-membrane or foulant-foulant) will bend the cantilever so the deflection can be captured.

Figure 2.11 Standard force-distance measurement curve (Powell, Hilal et al. 2017).

Figure 2.12 (a) AFM adhesion force measurement for foulant-cleaned membrane, and (b) foulant-fouled membrane by using foulant-coated tip.

Examples of AFM application in membrane fouling studies include Tang and co-workers (Tang, Kwon et al. 2009) discovered that flux decline was correlated to the adhesion forces between HA and membrane; the interaction force was strongly affected by solution chemistry, i.e., in the presence of divalent ions (Lee and Elimelech 2006) and increase of ionic strength due to shielding effect (Lee and Elimelech 2006, Miao, Wang et al. 2017).

2.3 Biofouling

2.3.1 Mechanism of Biofouling

Biofouling is persistent in SWRO desalination process and is often treated as the most serious type of fouling. Membrane biofouling is related to biological activities and formation of biofilms on the membrane surface. Although pretreatment processes are installed prior RO process, RO biofouling is still inevitable. This is because even with 99.9% removal of bacteria from the bulk solution, the survived bacteria can still attach, proliferate and form biofilm on RO membranes (Flemming 1997).

The formation of biofilm on membrane surface is closely related to the availability of organic constituents in the feed solution. In general, the mechanisms of biofilm formation can be categorized into four successive stages: (i) the attachment of organics onto the membrane surface, leading to the formation of a conditioning film that facilitates the subsequent bacteria attachment; (ii) the deposition of microorganisms onto the membrane surface; (iii) proliferation and production of exopolymeric substances (EPS) and soluble microbial products (SMP) to form a mature biofilm; and (iv) dispersal of biofilm, where cells and organics are released from the biofilm into the environment (Barker and Stuckey 1999, Flemming 2011).

2.3.2 Compositions of Biofilm

Extracellular polymeric substances (EPS) have been identified as the key components of biofilm. They are mainly made up of polysaccharides, proteins, lipids, extracellular DNA and humic substances (Herzberg, Kang et al. 2009). EPS also increase the cell hydrophobicity and enhance the cell adhesion onto membrane, which could result in severe flux decline (Matin, Khan et al. 2011).

In addition, RO biofouling could also give rise to the biofilm-enhanced osmotic pressure effect (BEOP), similar to the CEOP effect in colloidal fouling (Herzberg and Elimelech 2007). It was found that bacteria cells embedded in matrix of EPS (i.e., biofilm) has increased the hydraulic resistance and hindered the back-diffusion of salt, thus resulting in severe flux decline or increase in TMP.

2.3.3 Biofouling Potential

Biofouling potential is usually determined by the organic amount in the feed water which can be seen as nutrient for bacterial growth. Therefore, the bacteria growth is quantified by various method to assess the biofouling potential. The most common and direct methods are biodegradable dissolved organic carbon (BDOC) measurement and assimilable organic carbon (AOC) measurement (Wang, Tao et al. 2014, Terry and Summers 2018).

2.3.3.1 Biodegradable dissolved organic carbon (BDOC) measurement

The organic compounds in the water are mainly classified into biodegradable organic matters (BOM), and non-biodegradable organics. The BOM in water offers energy and carbon source for the microorganisms. Different BOM concentration could be various based on the water types such as wastewater and seawater (Servais, Billen et al. 1987). In addition, the BOM content can increase in some treatment processes such as oxidation and disinfection (Hozalski, Bouwer et al. 1999, LeChevallier 2013). Biodegradable dissolved organic carbon (BDOC) occupies the main portion in the BOM, which accounts for 21-34% (Huck 1990). Some studies have indicated that the use of ozone or chlorine for sterilizing the water could increase the amount of BDOC because of the degradation of organics (van der Kooij, Hijnen et al. 1989, Hureiki, Croué et al. 1994). It makes the organics more susceptible for the bacterial consumption. In addition, biofouling may become more serious in such case because it is hard to

ensure the whole process and setup are under sterilization. Once the bacteria appeared, they consume these degradable BOM and cause severe biofouling.

BDOC measurement is based on the amount of organics consumed by bacteria over a period of time (Terry and Summers 2018). BDOC value is obtained by subtracting the final concentration of the BDOC from the initial BDOC concentration. Generally, at least 10 days are necessary to achieve the complete consumption of the BDOC, which is quite time-consuming (Servais, Billen et al. 1987). Nowadays, for faster measurement, assimilable organic carbon (AOC) measurement becomes more popular.

2.3.3.2 Assimilable organic carbon (AOC) measurement

Assimilable organic carbon (AOC) are those organic matters can be consumed by the microorganisms. AOC generally occupies 0.1-9% of all DOC in water (Sim, Chong et al. 2017), which is part of the BDOC. Its main feature is that AOC can be rapidly consumed and evaluated by the growth of bacteria, while BDOC is calculated from the change in organic carbon (Wang, Tao et al. 2014). Both AOC and BDOC provide effective information for water stability. AOC is more popular because of its shorter measurement time (Jeong, Naidu et al. 2013).

AOC measurement is quantified by adding inoculum until it reaches the stationary phase (van der Kooij, Visser et al. 1982). The maximum bacterial growth is recorded. There are various methods to assess the growth of bacteria, such as bioluminescence, colony-forming units, turbidity, adenosine triphosphate (ATP), and flow cytometry (Sim, Chong et al. 2017). Among them, flow cytometry instrument has been regarded as the most popular tool to rapidly measure the AOC by quantifying the cell count (Hammes and Egli 2005, Elhadidy, Van Dyke et al. 2016). The growth yield which can be obtained by the standard calibration using acetate is needed to convert the cell count

to AOC value as $\mu\text{g/L}$ of acetate (Hammes and Egli 2005). Inoculum usually uses identified organisms or indigenous bacteria. Study shows that indigenous bacteria are more representative for the nature water (Elhadidy, Van Dyke et al. 2016). For example, seawater bacteria which can stand high salinity are suitable as the inoculum in AOC measurement for assessing seawater AOC than other inoculum which may hard to survive in the seawater condition. AOC becomes one of the most effective method to quantify the amount of organic carbon that can be assimilated by microorganisms in water, and it has been considered as a useful indicator to evaluate the impact of biofouling in many water treatment processes (van der Kooij 1992, Weinrich, LeChevallier et al. 2016).

In recent years, AOC measurement has become necessary in many studies to evaluate the performance of the pretreatment process such as organic removal (including AOC removal) (Charnock and Kjønnø 2000, Jeong, Naidu et al. 2013, Jeong, Naidu et al. 2016, Weinrich, LeChevallier et al. 2016). The results suggested that biofouling can be mitigated by the reduction of AOC value in seawater desalination pretreatment process (Jeong, Rice et al. 2014). Therefore, AOC measurement has become an important indicator to access the efficiency of the pretreatment process. Meanwhile, more studies have focused on the source of AOC in seawater. Some references have found that large amount of AOC could be produced where low molecular weight organics increased in the presence of ozone due to breakdown of large molecules to smaller one (van der Kooij, Hijnen et al. 1989, Hammes, Salhi et al. 2006). These studies offered more details of the AOC content and extended a better way to prevent biofouling.

2.4 Fouling Control

As the most economic method, RO in seawater desalination process still faces the challenge of fouling. Colloid particles easily form a cake layer on the membrane surface.

The organic compounds can form a conditioning layer on membrane and further result in biofouling. Scaling also occurs when the salt ions are oversaturated along the membrane module, although less problematic.

In order to prevent fouling, pretreatment is necessarily employed prior to RO process, which is an indispensable process to reduce the organic particles and colloids. **Table 2.2** lists the information of major pretreatments in seawater desalination process. Currently, in most pilot-scale desalination plants, sand filtration is the main used pretreatment method to remove particles when incorporated with additional coagulants (Potts, Ahlert et al. 1981). The results show that this strategy lowers the silt density index (SDI) and increases the removal of turbidity and suspended solids in effluent. However, complete removal to these particles and colloids is hardly achieved. The stable water quality is difficult to be guaranteed (Brehant, Bonnelye et al. 2002).

Common method for biofouling control in SWRO such as chlorination of raw seawater (i.e., disinfection) and subsequent de-chlorination by adding sodium bisulfite (SBS) to RO feed water after the pre-treatment step (Note that RO membrane has poor tolerance to free chlorine, i.e., the chlorine tolerance of RO is 2000 to 3000 ppm-hour exposure with a doubling of salt passage (Bartels, Wilf et al. 2005)) is not effective as the survived bacteria can proliferate and form mature biofilm on the RO membrane surface if nutrient is available (Khan, Hong et al. 2015). In addition, the disadvantage of chlorination includes the formation of harmful disinfection by-products such as trihalomethanes, haloacetic acids, halonitromethanes, haloacetonitriles, bromates, chlorites, iodo-acids etc. by reacting with natural organic matters, iodide and bromide ions in seawater (Richardson 2003, Huang, Fang et al. 2005, Yang, Shang et al. 2007).

In addition to chemical dosing, more recently, microfiltration (MF) and ultrafiltration (UF) become attractive as the pretreatment techniques because they can consistently/effectively remove the particles and colloids at low pressure (Jamaly, Darwish et al. 2014). Therefore, herein, membrane-based pretreatment is highlighted.

MF and UF membranes both efficiently retain large particles and macromolecules from water, which can produce high quality effluent and sustain high tolerance of chemical addition. Teng et al (Teng, Hawlader et al. 2003) found that UF with pore size of 0.01 μm could produce 78 $\text{L}/\text{m}^2\text{h}$ of water, and the TMP was increased slowly, indicating that less fouling potential for UF pretreatment process. Brehant et al (Brehant, Bonnelye et al. 2002) summarized that better water quality can be consistently obtained using UF pretreatment, comparing to conventional pretreatment strategies. In addition, UF membrane can greatly reduce the turbidity in seawater due to smaller pore size and reject over 98% of the algae and microorganisms (Ma, Zhao et al. 2007, Shon, Vigneswaran et al. 2008). Meanwhile, Leparc et al (Leparc, Rapenne et al. 2007) concluded that UF membrane was capable for lasting a long-term operation without chemical cleaning.

Recently, integrated coagulant and UF membrane is more appealing to further promote the performances of the pretreatment (Jeong, Kim et al. 2013). The addition of coagulant improves the performance of the UF membrane owing to the controlled UF fouling. However, overdosing of the coagulants may cause more severe RO fouling because of the addition of mineral salt. In addition, scaling also occurred easily in the bulk or on the membrane surface when the undesired salts and hardness ions oversaturated along the membrane module with the increase of the recovery and CP (Song, Gao et al. 2013). Moreover, the addition of anti-scalant (e.g. phosphate) is also prone to induce biofouling (Weinrich, Haas et al. 2013). Additionally, biopolymers and

LMW compounds still exist in the UF permeate, which has high biofouling potential and threat the subsequent RO process (Naidu, Jeong et al. 2013, Abdelkader, Antar et al. 2018). Therefore, some advanced pretreatment processes, such as membrane bioreactor (MBR) and gravity-driven membrane (GDM), have been proposed to improve the feed quality for RO (Jeong, Rice et al. 2014, Wu, Christen et al. 2017).

Table 2.2 List of major pretreatment methods in seawater desalination process.

Pretreatments	Advantages	Disadvantages	Market share
Chlorination	-Inactivation of microorganisms	-Disinfection by-products -Biofouling	30% (Darton and Gallego 2007)
Coagulation	-High efficiency of removing particulates -Reduction of SDI	-Overdosing of coagulant -Unstable process -Potential damage to the membrane system. -High cost	12% (Huehmer 2009)
MF/UF	-High removal of particulates -High removal of organics with large MW -Stable process -High permeability -Cost saving	-MF/UF fouling -Failure of removing organic with small MW	20% (Huehmer 2009)
Coagulation + UF	-High removal of particulates -High permeability -Stable process	-Overdosing coagulant -UF fouling	7.6% (Huehmer 2009)
NF	-High removal of dissolved organic matters (include organics with small MW) -Stable process	-Low permeability -NF fouling -Low recovery	Umm Lujj SWRO plant (Hassan, Farooque et al. 2002)

Due to the effective removal to biodegradable organic matters, membrane bioreactor (MBR) is very acceptable and environmentally friendly to control biofouling in the RO process (Meng, Chae et al. 2009). The applications of MBR as the pretreatment process

before RO have been widely reported (Achilli, Cath et al. 2009, Kitade, Wu et al. 2013). For example, Jeong's group (Jeong, Naidu et al. 2013) has used MBR to pretreat seawater, where powder activated carbon (PAC) was applied to absorb organics and bacteria. Results shows that this pretreatment successfully improved the RO recovery and extended the RO lifetime. Meanwhile, less foulant was observed on RO membrane surface, indicating is the well sustainable. Similar findings were also confirmed in other studies (Jeong, Rice et al. 2014). In addition to MBR, gravity-driven membrane (GDM) has also been successfully applied in the seawater pretreatment (Wu, Christen et al. 2017, Lee, Suwarno et al. 2019). Compared to MF/UF pretreatment, GDM is gravity-drive process, where there is zero energy consumption from the pump. In addition, high water quality can be obtained from the permeate of GDM because it is regarded as a bioreactor on the membrane surface, where the organic matter can be continuously consumed by the biofilm (Akhondi, Wu et al. 2015).

Nanofiltration (NF) membrane which has high rejection of the organic matter and the divalent ions has also been employed as an alternative pretreatment technique in SWRO process (Zhou, Zhu et al. 2015). Hassan et al. (Hassan, Al-Sofi et al. 1998) and Uhlinger (Uhlinger 2001) have proposed the low-cost NF+RO process, which showed the rejection of total dissolved salt (TDS) was over 90% at the pressure of 22 bar. In addition, the cost saved up to 27% compared with the single-stage SWRO. Fouling reduction in RO process was observed due to the high-quality feed from NF. A pilot study in Umm LUjj desalination plant showed that TDS of permeate achieved to 200 mg/L using NF as pretreatment, and water recovery increased to 56% in RO process where energy consumption was reduced 38% in comparison of conventional SWRO process (Hassan, Farooque et al. 2002). The advantage of NF pretreatment using in seawater desalination in terms of high water recovery and energy saving was also presented in other studies, demonstrating that NF can be considered as an advancement

in seawater pretreatment process prior to the RO (Zhou, Zhu et al. 2015). In addition, studies have been conducted to investigate different commercial NF membranes as seawater pretreatment, which revealed that NF270 was one of the most suitable membranes as it showed significant performance for fouling mitigation since it had high permeability and acceptable rejection of divalent ions (Llenas, Ribera et al. 2013).

2.5 Summary of Literature Review

Figure 2.13 shows the diagram of summary of literature review, and the highlighted in blue color is the focus of current study. RO technology becomes increasingly popular for seawater desalination. However, membrane fouling is the major challenge that impacts the performance of membrane and increases the water production cost. Among the different types of fouling, organic fouling and biofouling as well as the interplay between them need to be addressed.

Figure 2.13 Diagram of summary of literature review.

With regard to organic matters, model foulants such as alginate, bovine serum albumin, humic acid, etc. have been widely used to represent the natural organic compounds in order to simplify the actual organic fouling process. In recent years, advanced analytical tools such as LC-OCD, UV254, and F-EEM were applied to characterize the organic constituents in various water samples as well as foulants on membrane in order to identify the critical components that could be responsible for the RO fouling. In addition, the foulant-clean membrane and foulant-fouled membrane interactions were analysed by the XDLVO theory and AFM measurement to provide an understanding of the fouling mechanism.

Biofouling is generally recognized as the most persistence problem for RO operation. RO biofouling is associated with the formation of biofilm on the membrane surface. The organic compounds in water can form a conditioning layer (i.e., organic fouling) that facilitate the attachment of bacteria, and serve as the nutrient source for bacteria to proliferate that subsequently form a mature biofilm on the membrane surface. The exopolymer substances have been identified as the key component of a biofilm from the membrane autopsies. As a consequence of biofilm formation, an increase in hydraulic resistance and biofilm-enhanced osmotic pressure effect result in a drastic decline in flux or rapid rise in trans-membrane pressure. Furthermore, the assimilable organic carbon (AOC) was developed as an indicator of the biofouling potential of water samples.

In addition, the common pretreatment methods for seawater desalination process include coagulation/flocculation, ultrafiltration and combination of both. However, most of the dissolved organic matters in seawater are not successfully captured, thus the RO feed water still have high biofouling potential. Emerging technologies such as

membrane bioreactor (MBR) and nanofiltration (NF) membrane are gaining attention as seawater pretreatment technologies.

Despite large amount of research work on organic fouling and biofouling in RO process, the role of organic compositions in seawater on SWRO biofouling remains unclear, more importantly the interplay between them. The use of model foulants may not capture the actual SWRO fouling as natural organic matters have broad molecular weight distribution, physical and chemical properties. Therefore, this warrants further investigation on the effect of different dissolved organic compounds on biofouling in SWRO process in order to formulate an effective pretreatment that target at the culprit for fouling mitigation.

CHAPTER 3 Materials and Methods

3.1 Experimental Setups

3.1.1 Crossflow Setup

Figure 3.1 shows the schematic diagram of the crossflow setup. A typical filtration setup consists of feed tank, high pressure pump, pressure and conductivity transmitter, membrane module, flow meter, and mass flow controller. In the filtration process, the retentate and permeate is completely recycled back to the feed tank unless specified elsewhere. Digital pressure transducers (Ashcroft, USA) linked to a software (LabVIEW, National Instrument, USA) are used to record the pressure of feed, retentate and permeate. Mass flow controller (LIQUI-FLOW L30, Bronkhorst, Netherlands) is employed to record the permeate flux. Constant pressure was operated in the whole studies, and flux decline profile was recorded in the fouling process. The flow velocity was set at 0.17 m/s. Dissolved organic fractions of seawater was used as the RO feed solution, the operating temperature was set at 25 °C, and test duration was 6 days.

Figure 3.1 Schematic diagram of crossflow filtration setup.

Two types of membrane modules were used, i.e., module for flat sheet membrane and module for spiral wound membrane. In flat sheet membrane, two different size of flat sheet cells were selected, i.e., one was with area of 0.0186 m^2 , and another was with area of 0.0045 m^2 . Module with larger membrane area was to obtain higher volume of permeate, while module with smaller membrane area was to achieve stronger fouling phenomenon that can be observed in a short time.

In order to increase the efficiency of obtaining high permeate volume, spiral wound membrane element was applied with larger membrane area (2.4 m^2). The structure of the spiral wound membrane has been discussed in the **Section 2.1.2**.

3.1.2 Dead-end Setup

Figure 3.2 shows the schematic diagram of the dead-end filtration setup which consists of 1 L feed vessel and 200 ml membrane cell. The dead-end RO cell with an active membrane area of 0.002826 m^2 can operate under constant pressure provided by the compressed nitrogen gas. The permeate is collected in a beaker on a weighing balance which is connected to a computer for data acquisition using LabView software. The changing weight is recorded every 30s and can be converted to volume (liter) and flux ($\text{L}/\text{m}^2\text{h}$). Dissolved organic fractions of seawater and model foulants such as SA, BSA, and HA were used as the feed solution, the operating temperature was set at 25°C , and the test duration was 6 hours.

Figure 3.2 Schematic diagram of dead-end filtration setup.

3.2 Membranes

3.2.1 Microfiltration (MF) membrane

Microfiltration (MF) membrane (KAREI Filtration, Japan) with pore size of $0.2\ \mu\text{m}$ was to remove the suspended particles and bacteria during the filtration process.

3.2.2 Ultrafiltration (UF) Membrane

Commercial UF membranes were employed in this thesis. Two different flat sheet membranes were used which were GH (GE Osmonics Inc. USA) with molecular weight cut-off (MWCO) of 2kDa and XT (Synder Filtration, USA) with MWCO of 1kDa. In addition, one spiral wound UF membrane of XT (Synder Filtration, USA) with MWCO of 1kDa was also applied.

One hollow fiber UF membrane was employed to pretreat the seawater. The outside-to-inside hollow fiber UF membrane (outer diameter: 1.2 mm, effective length: 26 cm) was purchased from Toray company with MWCO of 150kDa. The UF module contained 18 hollow fibers with an effective area of $0.0186\ \text{m}^2$.

3.2.3 Nanofiltration (NF) Membrane

Commercial flat sheet NF membranes used in this thesis were NFG (Synder Filtration, USA), XN45 (GE Osmonics Inc.USA), NFW (Synder Filtration, USA), NF 270 (DOW, USA) and NF 90 (DOW, USA), respectively. In addition, one spiral wound NF membrane of NFW (Synder Filtration, USA) with MWCO of 0.3-0.5kDa was also applied.

Two in-house fabricated low-pressure hollow fiber NF membranes (i.e., NF1 and NF2) were used for seawater pretreatment process. The detailed fabrication procedure was summarized in the previous study (Liu, Shi et al. 2015). Briefly, hollow fiber NF membranes were fabricated by layer-by-layer (LBL) deposition with the introduction of the polyelectrolyte solution of poly (allylamine hydrochloride) (PAH, Sigma Aldrich) and poly (styrenesulfonic acid) sodium salt (PSS, Alfa Aesar) with sodium chloride (NaCl, Merck) and glutaraldehyde (GA, Sigma Aldrich) solution as the crosslinker throughout the lumen side. In this study, two types of LBL membranes (i.e., PSS+PAH+PSS+GA, and PSS+PAH+PSS+PAH+GA) were termed as NF1 and NF2 membrane. Each hollow fiber NF module consisted of 15 hollow fibers (inner diameter 0.75 mm, effective length: 26 cm) with an effective area of approximately 0.0093 m². In the pretreatment experiment, two NF modules were employed in parallel to achieve an effective area of 0.0186 m².

3.2.4 Reverse Osmosis (RO) Membrane

The RO membrane used in this thesis was commercial SW-30HR which was purchased from Dow Filmtec. Membranes were flushed with deionized (DI) water (Millipore, USA) for 1 min and soaked in DI water for 24 hours prior to use.

3.3 Sample Preparation

3.3.1 Raw Seawater

The seawater sample was collected from a R&D site next to a seawater reverse osmosis (SWRO) desalination plant in Singapore. As seawater was chlorinated before it was delivered to the collection tank, de-chlorination of the seawater by using adequate sodium bisulfite concentration (Acros Organics, USA) was performed. De-chlorinated seawater was stored at 4°C in the cold room and used within one week. The organic compositions of seawater were analysed by LC-OCD and F-EEM, and the detailed procedure are presented in **Section 3.4.1** and **Section 3.4.2**, respectively.

3.3.2 Synthetic Seawater

Synthetic seawater composed of 8g Na₂SO₄ (Merck, USA), 2.22g CaCl₂ (Merck, USA), 22g MgCl₂·6H₂O (Merck, USA), and 47.86g NaCl (Merck, USA) in 2L of DI water. The synthetic seawater was autoclaved prior to use.

3.3.3 Model Organic Solutions

Sodium alginate (SA), bovine serum albumin (BSA) and humic acid (HA) (all purchased from Sigma Aldrich), which represented polysaccharides, proteins and humic substances, respectively, were applied in this thesis. The concentrations of test solutions were adjusted to certain concentration by mixing certain amount of organic with DI water, with ionic concentrations equivalent to seawater (i.e., Na⁺, Ca²⁺, Mg²⁺), which was confirmed by TOC (TOC-VCSH, Shimadzu, Japan), liquid chromatography-organic carbon detector (LC-OCD Model 8, DOC-LABOR, Germany) and inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer, USA) measurements, respectively.

3.3.4 Bacterial Stock Solution

Vibrio sp. B2, which was isolated from a fouled SWRO membrane in previous work (Kim and Chong 2017), was selected as the model bacterium to study the organic transformation during bacteria growth in isolated dissolved organic fractions. The inoculum was prepared as following: the bacteria was first cultured in two Erlenmeyer flasks with 200 mL marine broth solution (37.4 g/L, BD) and incubated with shaking at 180 rpm and 37°C for 24 h. The bacteria free from marine broth was harvested by (i) centrifugation at 4000 rpm for 20 mins at room temperature, (ii) the supernatant was discarded, (iii) the pellets were washed with 0.85% NaCl solution; the above procedure was repeated 3 times, followed by centrifugation at 4000 rpm for 10 mins at room temperature. Subsequently, the bacteria was re-suspended into NaCl solution (35 g/L, Merck) to achieve an optical density OD_{600nm} of 0.1 (Shimadzu, model UV1800).

3.4 Analytical Methods

3.4.1 Liquid Chromatography-Organic Carbon Detector (LC-OCD)

Liquid chromatography-organic carbon detector (LC-OCD Model 8, DOC-LABOR, Germany) was employed to quantify the organic distribution based on the molecular weight (MW) in the seawater and the permeates. The organic compound was isolated into major fractions through size exclusion column (SEC). The organic fractions are categorized into biopolymers (BP, MW: >20kDa), humic substances (HS, MW: ~1000Da), building blocks (BB, MW: 300-500Da), low molecular weight acids (LMW-A, MW: <350Da), and neutrals (LMW-N, MW: <350Da) (Huber, Balz et al. 2011). Each water sample was pre-filtered through a 0.45 µm syringe filter prior to analysis. Quantification of the LC-OCD results were done using a customized software program (ChromCALC, DOC-LABOR, Karlsruhe, Germany).

3.4.2 Fluorescence-excitation emission matrix (F-EEM)

F-EEM is used to identify the organic species such as protein-like, humic-like and fulvic-like materials. Sample was filled into the 3 ml vial for F-EEM measurement, and a fluorescence spectrophotometer was used to scan over excitation wavelengths (Ex) from 200 nm to 500 nm and emission wavelengths (Em) from 250 nm to 550 nm, respectively. The increments of excitation and emission both were 10 nm. The fluorescence spectrophotometer was set at a speed of 1200 nm/min, and a PMT detector voltage of 600 V.

According to previous study, as shown in **Figure 3.3**, five distinguished regions were observed in EEM including Region I (Ex/Em=200-250/280-330nm); Region II (Ex/Em=200-250/330-380 nm); Region III (Ex/Em=200-250/380-550 nm); Region IV (Ex/Em=250-340/280-380 nm); and Region V (Ex/Em=250-400/380-550 nm) (Chen, Westerhoff et al. 2003).

Figure 3.3 Typical EEM peak values (Chen, Westerhoff et al. 2003).

3.4.3 Exopolymeric Substances (EPS) Measurement

The exopolymeric substances (EPS) in foulant solution which consists of polysaccharide and protein was quantified using the method described in previous study (Suwarno, Chen et al. 2012). In brief, for the measurement of polysaccharide content, sample solution (2 mL) was added into a mixture of 1 mL 5% (w/v) phenol solution and 5 mL of H_2SO_4 , and the solution was left to cool to room temperature. The UV-vis absorbance of the solution was measured using a UV spectrometer at 490 nm (UV-1800, SHIMADZU, Japan). Glucose (Merck, USA) was used as the calibration standard for this measurement. The protein concentration was measured using the Bicinchoninic Acid (BCA) Assay Kit (Pierce, product #23225). Sample solution (1 mL) was mixed with the working reagent (2 mL) and incubated in darkness for 2 h at room temperature. The solution was further measured at an absorbance of 562 nm by using UV spectrometer. Bovine serum albumin (BSA) solution was used as the standard to calibrate the protein concentration.

3.4.4 Assimilable Organic Carbon (AOC) Measurement

Assimilable Organic Carbon (AOC) analysis was used to quantify the biofouling potential in the sample based on the method developed by Hammes et al (Hammes, Berney et al. 2008). All glassware and plastic caps were cleaned following a protocol developed by Elhadidy et al. (Elhadidy, Van Dyke et al. 2016) to ensure that they were AOC-free. Briefly, the glassware and caps were acid- and alkaline-washed by an automated washer (Miele Professional) followed by rinsing with DI water. Subsequently, the glassware was soaked overnight in 0.2 M HCl solution (Sigma, USA), followed by flushing with DI water for at least 5 times to ensure that they are acid-free. Then, the glassware was covered with aluminum foil and dried in oven at 100°C. Subsequently, dried glassware was baked in muffle furnace at 450°C for 6 h. The plastic caps were soaked in foil-covered beaker with 10% sodium persulfate solution (Sigma,

USA) and then placed in 60°C water bath for at least 1 h. Lastly, caps were washed with DI water after soaking in sodium persulfate solution and followed by drying in oven at 100°C.

Indigenous inoculum was prepared by using raw seawater. Briefly, raw seawater (5L) which contains large particles, was filtered through 11 µm filter paper (Whatman, Grade 1, England) using vacuum pump. Subsequently, filtered seawater was passed through a 0.2 µm nucleopore track-etch membrane (Whatman, Grade 1, England) to achieve 500 ml suspended solution in the retentate with fairly concentrated viable bacteria count. This solution was then incubated at 30°C with 40 rpm for 21 days to ensure that the background AOC has been consumed completely. The cell count was measured using flow cytometer (BD Accuri C6, USA), and this solution was used as the inoculum for the AOC study. The sample (10 mL) was firstly filtered through a 0.22 µm PES syringe filter (Millipore, USA) into a 40 mL AOC-free vial. Subsequently, the sample was heated in 70°C water bath for 30 min to ensure that the residual bacteria in the solution was inactivated, and finally sample was allowed to cool down to room temperature. Each syringe filter was pre-washed by filtering with 100 ml of DI water prior to use. Prepared inoculum was injected into each vial to achieve an approximate cell count of 1×10^4 cells/mL, which was identified as the initial cell count ($N_{initial}$). Then, the inoculated samples were incubated in a temperature-controlled shaker-incubator (Model: ZQZY-70AF, Shanghai Zhichu Instrument Co., Ltd) at 30°C with 40 rpm. Cell count was measured using flow cytometer (BD Accuri C6, USA) every 24 h intervals, and the highest cell count (N_{final}) was recorded in order to calculate the AOC concentration of each sample. The sample without inoculum was prepared as negative control ($N_{negative}$). Prior to measurement all samples were stained with SYTO9 (Molecular Probes, USA) in the dark for 20 mins. Each AOC measurement was done in triplicates. The equation for AOC concentration is:

$$AOC (\mu g - C / L) = \frac{(N_{final} - N_{initial} - N_{negative}) (\frac{Cells}{L})}{Inoculum\ yield (\frac{Cells}{\mu g\ C})} \quad \text{Equation (3-1)}$$

The inoculum yield was evaluated by different standard concentration of sodium acetate solution with inorganic nutrient at seawater condition (35 g/L, NaCl). The acetate concentration of standard solution was prepared to 0 $\mu\text{g-C/L}$, 30.15 $\mu\text{g-C/L}$, 60.3 $\mu\text{g-C/L}$, 120.6 $\mu\text{g-C/L}$, and 241.2 $\mu\text{g-C/L}$, respectively. The mineral nutrient was prepared by mixing 306.8 mg of NH_4Cl , 576 mg of KNO_3 , and 68.4 mg of K_2HPO_4 into 200mL DI water as described in previous method (APHA 2012, Elhadidy, Van Dyke et al. 2016). Then, the standard solution and mineral stock were filtered through 0.2 μm PES syringe filter. Final concentration of sodium acetate solution was prepared by adding 5 μL of filtered mineral stock to 10 mL standard solutions. Indigenous inoculum was added into each standard solution to achieve an approximately cell count of 1×10^4 cells/mL. There were three replicates for each standard. Cell count was measured by flow cytometer daily until it achieved to maximum cell count. Corrected cell growth was obtained by counteracting the initial cell count and the value from the negative control. Lastly, inoculum yield was calculated by plotting corrected cell growth against acetate concentration in calibration process (as shown in **Figure 3.4**). In this study, the inoculum yield was 1.1623×10^5 cells/ $\mu\text{g-C}$.

Figure 3.4 Calibration curve by plotting the live cell count against the sodium acetate concentration using natural inoculum.

3.4.5 Confocal Laser Scanning Microscopy (CLSM)

The biofilm on the fouled membrane surface was characterized by confocal laser scanning microscopy (CLSM) analysis. The membrane coupon (3 cm × 4 cm) was stained with the LIVE/DEAD BacLight bacterial viability kit (Molecular Probes, L7012) according to the procedure provided by manufacturer. In brief, the staining reagent was prepared by combining 1.5 µL of SYTO 9 and 1.5 of µL PI in 0.5 mL of DI water. Subsequently, the membrane coupon was soaked in the staining reagent and incubated in dark for 30 mins at room temperature. Then, the membrane coupon was rinsed with 1 ml of DI water and placed on a glass slide. The microscopic observation and image acquisition were obtained by CLSM (Zeiss, model LSM710), and the biovolume (µm³/µm²) of biofilm was calculated by IMARIS software (Bitplane, version 7.3.1).

3.4.6 Modified Fouling Index (MFI) Measurement

The fouling potential of can be characterized via the MFI method (Jin, Lee et al. 2017). Fouling behavior assuming a cake filtration model can be expressed by the slope of the

plot of time divided by cumulative permeate volume (t/V) versus cumulative permeate volume (V) with a linear fitting, using following equation:

$$\frac{t}{V} = \frac{\mu R_m}{\Delta P \cdot A} + \frac{I\mu}{2\Delta P \cdot A^2} V \quad \text{Equation (3-1)}$$

Where R_m is membrane resistance, ΔP is pressure drop across filter, A is membrane surface area, μ is sample viscosity, and I is a measure of the membrane fouling potential of the sample. The term $\frac{I\mu}{2\Delta P \cdot A^2}$ according to this equation can serve as an index of the fouling tendency (i.e., MFI) when ΔP , μ , and A^2 are constant value (Jin, Lee et al. 2017).

3.4.7 Inorganic analysis

Salt concentration of the cations (i.e., Na^+ , Ca^{2+} , Mg^{2+}) and anions (i.e., Cl^- , SO_4^{2-}) were analyzed by an inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer, USA), and an ion chromatography system (IC, DIONEX ICS-1000), respectively.

3.4.8 Attenuated Total Reflectance - Fourier Transform Infrared Spectrometry (ATR-FTIR)

The functional groups of clean membrane and fouled membranes were identified by the FTIR (Prestige-21, Shimadzu)). In addition, for the powder sample, prior to measurement, one milligram of sample was mixed with 100 mg of potassium bromide (KBr). Transparent and hard slice with thickness of ~ 0.5 mm was formed by using a pressing tool. All the sample was measured 30 scans under a scanning range of 400-4000 cm^{-1} at 1 cm^{-1} resolution.

3.4.9 Atomic Force Microscopy (AFM) Measurement

The intermolecular forces between foulant-clean RO membrane and foulant-fouled membrane were measured with an atomic force microscopy (AFM, model XE-100, Park systems, Korea) to understand the organic fouling and biofouling behavior. A commercial AFM cantilever (Nanoscan, USA), which was coated with SiO₂ particles (5.0 μm in diameter), with a spring constant of 0.06 N/m was applied. Herein, the organic-coated cantilevers were prepared by soaking the tip into the solutions with expected foulant (>5 mg-C/L) at 4°C for 48 hours prior to use (Villacorte, Ekowati et al. 2015). The bacteria-coated cantilever tip was prepared by soaking the tip into the *Vibrio* sp. B2 stock solution with concentration of 6×10^6 cells/mL at 4°C for 48 hours prior to use. The tips were first examined for the adhesion force between tip and clean membrane surface (i.e., baseline), and then the foulant-coated probe was used to determine foulant-membrane and foulant-foulant interaction forces. The foulant-fouled membranes were prepared by using dead-end filtration method as shown in **Section 3.1.2**. An AFM fluid cell was utilized, and calibration was carried out to determine the spring constant of the organic-coated tips. All the force-curve measurements were taken from at least 5 different locations and tested 6 times for each point to obtain the average results.

3.4.10 Extend Derjaguin-Landau-Verwey-Overbeek (XDLVO) Theory

According to the XDLVO theory, the interfacial free energies between solid materials i.e., foulant-foulant and foulant-membrane, can be calculated from the surface tension-contact angles measurements (Goniometer) and surface charge-zeta potential measurements (SurPASS electrokinetic analyzer). In this study, the surface tension was determined by two polar probe liquids and one non-polar probe liquid. The properties of probe liquids used for contact angle measurements are listed in **Table 3.1**. The

detailed information of XDLVO theory can be found in the literature review (**Section 2.2.4**).

Table 3.1 Surface tension properties of probe liquids (Hwang, Lee et al. 2011)

	γ^{LW}	γ^+	γ^-	γ^{AB}	γ^{TOT}
DI water	21.8	25.5	25.5	51.0	72.8
$\text{Na}^+ + \text{Cl}^-$	21.8	25.5	25.5	51.0	72.8
$\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{Cl}^-$	21.8	25.5	25.5	51.0	72.8
Glycerol	34	3.9	57.4	29.9	63.9
Diiodomethane	50.8	0	0	0	50.8

3.4.11 Field Emission Scanning Electron Microscope (FE-SEM)

The surface morphology of the membrane autopsy (3 cm $\times$ 4 cm) was identified by a field emission scanning electron microscope (FE-SEM, Jeol JSM-7600F) at acceleration voltage of 5 kV, with the magnitude of 10000x, respectively. Before measurement, membrane coupons were dried in a freeze drier (Martin Christ Alpha 2-4). Each image of the sample was captured at three different positions.

CHAPTER 4 Fouling Behavior of Isolated Dissolved Organic Fractions from Seawater in Reverse Osmosis (RO) Desalination Process

This chapter describes the fractionation process of isolating the organic matter in seawater based on the molecular weight. In addition, the organic fouling mechanism of each fraction was studied. The fractionation process was well described and it could be practically applied in other type of water such as surface water and wastewater. The methods using AFM and XDLVO theory could also be considered as a way for fouling prediction.

4.1 Introduction

As described in **Chapter 1 & 2**, smaller MW compounds (i.e., <1 kDa) which have a high presence in seawater (Penru, Simon et al. 2013) and may cause severe RO fouling have not been well understood since these small MW organics were not the focus in previous studies. An understanding of the fouling behavior of these small MW compounds in seawater is necessary. Therefore, considering the properties associated with their MWs, in this study, the focus was on the impact on RO fouling by different organic fractions, i.e., (i) MW: >1 kDa, (ii) MW: 350 – 1000 Da, and (iii) MW: <350 Da, in seawater isolated by membrane technique.

The atomic force microscopy (AFM) and the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory have been widely used to analyze the interaction forces and energies between foulant-membrane and foulant-foulant, which are powerful methods for fouling mechanism exploration (Li and Elimelech 2004, Jin, Huang et al. 2009, Tiraferri, Kang et al. 2012, Li, Li et al. 2015, Ding, Yang et al. 2016). However, little studies were found to apply AFM method and XDLVO model to understand the RO

fouling behavior of natural DOM in seawater (Villacorte, Ekowati et al. 2015). In addition, seawater consists of large amount of divalent ions such as Ca^{2+} and Mg^{2+} , but the influence of divalent ions under high salinity condition on RO organic fouling still remain elusive.

This study aimed to investigate the fouling mechanism by using isolated organic fractions from seawater. First, DOM in seawater was fractionated into different fractions based on their MWs using membrane technique. Then, the isolated organic fractions and their corresponding model foulants were characterized by size exclusion liquid chromatography and fluorescence spectroscopy, and were compared in term of their fouling potentials. In addition, SWRO fouling of the isolated organic fractions were performed. The interaction force and interfacial energy were examined by AFM force-distance measurement and XDLVO theory.

4.2 Materials and Methods

4.2.1 Fractionation and Concentration of DOM in Seawater

4.2.1.1 Seawater Sample

The collection of seawater sample was described in **Section 3.3.1**. Total of 15 seawater samples were collected over a 9-month period and total volume of seawater used in this chapter was ~1200 L. The concentrations of organic compounds were quantified by LC-OCD, duplicate measurements were made for each sample.

4.2.1.2 Membrane Characterization and Selection

Commercial UF and NF membranes were employed to isolate and concentrate the organic constituents from seawater. The investigated membranes included UF membranes: GH and XT; NF membranes: NFG, XN45, NFW, NF 270 and NF 90. The

contact angles of the membranes were determined using a goniometer (model DSA25, KRUSS GmbH, Germany). The contact angle of each sample was measured at five random positions. The surface charge of membrane was obtained by SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) at standard condition of 10 mM KCl solution. A series of neutral organic solutes such as ribose (MW: 150.13 g/mol), glucose (MW: 180.16 g/mol), sucrose (MW: 342.29 g/mol), raffinose (MW: 594.52 g/mol), and α -Cyclodextrin (MW: 972.84 g/mol) at concentration of 200 mg/L were used to characterize the molecular weight cut offs (MWCOs) of NF membranes. A bench-scale dead-end filtration setup was used, and the MWCO was determined from approximate MW that was 90% rejected by the membrane (Liu, Shi et al. 2015).

The selection of UF and NF membranes for subsequent isolation process were based on the rejection of targeted organic component. The LC-OCD was applied to detect the distribution and concentration of targeted organic fractions in the feed and permeate. In addition, the concentration of ionic species in seawater was measured by an ICP-OES. Prior to measurement of the rejection properties using a dead-end filtration cell, the membranes were compacted with DI water at 3 bar for 3 hours.

4.2.1.3 Fractionation and Concentration Protocol

The fractionation and concentration procedure of organics from seawater by the selected membranes is illustrated in **Figure 4.1**. Three stages were involved: (i) seawater was pretreated by a 0.2 μ m MF membrane to remove the suspended particles, followed by (ii) filtration through an NF membrane for separating the LMW fraction (F. LMW, permeate) from the BP and HS&BB fractions (retentate). Discontinuous-diafiltration was performed where DI water (i.e., ~300 L) was added to the system and retentate was recycled until all the LMW compounds were separated, (iii) the NF retentate which contained BP and HS&BB compounds was then filtered through an UF

membrane for separating the BP fraction (F.BP, retentate) from the HS&BB fraction (F.HS&BB, permeate). Similarly, discontinuous-diafiltration (i.e., ~300 L of DI water) was performed in this step. High crossflow rate (0.39 m/s) and low flux (≤ 10 L/m²h) were applied in the UF/NF fractionation process to minimize membrane fouling by the organic compounds. The concentration of isolated organic fractions was conducted in stage (ii) and (iii) simultaneously through volume reduction by discharging the unwanted permeate. It is worth noting that due to the separation characteristics of membranes and the dilution effect of added DI water, the concentration of ions appeared to be different in each of the fractionated solutions. Thus, inorganic salts such as NaCl, MgCl₂·6H₂O, and CaCl₂ (Merck, USA) were added to adjust the concentration of ions in F.BP and F.HS&BB to be same as the original seawater. Note that the F.LMW after fractionation process contained high concentration of salts, no suitable NF/RO membrane was found to be able to remove the salts, thus ED was tested to separate LMW from salt ions.

Figure 4.1 Illustration of fractionation and concentration of organics in seawater by membrane technique. (i) MF membrane: pressure = 0.06 bar, dead end filtration mode; (ii) Operating conditions of NF membrane: pressure = 2.0 bar, initial flux = 8 L/m²h, crossflow velocity = 0.39 m/s; (iii) UF membrane: pressure = 0.16 bar, initial flux = 10 L/m²h, crossflow velocity = 0.39 m/s. Spiral wound membrane elements, 2.5-inch module with membrane area of 2.4 m², were employed in UF/NF processes.

4.2.2 Comparison of Model Foulants and Isolated Organic Fractions

Sodium alginate (SA), bovine serum albumin (BSA) and humic acid (HA) were applied for comparison with the isolated organic fractions from seawater. No common model foulant was used to represent the LMW in the literature. The stock solutions were prepared by filtering with a 0.2 μm syringe filter to remove the insoluble components. The concentrations of test solutions were adjusted to ~1 mg-C/L, with ionic concentrations equivalent to seawater (i.e., Na⁺, Ca²⁺, Mg²⁺), which was confirmed by TOC and ICP-OES measurements, respectively. Both model and isolated organic

solutions were analyzed by LC-OCD and F-EEM. In addition, the fouling potentials of isolated organic fractions and their corresponding model foulants were characterized via the Modified Fouling Index (MFI) method (Jin, Lee et al. 2017).

Here, SW-30HR RO membrane and dead-end filtration cell were used to retain all organic compounds. The feed organic concentrations were set at 1 mg-C/L and salt concentrations were similar to seawater. The stabilization of membrane was conducted for 12 h at 55 bar with DI water, followed by filtration of test solution. The flux was converted from the weight of collected permeate recorded by an electric balance (OHAUS, USA) as described in **Section 3.1.2**.

4.2.3 Bench-Scale RO Fouling Study of Isolated Organic Fractions

A laboratory-scale crossflow RO filtration setup was employed for fouling experiments as described in **Section 3.1.1**. A 0.2 μm cartridge filter was installed in the circulation loop to prevent bacteria growth in the system. The initial flux was set at 0.17 m/s and 20 L/m²h, respectively. The flux decline profile was used as the fouling indicator. The fouling process lasted for 6 days. In addition, the effects of monovalent and divalent ions on RO organic fouling were studied. Two types of salt solution at seawater concentrations were tested, (i) solution contained Na⁺ only, and (ii) solution contained Na⁺, Ca²⁺ and Mg²⁺ (by adding NaCl, MgCl₂·6H₂O, and CaCl₂).

At the end of experiment, membrane autopsy studies were performed. The foulants were extracted from fouled membrane surface by immersing membrane coupon into 25 ml of DI water and ultrasonication for 30 min, followed by 1 min vortex. The foulant solution was analyzed by LC-OCD. Note that only small volume of concentrated F.LMW (15 mL, >5mg/L) was obtained via SPE method, thus no SWRO fouling test that required large volume (~20L) was conducted for F.LMW; AOM.LMW as a

surrogate of F.LMW was tested instead (**Appendix A**). An electrodialysis unit (PCCell, GmbH, Germany) was used to remove the salt.

4.2.4 Adhesion and Cohesion Force Measurements

The intermolecular forces between isolated organic fractions and clean RO membrane (i.e., foulant-membrane) as well as organic-fouled membrane (i.e., foulant-foulant) were measured with an atomic force microscopy to understand the fouling behavior. A detailed protocol was shown in **Section 3.4.9**. Due to the concentration of F.LMW by membrane method would further increase the salt concentrations, herein, small volume with high concentration of F.LMW (i.e., 15 mL, >5 mg-C/L) that was free of salt was achieved by filtering ~5L of F.LMW through SPE cartridges (C18 Sep-Pak Vac, 6cc, 1.0g) according to the procedure in previous study (Jeong, Kim et al. 2013).

4.2.5 XDLVO Theory Analysis

A detailed procedure was summarized in **Section 3.4.10**. The functional groups of RO membrane and isolated organic fractions were identified by the ATR-FTIR. Prior to measurement, one milligram of isolated organic fraction was extracted as powder by the SPE method and freeze dried, followed by mixing with 100 mg of potassium bromide (KBr).

4.3 Results and Discussion

4.3.1 Performance of Fractionation and Concentration Process

4.3.1.1 Seawater Compositions

The organic and ionic concentrations of seawater are summarized in **Table 4.1**. The samples ($n = 15$) were collected and characterized over a nine-month period. It was found that the concentration of organics remained relatively constant; the average DOC

was 1175.4 ± 69.3 $\mu\text{g/L}$. In details, the concentration of HS was 495.3 ± 72.1 $\mu\text{g/L}$, which occupied the largest portion (42%), while the concentration of BB was 182.6 ± 33.8 $\mu\text{g/L}$ (16%). It shall be noted that BB is the breakdown product of HS which has a lower MW (Huber, Balz et al. 2011), and in current study, the terms HS and BB were combined as HS&BB, which occupied 58% of total DOC. The concentration of LMW compounds showed more obvious fluctuations (i.e., the highest reading was 504 $\mu\text{g/L}$ and the lowest reading was 223 $\mu\text{g/L}$). This could be caused by the variations of microorganisms bioactivity in seawater which was related to organics photolysis resulting in a series of radical and fragmentation reactions (Jeong, Naidu et al. 2016). Moreover, the oxidation processes could also break down the organics from large MW to smaller MW (Filloux, Gernjak et al. 2016). In contrast to wastewater or river water, BP was present at a low concentration in seawater, thus large volume of seawater (~ 1200 L) was required for the isolation process to collect sufficient amount of BP. Furthermore, high concentration of salt (**Table 4.4**) may impose high osmotic pressure effect in the isolation process with NF membrane.

Table 4.1 Compositions of seawater in this study (n = 15)

Parameter	Value
DOC ($\mu\text{g/L}$)	1175.4 $\pm$ 69.3
HOC ($\mu\text{g/L}$)	63.2 $\pm$ 29.1
Biopolymers ($\mu\text{g/L}$)	79.0 $\pm$ 22.8
Humic substances ($\mu\text{g/L}$)	495.3 $\pm$ 72.1
Building blocks ($\mu\text{g/L}$)	182.6 $\pm$ 33.8
LMW ($\mu\text{g/L}$)	355.3 $\pm$ 116.9
Ca ²⁺ (mg/L)	362.1 $\pm$ 0.9
Mg ²⁺ (mg/L)	1252.3 $\pm$ 8.7
Na ⁺ (mg/L)	10600 $\pm$ 125
Conductivity (mS/cm)	47.5 $\pm$ 0.2

DOC: dissolved organic carbon; HOC: hydrophobic organic carbon; LMW: low molecular weight compounds

4.3.1.2 Membrane Selection, Fractionation Performance and Mass Balance

In this study, isolated organic fractions from seawater were obtained by membrane filtration technique. Some important technical parameters such as contact angle, surface charge, and MWCO of the applied commercial UF and NF membranes were summarized in **Table 4.2**. All the measured MWCOs of the membranes were slightly larger than the specifications provided by the manufacturers. The information on the standards used and methods of characterization by different suppliers were not available. In this study, spherical and uncharged organics and uniform approach were applied for measuring the MWCOs of different membranes, which could provide a more comprehensive and precise information to allow comparison of different membranes.

It is worth to note that the criteria of the membrane selection is based on the MW of organics defined by LC-OCD (i.e., BP, HS&BB, and LMW compounds).

Table 4.2 Contact angle, zeta potential (pH = pH_{sw}), molecular weight cut off (MWCO) and material of UF and NF membranes

Membrane	Contact Angle (°)	Surface charge (mV) (pH = pH _{sw})	Tested MWCO (Da)	Manufacturer's MWCO (kDa)	Material
GH	58.2±3.6	-42.3±3.4	N.A	2.0	PA
XT	59.5±3.7	-39.8±2.1	1144±91	1.0	PES
NFG	41.3±2.5	-27.1±1.5	1022±53	0.6-0.8	PA
XN45	53.9±1.5	-49.2±4.2	523±22	0.3-0.5	PPA
NFW	35.5±1.1	-36.0±2.2	536±38	0.3-0.5	PA
NF270	9.5±2.2	-47.5±1.8	538±44	N.A	PA
NF90	75.2±4.2	-45.5±3.6	258±12	N.A	PA

N.A: not applicable

PA: polyamide

PES: polyethersulfone

PPA: polyphthalamide

The organic and salt rejections for various membranes were presented in **Figure 4.2**. The organics can be grouped into 4 main groups (I, tyrosine protein-like; II, protein-like; III, fulvic-like; and IV, microbial by-product-like) based on the rejection properties. In comparison to other membranes, Group II membranes: XT and NFG exhibited an 80% rejection of BP while allowing the passage of HS&BB and LMW, i.e., rejection < 25%. It is worth to mention that the lower salt rejection of the membrane is desired to minimize the osmotic pressure effect during the isolation process. Therefore, XT (UF

membrane) with larger pore size (**Table 4.2**) and negligible salt rejection relative to NFG was selected for isolating the BP fraction into the retentate. **Figure 4.2a** illustrates when using GH (Group I membrane) with MWCO of ~2 kDa, the rejection of BP was only ~40%, contrary to the 80% rejection by XT with MWCO of ~1 kDa, thus GH was not suitable in this work (**Figure 4.3**). This observation also suggested that majority of BP in the seawater in this study has molecular weight smaller than the value of 20 kDa reported in previous study (Huber, Balz et al. 2011). A similar result was also found in another study which concluded that seawater organics contained aromatic proteins in the range of >1 kDa (Penru, Simon et al. 2013). The Group III membranes: XN45, NFW and NF270, showed greater than 80% rejection of BP and HS&BB while less than 20% rejection of LMW (**Figure 4.2a**). It shall be noted that the rejection properties of NF membranes are governed by the interplay of steric effects (size exclusion), electrostatic effect (Donnan exclusion), and dielectric exclusion (Labban, Liu et al. 2017). Since the NFW membrane showed the best separation of LMW from BP and HS&BB, as well as a relatively lower salt rejection among all the NF membranes in the same group (**Figure 4.2b**), it was the most suitable for isolating the LMW fraction into the permeate. The NF90 (Group IV) showed the greatest rejection for most of organic compounds as well as divalent ions while allowing the passage of monovalent ions, it could be the most suitable for concentration purpose, but not for organic fractionation. Hence, by comprehensively considering the organic and salt rejections of all membranes, XT and NFW membranes were selected for the subsequent isolation process as the UF and NF membrane, respectively.

Figure 4.2 (a) Organic rejections, and (b) Salt rejections by different UF and NF membranes (seawater as feed, measurements with three repetitions (error bar for $n = 3$) were obtained from dead-end filtration at 2 bar except NF90 at 30 bar).

Figure 4.3 LC-OCD analysis of organic rejection of GH and XT membranes.

The fractionation performance of selected membranes was further investigated by comparing the LC-OCD chromatograms of seawater and the isolated organic samples. The fractionation process was completed when the expected organic fractions were achieved in each organic fraction. As depicted in **Figure 4.4a**, DOM in seawater was successfully fractionated and concentrated into three main fractions (i.e., F.BP, F.HS&BB, and F.LMW); BP was dominant in the F.BP with ~95% of total DOC content, HS&BB was dominant in the F.HS&BB with 93% of total DOC content, and LMW was dominant in the F.LMW with 87% of total DOC content (**Figure 4.4b**). From the

F.BP chromatogram (**Figure 4.4a**), there were two peaks appeared at the elution time of 31 min and 37 min, respectively, indicated that the biopolymers were made up of two different types of organics, while the distinction was not observed in the original seawater chromatogram possibly due to overlapping of peaks at very low concentration. In addition, small amount of other organics still present in each main fraction (**Figure 4.4b**) due to the non-perfect rejection properties of membranes (**Figure 4.2**) as well as the duration of diafiltration process, i.e., longer filtration time allows higher purity but requires larger amount of DI water to be added, which needs to be removed to get the desired concentration.

Figure 4.4 (a) LC-OCD chromatograms of natural seawater and fractionated organics (i.e. BP, HS&BB and LMW fractions), and (b) proportion of organics in each isolated organic fraction, calculated from LC-OCD analysis results.

The recovery of organic compounds was critical to determine the efficiency of the membrane technique for fractionation of organics in seawater. The mass balance of organic compounds for the fractionation and concentration process for one batch of 285 L of seawater was performed (**Table 4.3**). According to the LC-OCD data and mass balance calculation, 82% of BP was collected into the F.BP while 5% of BP was loss into the F.HS&BB, and remaining 13% of BP (~2 mg) was unaccounted for, which could be attributed to adsorption onto tubings and membranes. Similarly, only 84% of

LMW was collected into the F.LMW, with 17% loss into the F.HS&BB. On the other hand, high recovery of HS&BB was achieved with 95% of HS&BB was collected into the F.HS&BB. Unlike BP, all HS&BB and LMW were accounted for, indicated insignificant degree of adsorption onto tubings and membranes. Overall, >80% recovery of organic compounds can be achieved by the membrane technique for fractionation, compared to other techniques which have lower efficiency with recovery of ~21% (Park, Nam et al. 2019).

Table 4.3 The recovery of organic compounds in the fractionation and concentration process by membrane technique in one batch of experiment with initial volume of 285 litres of seawater.

	BP (mg)	Recovery	HS&BB (mg)	Recovery	LMW (mg)	Recovery
Seawater	20.52±1.23	-	216.32±1.05	-	89.21±0.56	-
F.BP	16.83±0.49	82%	< 0.44	< 0.2%	< 0.21	< 0.2%
F.HS&BB	1.03±0.02	5%	205.49±1.57	95%	15.33±0.78	17%
F.LMW	<0.15	<0.7%	10.97±0.46	5%	74.93±0.32	83%

Due to the rejection properties of membranes and dilution effect from the added water during diafiltration process, each fraction contained different salinity at the end of fractionation process, thus salt adjustment to seawater concentration (i.e., same amount of total dissolved solids as measured by conductivity reading) was performed before used for further studies. **Table 4.4** describes the ionic concentration of F.BP and F.HS&BB before and after salt adjustment. No adjustment of salt was conducted for F.LMW as it contained high concentration of salt after the fractionation process.

Table 4.4 Ions concentrations in each organic fraction before and after salt adjustment.

	F.BP			F.HS&BB			F.LMW	
	after isolation			after isolation			after isolation	
	process	Na	CaMgNa	process	Na ⁺	CaMgNa	process	CaMgNa
Ca ²⁺ (mg/L)	<0.30	<0.23	331.5	64.51	<1.29	450.9	221.9	462.4
			±1.5	±2.2		±1.7	±3.3	±2.1
Mg ²⁺ (mg/L)	<1.32	<0.97	1287	197.2	<3.92	1292	787.3	1268
			±13	±2.4		±13	±21	±22
Na ⁺ (mg/L)	<0.28	16600	10510	32.8	17090	10090	10820	10879
		±101	±95	±4.15	±85	±67	±88	±54
Conductivity	<0.13	47.93	48.33	5.78	48.76	48.25	46.23	49.31
(mS/cm)		±0.65	±0.36	±0.14	±0.62	±0.22	±0.85	±0.55

Note: N.D.: not detectable

4.3.2 Chemical Analysis and Fouling Potential of Model Organic Foulants and Isolated Organic Fractions

Figure 4.5 shows the comparison of LC-OCD chromatograms of isolated organic fractions and model foulants such as SA, BSA, and HA. Different elution times were observed for SA (30 min) and BSA (34 min), which were corresponded to the two peaks in F.BP, thus the biopolymers in seawater were mainly made up of polysaccharides-like and protein-like compounds. Whereas the elution time of HA was 40 min, which showed greater MW than the natural organics (HS&BB) in seawater. Both F.LMW and AOM.LMW had similar elution time at ~70 min.

Figure 4.5 LC-OCD chromatograms of (a) F.BP and model foulants of SA and BSA, (b) F.HS&BB and model foulant of HA, and (c) F.LMW and model foulant of AOM.LMW.

Refer to the FEEM results in **Figure 4.6a**, seawater consists of tyrosine protein-like (I; Em: 250-330 nm, Ex: 200-250 nm), protein-like organics (II; Em: 330-380 nm, Ex: 200-250 nm) and fulvic-like organics (III; Em: 380-550 nm, Ex: 200-250 nm). It has higher intensity (i.e., higher concentration) for fulvic-like organics (III) but lower intensity for humic-like organics (V; Em: 380-550 nm, Ex: 250-400 nm); the fulvic-like organics have been reported to have smaller MW than humic-like compounds, which could explain the different MW distribution of F.HS&BB and model HA (Perminova, Frimmel et al. 2003). In addition, no obvious signal was observed for microbial by-product-like organics (IV; Em: 250-380 nm, Ex: 250-320 nm). As shown in **Figure 4.6b**, F.BP displayed higher concentrations of tyrosine protein-like compounds (I) than tryptophan protein-like compounds (II), and the intensities corresponding to humic-like, fulvic-like and microbial by-product-like organics were undetectable. SA displayed a weak intensity in region I, while BSA had a strong signal in protein-like materials (II) and microbial by-product-like organics (IV), with 30 times higher in intensity than F.BP. The F.HS&BB (**Figure 4.6c**) was composed of protein-like (I, II), fulvic-like (III) and humic-like (IV) organics. Since F.HS&BB was made up of 93% HS&BB, 7% LMW and residual BP (**Figure 4.6b**), the intensity in region II may be contributed by the LMW, which was rich in tryptophan protein-like organics (II); while the intensity in region I may be due to the residual BP from the fractionation process or natural humic-

fulvic substances that contains protein-like materials (Rodriguez 2011, Yu, Song et al. 2014). The comparison of F.HS&BB and HA appeared to show significant difference in their fluorescence intensities. This could be attributed to the fact that certain amount of the organics in seawater are non-fluorescent. In another word, seawater contains more photochemically degraded DOM or relatively less aromatic DOM compared to other water sources such as ground water and surface water (Zhou, Guo et al. 2016). On the other hand, AOM.LMW which was derived from marine algae, was rich in tryptophan protein-like organics (II) similar to F.LMW.

Figure 4.6 FEEM spectroscopy of (a) seawater, (b) F.BP, (c) F.HS&BB, (d) F.LMW, (e) SA, (f) BSA, (g) HA, and (h) AOM.LMW.

The fouling potential of isolated organic fractions and model foulants are illustrated in **Figure 4.7**. The fouling potentials of isolated organic fractions are in the following order: F.BP > F.LMW > F.HS&BB. It was found that the corresponding model foulants

had overestimated the fouling potentials of isolated organic fractions i.e. the MFI values of model foulants were higher. In this regard, the fouling potential is highly associated with the physicochemical properties of the foulant solutions.

Figure 4.7 Plot of t/V vs. V (t = filtration time, V = cumulated volume) for (a) model organic foulants, and (b) isolated organic fractions. The MFI value, which represents fouling potential, is the slope of the fitted line in the cake filtration stage.

The above analyses show that DOM in seawater have different characteristics than those model foulants, such as SA, BSA and HA, which are commonly used in membrane fouling studies, thus they may not provide a complete representation of RO membrane fouling by DOM in seawater. Therefore, they were not included in the subsequent studies. Only the AOM.LMW which has similar properties as F.LMW was further investigated in the RO fouling test.

4.3.3 Foulant-Membrane and Foulant-Foulant Interactions

4.3.3.1 Adhesion and Cohesion Force Measurement by AFM

To further explore the fouling behaviors, the adhesion forces between the isolated organic fractions and the clean RO membrane surface as well as organic-fouled membrane surface were measured under different salt conditions. **Figure 4.8** shows the retraction force-distance values of foulant-membrane and foulant-foulant, and the

force-distance curve with frequency distributions are shown in **Figure 4.9**. In all cases, the magnitude of adhesion forces of foulant-membrane was larger than that of foulant-foulant for all isolated organic fractions (**Figure 4.8**), for example, the interaction forces of F.BP-RO compared to F.BP-F.BP in solution of Na^+ and $\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$ were higher by 1.5x and 1.9x, respectively. The results suggested that foulant-membrane interaction was dominant, as such initial fouling was the key driver in SWRO organic fouling. In addition, the foulant-membrane interaction was in the following order: F.BP-RO > F.LMW-RO > F.HS&BB-RO. This result agrees with previous studies that biopolymer is the major foulant in SWRO process (Li, Lee et al. 2016). Meanwhile, the retraction forces of F.LMW-RO were -1.21 ± 0.88 mN/m (Na^+ condition) and -2.94 ± 0.45 mN/m ($\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$ condition), respectively; these values were relatively smaller than that of F.BP-RO (-4.16 ± 0.53 and -6.40 ± 0.95 mN/m, respectively) but higher than that of F.HS&BB-RO (-1.09 ± 0.17 and -1.19 ± 0.22 mN/m). Therefore, the role of LMW in membrane fouling shall not be overlooked (i.e., previous studies did not pay much attention to LMW compounds); moreover, a recent study found that LMW may trigger biofouling in RO process (Jeong, Naidu et al. 2016). However, the low adhesion force of F.HS&BB-RO was in conflict with other studies, which showed a stronger adhesion force by using model humic-like organic, particularly in the presence of divalent ions. Again, this is a clear indication that HS&BB in seawater has significantly different features compared to typical model foulants used in lab studies, that could result in different fouling behavior on RO membrane.

Figure 4.8 Retraction force-distance values of foulant-membrane and foulant-foulant under salt conditions of (a) Na⁺, and (b) Na⁺, Ca²⁺, and Mg²⁺.

In comparison, the presence of divalent ions showed greater impact on the interaction forces of F.BP-RO and F.LMW-RO as well as F.BP-F.BP and F.LMW-F.LMW than F.HS&BB-RO and F.HS&BB-F.HS&BB. For instance, the calcium-carboxylate complexation has a critical role in the SWRO organic fouling: (i) the foulant-calcium-foulant interaction can be explained by the “egg-box” model (Grant, Morris et al. 1973) as biopolymers mainly consists of polysaccharides and proteins and LMW also consists of protein-like compounds (**Figure 4.6d**), in which Ca²⁺ binds preferentially to the oxygen atoms of the carboxylate groups in a highly organized manner and form bridges between adjacent molecules resulting in the egg-box-shaped gel network (Lee and Elimelech 2006); (ii) in foulant-calcium-membrane interaction, Ca²⁺ formed bridges between the carboxylate functionality on membrane and foulant interfaces, in which the attraction appeared to be much stronger than in (i). The presence of divalent ions in F.HS&BB did not have significant effect on foulant-foulant and foulant-membrane interactions perhaps due to lack of binding sites on the organic compounds.

Figure 4.9 Retraction force-distance curves of foulant-membrane and foulant-foulant under salt conditions of (a) Na⁺, and (b) Na⁺, Ca²⁺, and Mg²⁺, with frequency distribution histogram.

Figure 4.9 continued. Retraction force-distance curves of foulant-membrane and foulant-foulant under salt conditions of (a) Na^+ , and (b) Na^+ , Ca^{2+} , and Mg^{2+} , with frequency distribution histogram.

4.3.3.2 Interfacial Free Energy

Using the XDLVO theory (van Oss 1993, Van Oss 2006), the interfacial free energy of foulant-membrane and foulant-foulant interactions can be estimated indirectly from the surface tension-contact angle and surface charge-zeta potential measurements. The contact angles measured by different probe liquids and zeta potentials of clean and organic-fouled membranes are listed in **Table 4.5**, in which significant differences between clean and organic-fouled membrane are observed. In general, the organic-fouled membranes were more hydrophilic and negatively charged than the clean

membrane, which was not surprising as majority of the DOM in seawater were hydrophilic (i.e., only 5% of DOC was HOC). The calculated surface tensions and interfacial free energies of foulant-foulant (i.e., cohesion energy) and foulant-membrane (i.e., adhesion energy) are summarized in **Table 4.6**.

Table 4.5 Contact angle and zeta potential of clean RO membrane and fouled RO membranes with isolated organic fractions.

Membrane/Fouled	Contact angle (°)					Zeta potential (mV)
	DI water	Glycerol	Diiodomethane	Na ⁺	Na ⁺ +Ca ²⁺ +Mg ²⁺	
Clean	65.6 ± 4.2	69.5 ± 3.2	40.1 ± 2.8	75.3 ± 2.2	89.4 ± 1.9	-15.8 ± 0.5
F.BP	53.3 ± 1.2	51.7 ± 6.4	43.5 ± 2.4	72.8 ± 0.9	74.7 ± 2.6	-45.6 ± 0.4
F.HS&BB	42.1 ± 1.5	40.8 ± 4.5	12.4 ± 3.4	44.9 ± 3.3	46.5 ± 4.4	-52.0 ± 0.1
F.LMW	62.4 ± 3.5	61.3 ± 2.5	29.9 ± 5.2	68.4 ± 3.8	70.2 ± 3.2	-30.4 ± 0.9
AOM.LMW	65.2 ± 2.8	84.2 ± 4.6	42.6 ± 1.3	75.8 ± 1.8	80.3 ± 8.3	-23.7 ± 2.1

Note: Refer to Table 3 for concentration of solution with Na⁺ and Na⁺+Ca²⁺+Mg²⁺

It is worth noting that positive value of free energy means repulsion while negative value means attraction. It was found that all the free energies were negative values, meaning high potential of membrane fouling by DOM in seawater; and the magnitude of adhesion energies were higher than the cohesion energies, which suggested that initial fouling was dominant in SWRO process, and agreed with the AFM measurements. In addition, F.BP demonstrated the highest free energies for all test conditions (**Table 4.6**), followed by F.LMW. The role of electrostatic double layer, i.e., ΔG_{EL} , was negligible at high ionic strength such as seawater due to the electrostatic shielding effect (Tang, Chong et al. 2011). Particularly, the Lewis acid-base (AB) interaction was observed as the primary factor in the foulant-foulant and foulant-membrane interactions by F.BP and F.LMW; though LW interaction was more important in the case of F.HS&BB-F.HS&BB. It has been reported that van der Waals

force has a lower contribution for the attraction of different solid materials, compared with the short-range acid-base (AB) interaction when two solid materials immersed in a polar solvent (i.e., water) (Brant and Childress 2002). From the ATR-FTIR analysis (**Figure 4.10**), F.BP contained high intensity of O-H and N-H in the vicinity of 3400 cm^{-1} (Belfer, Purinson et al. 1998) that can interact with the C=O group in the RO membrane, while these functional groups were insignificant in F.HS&BB and F.LMW. It indicated that F.BP contained high amount of polysaccharide-like organics, a major contributor in RO fouling due to its sticky feature (Jermann, Pronk et al. 2007). Therefore, the interaction energies of foulant-foulant and foulant-membrane were higher for F.BP than F.HS&BB and F.LMW. The impact of divalent ions was similar to the AFM results where greater free energies were observed especially for foulant-membrane.

Figure 4.10 ATR-FTIR spectra of RO membrane and isolated organic fractions.

Table 4.6 Surface tension and interfacial free energy of foulant-membrane and foulant-foulant (mJ/m²)

	Surface Tension (mJ/m ²)					Free Energy (mJ/m ²)			
	γ^{LW}	γ^+	γ^-	γ^{AB}	γ^{TOT}	ΔG^{LW}	ΔG^{AB}	ΔG^{EL}	ΔG^{TOT}
Na⁺									
F.BP-RO	-	-	-	-	-	-4.796	-42.570	-1.685	-49.051
F.BP-F.BP	37.807	2.407	4.424	6.526	44.333	-4.379	-41.232	0.460	-45.151
F.HS&BB-RO	-	-	-	-	-	-7.697	-15.230	-2.533	-25.460
F.HS&BB-F.HS&BB	49.615	0.422	26.555	6.697	56.312	-11.279	1.819	0.597	-8.863
F.LMW-RO	-	-	-	-	-	-6.433	-33.542	-0.336	-40.312
F.LMW-F.LMW	44.274	0.046	12.195	1.501	45.775	-7.879	-30.123	0.204	-37.797
AOM.LMW-RO	-	-	-	-	-	-4.918	-18.425	-0.047	-23.390
AOM.LMW-AOM.LMW	38.273	1.736	21.067	12.095	50.368	-4.605	-6.865	0.124	-11.347
Na⁺+Ca²⁺+Mg²⁺									
F.BP-RO	-	-	-	-	-	-4.796	-57.599	-1.685	-64.080
F.BP-F.BP	37.807	2.667	3.203	5.845	43.652	-4.379	-44.555	0.460	-48.474
F.HS&BB-RO	-	-	-	-	-	-7.697	-37.534	-2.533	-47.764
F.HS&BB-F.HS&BB	49.615	0.492	24.565	6.950	56.565	-11.279	-1.626	0.597	-12.308
F.LMW-RO	-	-	-	-	-	-6.433	-56.427	-0.336	-63.197
F.LMW-F.LMW	44.274	0.083	10.298	1.853	46.127	-7.879	-35.055	0.204	-42.730
AOM.LMW-RO	-	-	-	-	-	-4.918	-44.126	-0.047	-49.091
AOM.LMW-AOM.LMW	38.273	1.243	14.537	8.503	46.776	-4.605	-19.468	0.124	-23.950

F.BP: Biopolymer fraction

F.HS&BB: Humic substance & building block fraction

F.LMW: Low molecular weight fraction

AOM.LMW: Low molecular weight fraction of algal organic matter

RO: Reverse osmosis

4.3.4 RO Fouling of Isolated Organic Fractions

The flux decline profiles and the amount of foulants extracted from the organic-fouled RO membranes were illustrated in **Figure 4.11** and **Figure 4.12**, respectively. As mentioned above, no fouling test for F.LMW was conducted, AOM.LMW was used as a surrogate of F.LMW instead. Both results clearly showed that the membrane fouling caused by F.BP was more severe than that by F.HS&BB, in which (i) more than 10% decline in flux was observed, (ii) significant amount of foulants (i.e., biopolymer) were detected, especially in the presence of divalent ions. In addition, the flux decline mainly happened at the early stage of fouling process. These observed flux decline patterns for F.BP and F.HS&BB in Na^+ and $\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$ were well-correlated to the stronger interaction of foulant-membrane according to XDLVO and AFM analyses. At the later stage of fouling, the rate of flux decline gradually slowed down due to weaker cohesion forces between foulant and foulant. Similar to F.BP and F.HS&BB, it was found that the RO membrane fouling of AOM.LMW, a surrogate of LMW, can also be predicted via the foulant-foulant and membrane-foulant interactions (**Table 4.7** and **Figure 4.11**). The results also supported the findings that biopolymer has greater impact than AOM.LMW on RO membrane fouling.

Figure 4.11 Flux decline curves under different salt conditions for (a) F.BP, (b) F.HS&BB, and (c) AOM.LMW (force-distant curve was shown in the graph).

Figure 4.11 continued. Flux decline curves under different salt conditions for (a) F.BP, (b) F.HS&BB, and (c) AOM.LMW (force-distant curve was shown in the graph).

Figure 4.12 LCOCD analysis of foulants extracted from organic-fouled RO membrane by (a) F.BP, (b) F.HS&BB as feed solutions, and (c) AOM.LMW.

Figure 4.12 continued. LCOCD analysis of foulants extracted from organic-fouled RO membrane by (a) F.BP, (b) F.HS&BB as feed solutions, and (c) AOM.LMW.

4.4 Conclusions

In this study, seawater DOM was fractionated into three major fractions based on their MW using UF/NF membranes with different MWCOs, followed by the comparison with corresponding model foulants in terms of their characteristics and fouling potential. The fouling mechanisms of isolated organic fractions and the influence of ionic species were investigated by AFM analysis, XDLVO theory and RO fouling experiments. The conclusions are summarized as follow:

- (i) Membrane technique was successfully applied, with recovery of >80%, to fractionate the DOM in seawater into three main fractions: biopolymer (F.BP, MW: >1000 Da), humic substances and building block, (F.HS&BB, MW: 350 – 1000 Da) and low molecular weight compounds (F.LMW, MW: <350 Da);
- (ii) The biopolymer in seawater was mainly made up of polysaccharides-like and protein-like compounds, the HS&BB showed smaller MW, all isolated organic fractions showed lower fluorescence intensities, and had lower fouling potentials than common model foulants used in SWRO fouling studies;

(iii) From the SWRO fouling tests, AFM measurements and XDLVO theory analysis, the F.BP was found to be the major contributor, followed by F.LMW, while F.HS&BB showed negligible impact to membrane fouling. In addition, initial fouling (i.e., foulant-membrane interaction) was the key driver and fouling was exacerbated in the presence of divalent ions, i.e., Ca^{2+} -carboxylate complexation between foulant and membrane as well as foulant and foulant;

This chapter offered a detailed protocol of fractionation process from seawater organic matters, which provided the possibility to explore more information from these fractions on membrane fouling. Isolated organic fractions are more competitive with the model organics. In addition, in this chapter, the implication is that existing seawater pre-treatment method such as MF/UF is only able to partially remove the large MW biopolymer, and not effective towards the small MW biopolymer, humic substances as well as LMW, thus the RO fouling may only be delayed but cannot be prevented. The NF membrane (i.e., MWCO $\sim$ 300-500 Da) can remove majority of the DOMs in seawater but the cost associated with NF pre-treatment needs to be considered. In addition, the biofouling potential and the role of these DOMs in seawater on SWRO fouling are not fully understood, and need further investigations in future studies.

CHAPTER 5 Impact of Isolated Dissolved Organic Fractions from Seawater on Biofouling in Reverse Osmosis (RO) Desalination Process

This chapter describes the biofouling potential of each isolated dissolved organic fractions, their bio-transformation with the existence of bacteria, and their biofouling behavior. Modified AOC method which is suitable for seawater condition was conducted to analyze the biofouling potential in seawater. Bio-transformation gave the insight of how the organic matter was affected by the bacteria. All the information provided a good understanding of biofouling mechanism.

5.1 Introduction

From SWRO organic fouling study in **Chapter 4**, the rate of fouling was in the order of $F_{BP} > F_{LMW} > F_{HS\&BB}$. However, the effect of these isolated organic fractions on SWRO biofouling behavior has not been systematically investigated.

The aims of this study are to investigate the biofouling potential of the isolated organic fractions from seawater and to evaluate their impacts on membrane biofouling in SWRO desalination process. First, three major dissolved organic fractions were isolated from seawater by a membrane-based fractionation and concentration process using a combination of ultrafiltration (UF) and nanofiltration (NF) membranes. Second, the biofouling potential of the isolated dissolved organic fractions was characterized by the AOC measurement. Third, the organic transformation that occurred during the bacteria growth was examined. Fourth, the bacteria-clean/fouled membrane interactions were characterized by atomic force microscopy (AFM) analysis. Last, the impact of isolated dissolved organic fractions on SWRO biofouling was investigated using a laboratory cross-flow RO setup.

5.2. Materials and Methods

5.2.1 Fractionation and Concentration of Dissolved Organic Fractions from Seawater

The collection of seawater was described in **Section 3.3.1**. Additional inorganic salts such as NaCl, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, and CaCl_2 were added to adjust the ions concentrations to level similar to seawater. ICP-OES was used to measure the ionic concentration.

5.2.2 Assimilable Organic Carbon (AOC) Measurement

As shown in **Figure 5.1**, to obtain the growth medium, each isolated dissolved organic fraction (10 mL, $\sim 0.5 \text{ mg-C/L}$) was first filtered through a $0.22 \mu\text{m}$ PES syringe filter (Millipore, USA) into a 40 mL AOC-free vial. The protocol of AOC measurement can refer to **Section 3.4.4**.

Figure 5.1 The illustrations of (i) inoculum preparation, (ii) sample preparation and (iii) cell count measurement in AOC analysis.

5.2.3 Organic Transformation During Bacteria Growth in Isolated Dissolved Organic Fractions

Vibrio sp. B2 was selected as model bacterium. The preparation of the stock solution was described in **Section 3.3.4**. The preparation of growth medium of isolated dissolved organic fraction was same as described in **Figure 5.1(ii)**. The *Vibrio* sp. B2 inoculum was injected into each vial to achieve an approximate cell count of 6×10^5 cells/mL, then was incubated at 30°C and 40 rpm for 3 days. A blank test with only the salts solution, i.e., carbon-free synthetic seawater, was conducted to analyze the background from the inoculum alone (Supporting Information). The organic compounds in each test solution were characterized by the LC-OCD and F-EEM analyses.

5.2.4 Atomic Force Microscopy (AFM) Measurement

The adhesion and cohesion force between bacteria-virgin RO membrane, bacteria-F.BP, bacteria-F.HS&BB, bacteria-F.LMW, and bacteria-bacteria were examined by AFM. The procedure was described in **Section 3.4.9**.

5.2.5 Impact of Isolated Dissolved Organic Fractions on SWRO biofouling

5.2.5.1 RO system and Biofouling Experiment

The RO setup has been described in **Section 3.1.1**. The commercial RO membrane (SW30-HR, DOW FilmTec, USA) with an effective area of 0.0045 m² was used. The RO membrane was soaked in DI water for 24 h prior use and was compacted at 6.1 MPa for at least 12 hours with DI water to achieve a stabilized permeate flux. Then, the DI water in feed tank was replaced to the test solution with isolated dissolved organic fraction (DOC = 0.5 mg-C/L). The initial flux was set at 30 L/m²h and crossflow velocity of 0.17 m/s. The RO system was operated in a fully recycled mode, where the retentate and permeate were returned to the feed tank to maintain constant volume and

concentration. To initiate biofouling, the *Vibrio* sp. B2 stock solution (**Section 3.3.4**) was injected at a flowrate of 0.5 mL/min by an injection pump (ELDEX, Model 5979 OptosPump 2HM) into the feed line to achieve an average cell concentration of 1.5×10^4 cells/mL. The bacteria stock solution was replaced every 2 days. To prevent the feed tank from turning into a bioreactor, 2 units of 0.2 μm cartridge filters were installed at the retentate line before returning to the feed tank and the feed solution was replenished daily. The biofouling experiments lasted for 6 days.

5.2.5.2 Membrane Autopsy Analysis

The fouled membrane was taken out from RO crossflow cell after 6-day operation. The extraction of foulant can refer to **Section 4.2.3**. The foulant solution was further analyzed using LC-OCD, F-EEM, and EPS analysis. Biofilm on membrane surface was analyzed by confocal laser scanning microscopy (CLSM). The procedure of CLSM was summarized in **Section 3.4.5**.

5.3 Results and Discussion

5.3.1 Isolated Dissolved Organic Fractions from Seawater

As shown in **Figure 5.2**, the dissolved organic content in seawater contained 6% BP, 52% HS&BB and 42% LMW. These dissolved organic compounds were successfully fractionated and concentrated into three major fractions, i.e., F.BP (MW >1000 Da), F.HS&BB (MW 350-1000 Da) and F.LMW (MW <350 Da). For each fraction, the final organic concentration was adjusted to DOC = 0.5 mg-C/L while the ions concentrations were adjusted to level similar to the original seawater as summarized in **Table 5.1**. These solutions will be used in the subsequent tests.

Table 5.1 Concentration of dissolved ions in isolated dissolved organic fractions before and after ionic adjustment.

	Original (mg/L)			Conductivity	Adjusted (mg/L)			Conductivity
	Ca ²⁺	Mg ²⁺	Na ⁺	mS/cm	Ca ²⁺	Mg ²⁺	Na ⁺	mS/cm
Seawater	371.1 ± 0.9	1189 ± 9	10589 ± 101	47.2 ± 0.2	No adjustment of ions concentration			
F.BP	<1.4	<3.2	<0.9	< 0.3	361.5 ± 1.8	1213 ± 16	10670 ± 105	47.3 ± 0.2
F.HS&BB	34.5 ± 3.2	153.1 ± 2.8	21.6 ± 3.6	4.4 ± 0.1	400.3 ± 0.9	1198 ± 18	10790 ± 97	47.9 ± 0.2
F.LMW	313.9 ± 2	1109 ± 9	10310 ± 30	46.2 ± 2.1	391.9 ± 3.3	1122 ± 15	10770 ± 121	47.8 ± 0.1

Figure 5.2 LC-OCD analysis of organic compounds in original seawater and isolated dissolved organic fractions. The percentage value is the % ratio of DOC of BP, HS&BB, or LMW to total DOC (the chromatograph of each fraction can refer to Figure 4.4).

5.3.2 Assimilable Organic Carbon (AOC) Analysis

The biofouling potential of each isolated dissolved organic fraction was characterized by the AOC content, which was based on the growth curve of indigenous bacteria at DOC = 0.5 mg-C/L (**Figure 5.3**), are summarized in **Table 5.2**. The contribution of AOC and DOC from each organic compound in seawater is summarized in **Table 5.3**. The F.LMW showed the highest growth rate of 0.60 d⁻¹ and AOC value was 172 ± 15 µg-C/L; F.BP displayed much slower cell growth of 0.20 d⁻¹ and AOC value was 101 ±

32 $\mu\text{g-C/L}$; F.HS&BB showed the lowest cell growth of 0.16 d^{-1} and AOC value was $43 \pm 13 \mu\text{g-C/L}$. Thus, the AOC/DOC ratio was in the sequence of F.LMW ($\sim 35\%$) > F.BP ($\sim 19\%$) > F.HS&BB ($\sim 8\%$). Typically, humic substances showed high resistance to biodegradation (van der Kooij, Hijnen et al. 1989), thus there was poor correlation between AOC and HS&BB (Jeong and Vigneswaran 2015). Unlike HS&BB, LMW which composed of high proportion of protein-like organics (**Chapter 4**) as well as BP which mainly composed of protein and polysaccharides (Villacorte, Ekowati et al. 2017), could serve as the nutrient source in supporting microbial growth, thus both gave higher AOC/DOC readings. In addition, when comparing F.LWM with F.BP, the cell growth rate was $\sim \times 3$ higher while the AOC concentration was only about $\times 1.7$ higher, could be attributed to the smaller molecular weight of LMW ($\text{MW} < 350 \text{ Da}$) compared to BP ($\text{MW} > 1000 \text{ Da}$), which was more readily consumed by microorganisms (Passow 2002, Villacorte, Ekowati et al. 2017). This finding was important as water samples with the same amount of AOC but different organic compositions, could potentially result in different SWRO biofouling rates.

Figure 5.3 Growth curve of indigenous inoculum in different isolated dissolved organic fractions from seawater. Initial concentration of organic in each fraction = 0.5 mg-C/L (Error bars for n = 3).

Table 5.2 AOC/DOC of isolated dissolved organic fractions.

	AOC ^a	DOC ^b	AOC/DOC
	($\mu\text{g-C/L}$)	($\mu\text{g-C/L}$)	(%)
Seawater (diluted) ^c	102 $\pm$ 35	523 $\pm$ 20	19.5
F.BP	101 $\pm$ 32	534 $\pm$ 29	18.9
F.HS&BB	43 $\pm$ 13	518 $\pm$ 47	8.3
F.LMW	172 $\pm$ 15	494 $\pm$ 50	34.8

^a Measured value based on growth test of indigenous bacteria.

^b Measured value by LC-OCD analysis.

^c Seawater was diluted so that DOC was ~ 0.5 mg/L and salts concentrations were adjusted to level equivalent to original seawater.

Overall, the ratio of AOC/DOC for seawater was only $\sim 20\%$. The cell growth curve of seawater followed similar trend as F.LMW since LMW contributed $\sim 73\%$ of AOC in seawater (**Table 5.3**). Although HS&BB was the largest portion of organic compounds in seawater (i.e., $\sim 52\%$ of DOC), it did not play a significant role in supporting the microbial growth, i.e., contributed to $\sim 21\%$ of AOC in seawater. Meanwhile, BP which accounted for only 6% of DOC in seawater, contributed only $\sim 5\%$ of AOC in seawater. The findings suggested that the contribution to biofouling potential of seawater was in the order of LMW $\gg$ HS&BB $>$ BP; which corroborated the linear correlation between LMW and AOC in treated seawater by MBR (Hammes, Salhi et al. 2006, Jeong, Kim et al. 2013, Naidu, Jeong et al. 2013).

Table 5.3 Contribution of AOC and DOC by different organic compounds in seawater.

	DOC ^a		AOC ^b		AOC/Total DOC
	($\mu\text{g-C/L}$)	(%)	($\mu\text{g-C/L}$)	(%)	(%)
BP	70 ± 8	5.9	13	5.5	1.1
HS&BB	617 ± 12	51.8	51	21.2	4.3
LMW	505 ± 19	42.3	176	73.3	14.8
Total	1192	100	240	100	20.1

^a Measured value by LC-OCD.

^b Calculated value based on measured value of DOC in original seawater (Figure 5.2) and AOC/DOC ratio (Table 5.2).

5.3.3 Organic Transformation During Bacteria Growth in Isolated Dissolved Organic Fractions

The bio-transformation of organics during bacteria growth of *Vibrio* sp. B2 in isolated dissolved organic fractions and carbon-free synthetic seawater (blank) are shown in **Figure 5.4a** and **Figure 5.5**, respectively. In the blank test, maximum increase in BP, HS&BB and LMW were only ~ 10 , ~ 10 and ~ 30 $\mu\text{g-C/L}$, respectively, after 3-day incubation. In F.BP as nutrient source, the concentration of BP decreased while the concentration of LMW increased to 142 ± 63 $\mu\text{g-C/L}$, due to biodegradation of larger molecules of BP into smaller molecules of LMW that would be more favourable for assimilation (Naidu, Jeong et al. 2013, Naidu, Jeong et al. 2015); HS&BB was also released as the concentration increased (73 ± 22 $\mu\text{g-C/L}$) but the amount was much less than LMW. The bacteria could also generate BP through SMP and EPS production (Villacorte, Ekowati et al. 2017), but it was difficult to distinguish the BP produced as microbial product from the indigenous BP in F.BP. While in F.HS&BB as nutrient source, only small amount of BP and LMW (i.e., taking into account the LMW impurities in F.HS&BB (**Figure 5.2**) as well as LMW release in blank test) were

produced as humic substances were slowly or non-biodegradable and the microbial growth was not favoured. On the other hand, in F.LMW as nutrient source, a decrease in LMW was observed as LMW was easily consumed by bacteria for proliferation. An increase in BP ($58 \pm 21 \mu\text{g-C/L}$) and HS&BB ($74 \pm 39 \mu\text{g-C/L}$) was also noted, mainly due to the production of SMP and hydrolysis of EPS secreted by bacteria.

From the F-EEM analysis, F.BP and F.LMW mainly consisted of protein-like organics in region I and II, respectively, while F.HS&BB was a mixture of protein-like (region I, II), fulvic-like (region III) and humic-like (region IV) organics. After 3-day incubation, the results clearly showed the transformation of organics in all test solutions to protein-like (region II), microbial by-product-like (region IV), and humic-like (region V) organics. The organic transformation was critical as reported from previous study, microbial by-product-like organics were identified as an important foulant in membrane processes (Yu, Qu et al. 2015).

Figure 5.4 Bio-transformation of organics by *Vibrio* sp. B2 (Kim and Chong 2017) as inoculum in different isolated dissolved organic fractions from seawater (a) LC-OCD, and (b) FEEM analysis (Error bars for $n = 3$).

Figure 5.4 continued. Bio-transformation of organics by *Vibrio* sp. B2 (Kim and Chong 2017) as inoculum in different isolated dissolved organic fractions from seawater (a) LC-OCD, and (b) FEEM analysis (Error bars for $n = 3$).

Figure 5.5 Organic concentration during growth test of *Vibrio* sp. B2 (Kim and Chong 2017) as inoculum in carbon-free solution (Error bars for n = 30).

5.3.4 Bacteria-clean/fouled Membrane Interactions

From the AFM analysis (**Figure 5.6**), it can be seen that interaction of bacteria and clean membrane surface was not favoured. However, the presence of organics had modified the membrane surface, causing greater adhesion of bacteria to the organic-fouled membrane as compared to clean membrane, and the magnitude of interaction force was in the following order: bacteria-BP > bacteria-LMW > bacteria-HS&BB. First, the results suggested that organic conditioning film was an important precursor to biofouling as bacteria-membrane interaction was the weakest. Second, in previous study, BP was identified as the major contributor of organic fouling in RO due to its sticky nature that caused highest degree of BP-membrane interaction as compared to HS&BB and LMW (**Chapter 4**). Similarly, the effect of bacteria-BP fouled membrane interaction was also more pronounced. In addition, once the bacteria colonized the membrane, more bacteria attachment was expected since bacteria-bacteria interaction was greater than bacteria-organic-fouled membrane interaction.

Figure 5.6 AFM analysis of interaction of bacteria-clean RO membrane, bacteria-BP-fouled membrane, bacteria-HS&BB-fouled membrane, bacteria-LMW fouled membrane, and bacteria-bacteria (Error bar for $n = 30$).

5.3.5 Impact of Isolated Dissolved Organic Fractions on SWRO Biofouling

In the crossflow RO experiments to simulate SWRO biofouling in different isolated dissolved organic fractions, the characteristics of test solution in the feed tank remained unchanged (i.e., concentration and organic compositions) as shown in **Figure 5.7**. This was important so the feed tank and recirculating lines did not turn into a bioreactor that could impact the biofouling process. The flux decline rate during biofouling process was compared with the control without bacteria injection (i.e., organic fouling in our previous study (**Chapter 4**)) as shown in **Figure 5.8**. The impact of isolated dissolved organic fractions (at DOC = 0.5 mg-C/L) on biofouling based on the % flux decline rate after 140 h of operation was in the order of F.LMW > F.BP >> F.HS&BB. When compared to the control, significant difference in the flux decline rate was noted between biofouling and control (30% vs. < 5%) in F.LMW, while it was 20% vs. 12.5% in F.BP. Insignificant effect on flux decline rate was observed in both biofouling and control in F.HS&BB, i.e., < 10%.

Further analysis of membrane autopsy also supported the flux decline profile. From the CLSM imaging (**Figure 5.9**) and quantification of biovolume of live cells on RO

membranes (**Figure 5.8a**), higher value of $15.5 \pm 0.5 \mu\text{m}^3/\mu\text{m}^2$ was noted for bio-fouled membrane in F.LMW than $12.5 \pm 1.3 \mu\text{m}^3/\mu\text{m}^2$ in F.BP. Whereas lowest value of $4.9 \pm 1.1 \mu\text{m}^3/\mu\text{m}^2$ was reported in F.HS&BB. It shall be noted that the biovolume of dead cells on RO membranes was negligible. The results agreed well with the AOC measurement, i.e., $\text{F.LMW} > \text{F.BP} > \text{F.HS\&BB}$, where greatest microbial growth rate was observed in F.LMW as nutrient source.

Figure 5.7 Monitoring of organic profile in feed tank during SWRO biofouling test with different isolated dissolved organic fractions from seawater as RO feed (a) F.BP, (b) F.HS&BB, and (c) F.LMW.

Figure 5.8 Flux decline profile of RO biofouling by *Vibrio* sp. B2 (Kim and Chong 2017) in different isolated dissolved organic fractions from seawater. The control experiments were tests without the presence of bacteria, taken from our previous work (Chapter 4). Concentration of organic in each fraction = 0.5 mg-C/L.

Figure 5.9 CLSM image of biofouled membrane coupon in RO biofouling test with different isolated dissolved organic fractions from seawater as RO feed (a) F.BP, (b) F.HS&BB, and (c) F.LMW.

In addition, the LC-OCD analysis (**Figure 5.10b**) of foulant extracted from the biofouled membrane also revealed that least biofouling occurred in F.HS&BB as RO feed. Several remarks could be made for biofouling in F.BP and F.LMW as RO feed:

- (i) In F.BP as RO feed, by comparing the feed and foulant compositions and amount, it was found that despite there was no LMW in the F.BP feed solution (**Figure 5.2** and **Figure 5.7**), large amount of LMW was detected in the foulant (**Figure 5.10b**). In addition, the amount of BP detected in biofouled membrane was much higher than the control, i.e., organic-fouled membrane. First, the large amount of LMW in foulant was due to the biodegradation of larger molecules of BP into smaller molecules of LMW for easy consumption by bacteria to proliferate. This hypothesis was supported by the biotransformation data in **Figure 5.4**. Second, the results suggested that the amount of BP generated as SMP and EPS by bacteria far

exceeded the deposition of indigenous BP from F.BP feed solution. Note that LMW could also be generated as part of the SMP and EPS.

- (ii) In F.LMW as RO feed, the deposition of LMW originated from F.LMW onto clean RO membrane was less favourable compared to BP in F.BP due to weaker LMW-membrane interaction (Chapter 4). However, when LMW was consumed for microbial growth, BP was generated as SMP and EPS, i.e., biotransformation of LMW by bacteria as shown in **Figure 5.4**. Hence, RO membrane surface could be modified as such it promoted subsequent bacteria deposition. Since the amount of BP produced via biotransformation was relatively lower than the availability of BP in F.BP, the initial biofouling rate in F.LMW was slower than F.BP (**Figure 5.8**, from 0 to 30 h). However, once the BP conditioning layer was formed on the membrane, with the continuous supply of LMW in F.LMW, in which the amount was much higher than LMW obtained from the biodegradation of BP in F.BP, resulted in greater microbial growth and production of SMP and EPS (i.e., BP and LMW), thus the biofouling rate in F.LMW surpassed F.BP beyond 30 h (i.e., 30% vs. 20% in flux decline after 140 h).
- (iii) By comparing the flux decline profile and compositions of foulants extracted from fouled membranes and controls, it was noted the sequence of flux decline was F.LMW (30%) > F.BP (20%) > control F.BP (12.5%) >> control F.LMW (<5%), the amount of BP in foulant was in the order of F.LMW > F.BP > control F.BP >> control F.LMW, the amount of LMW in foulant was in the order of F.BP > F.LMW >> control F.BP > control F.LMW. There was a good correlation between flux decline and amount of BP in foulant. Note that majority of BP in foulant was accumulated through generation of SMP and EPS rather than from deposition of indigenous species. Based on these results and CLSM analysis, it was suggested that biofilm with high number of cells embedded in matrix of SMP and EPS (i.e., in particular BP) could result in high hydraulic resistance and biofilm enhanced

osmotic pressure effect that lower the flux.

The EPS (**Figure 5.10c**) and F-EEM analyses of foulants extracted from biofouled membranes also supported the remarks above. The amount of EPS in foulant was in the order of $F_{LMW} > F_{BP} > F_{HS\&BB}$. It was noted that proteins occupied a large portion of EPS compared to polysaccharides, which agreed well with previous work (Jeong et al. 2013). Similarly, F-EEM analysis revealed that the foulant was mainly composed of tyrosine protein-like (Region I), protein-like organics (Region II), and microbial by-product-like organics (Region IV).

Overall, these findings are critical in providing the guidance for selection of efficient seawater pretreatment method to mitigate membrane biofouling. Most of the reported work focused on removing the biopolymer fraction by methods such as coagulation/flocculation and membrane filtration or combinations prior RO process (Jeong, Kim et al. 2013, Shutova, Karna et al. 2016). However, based on the AOC/DOC ratio of organics in seawater (**Table 5.2**) and SWRO biofouling test in this study, the role of indigenous BP in SWRO biofouling was less critical owing to its relatively low concentration (i.e., only accounted for 6% of DOC and 5% of AOC in seawater). On the other hand, LMW which accounted for >70% of AOC and 42% of DOC in seawater, played a significant role in SWRO biofouling by supporting microbial growth that contributed to the build-up of SMP and EPS (i.e., generation of BP). Even though HS&BB occupied about 52% of DOC in seawater, i.e., major organic compound, it had marginal role in SWRO biofouling. Therefore, seawater pretreatment prior RO process shall focus on the removal of AOC rather than the removal of biopolymer.

Figure 5.10 (a) Biovolume ($\mu\text{m}^3/\mu\text{m}^2$) of live and dead cells, (b) LC-OCD, (c) EPS (protein and polysaccharide), (d) FEEM of biofouled RO membranes by *Vibrio* sp. B2 (Kim and Chong 2017) in different isolated dissolved organic fractions from seawater. The control experiments in (b) were tests without the presence of bacteria, taken from our previous work (Chapter 4).

5.4. Conclusions

Natural organic matters (NOM) in seawater are critical in supporting bacterial growth and biofilm formation that eventually lead to severe membrane biofouling in the seawater reverse osmosis (SWRO) desalination process. To study the mechanisms of SWRO biofouling, isolation and concentration was performed using a membrane-based technique to separate the dissolved organic compounds in seawater into 3 major fractions according to their molecular weights (MWs), namely, fractions of biopolymers (F.BP, MW >1000 Da), humic substances and building blocks (F.HS&BB, MW 350-1000 Da), and low molecular weight compounds (F.LMW, MW <350 Da). The biofouling potential of the isolated dissolved organic fractions was characterized by assimilable organic carbon (AOC) content and their impact on SWRO biofouling was evaluated using *Vibrio* sp. B2 as model bacteria in a crossflow RO system. The findings are summarized below:

- (i) The AOC/DOC ratio of the isolated dissolved organic fractions was in the order of F.LMW (~35%) > F.BP (~19%) > F.HS&BB (8%), and for seawater was ~20%. The organic compositions of seawater were BP ~6%, HS&BB ~52% and LMW ~42%, thus the main contributor to AOC in seawater was LMW (>70%);
- (ii) In SWRO biofouling study using isolated dissolved organic fractions at DOC = 0.5 mg-C/L as RO feed, F.LMW caused the most severe flux decline (30%), followed by F.BP (20%), while insignificant effect in F.HS&BB (<10%). The membrane autopsies data (i.e., CLSM, LC-OCD, EPS and FEEM analysis) supported these findings;
- (iii) In F.BP as RO feed, the BP preferentially formed a conditioning layer on the RO membrane due to strong interaction of BP-membrane, followed by the deposition of bacteria due to greater interaction of bacteria-BP than bacteria-membrane. The BP was then biodegraded to LMW, which could be easily assimilated by bacteria for proliferation. BP and LMW was generated as SMP and EPS. Note that the hypothesis of biotransformation of organics was supported by the data obtained from microbial growth in batch test;
- (iv) On the other hand, in F.LMW as RO feed, due to weaker interaction of LMW-membrane, the deposition of LMW onto membrane was not favourable. But bacteria consumed LMW and produced BP as a by-product, which could then

form a conditioning layer on the membrane surface. This process was slower than the direct deposition of BP in F.BP, thus slower flux decline rate was observed in F.LMW as compared to F.BP during the initial stage of biofouling. However, due to continuous supply of LMW in F.LMW, in which the amount was much higher than the amount of LMW generated through biodegradation of BP in F.BP, rapid microbial growth and generation of SMP and EPS were observed, thus biofouling rate in F.LMW surpassed F.BP at the later stage of biofouling process;

- (v) The large amount of BP and LMW presence (i.e., HS&BB was insignificant) in the foulants of biofouled membranes in F.BP and F.LMW as RO feed were not from the deposition of indigenous BP and LMW from the bulk feed solution, but rather from the generation of BP and LMW during microbial growth on the membrane surface through biodegradation of BP in F.BP and production of SMP and EPS in both F.BP and F.LMW. The accumulation of bacteria cells embedded in matrix of SMP and EPS (i.e., in particular BP) formed a biofilm that caused an increase in hydraulic resistance and biofilm-enhanced osmotic pressure effect, thus decline in flux.

Based on the above information obtained for isolated dissolved organic fractions, when translated to actual seawater, the following conclusion could be made. Even though HS&BB was the major organic compound in seawater (~52%), it had marginal role in SWRO biofouling. Meanwhile, the role of indigenous BP in SWRO biofouling was less critical owing to its relatively low concentration. On the other hand, LMW which accounted for >70% of AOC and ~42% of DOC in seawater, played a significant role in SWRO biofouling by supporting microbial growth that contributed to the build-up of SMP and EPS (i.e., in particular BP). Therefore, seawater pretreatment prior RO process shall focus on the removal of LWM (i.e., AOC) rather than the removal of biopolymer.

CHAPTER 6 Mitigating Reverse Osmosis (RO) Fouling in Seawater Desalination Process by Removing Low Molecular Weight (LMW) Organic Compounds with Nanofiltration (NF) Pretreatment

This chapter describes the fouling mitigation by using NF pretreatment. Chapter 4 & 5 have discussed the organic fouling and biofouling mechanisms, therefore, a novel pretreatment method was came up with to effectively reduce the fouling in SWRO process. Many studies have shown the advantages of using UF membrane as the pretreatment process, but with the development of the material science, ground-breaking membrane fabrication process has thrived. Therefore, using NF membrane as the pretreatment process could be an alternative option in seawater desalination process.

6.1 Introduction

Conventional pretreatment such as ultrafiltration (UF), pore size 0.1 – 0.001 μm , could only remove particulate matters and large molecular weight (MW) organic compounds based on size exclusion mechanisms (Anis, Hashaikh et al. 2019, Badruzzaman, Voutchkov et al. 2019). As shown in **Chapter 6**, LMW (MW < 350 Da) accounted for more than >70% of AOC in seawater, thus resulted in severe SWRO biofouling. Therefore, seawater pretreatment prior RO process shall focus on the removal of AOC (i.e., LMW). In this study, NF pretreatment was assessed and its performance was compared with conventional UF pretreatment. SWRO fouling phenomenon by using NF permeate as RO feed water was also examined.

6.2 Materials and Methods

6.2.1 NF pretreatment and RO fouling experiment

The collection of seawater has been described in **Section 3.3.1**. The schematic diagram of seawater treatment process is illustrated in **Figure 6.1**. In this study, one type of hollow fiber UF membrane and three types of NF membranes (i.e., NF270,

NF1, and NF2) were employed to pretreat the raw seawater (**Section 3.2**). MWCOS of NF membranes were determined followed the method in **Section 4.2.1.2**. It should be noted that a crossflow setup (with an effective area of 0.0186 m^2) was used for NF270 pretreatment process. The operating pressure of NF process was set at 4 bars. All NF processes were divided into two stages to evaluate the membrane performance: (i) concentration stage up to 50% recovery (i.e., against the elevated concentration of organic/inorganic substances), where the retentate was completely recycled to the feed tank, while the permeate was collected into a container. 20 L of raw seawater (i.e., feed water) was used to obtain 10 L of permeate; and (ii) long-term performance at concentration equivalent to 50% recovery (i.e., extended test for another 72 hours after step (i)). Here, the retentate and permeate were fully recycled back to the feed tank.

Then, the collected permeates from pretreatment process were further employed as feed water for the downstream RO process. A crossflow RO setup (with effective area of 0.0045 m^2) was used for the fouling study. Commercial SW-30HR was used in this study. The description of the RO system can refer to **Section 3.1.1**. Initial water flux was set at $30 \text{ L/m}^2\text{h}$. The flux decline profile was regarded as fouling indicator and the operation duration was 6 days.

Figure 6.1 Diagram of the seawater pretreatment process and fouling experiment.

6.2.2 Analytical Methods

6.2.2.1 Water Quality Measurement

Raw seawater and all the permeate samples (50 mL) from UF and NF pretreatment processes were collected and analyzed by turbidity meter (Hach, US), ICP-OES (Section 3.4.7), IC (Section 3.4.7), LC-OCD (Section 3.4.1), and AOC (Section 3.4.4).

6.2.2.2 Membrane Autopsy Analysis

After the fouling process, the autopsy of fouled membranes was performed. For hollow fiber NF membranes, 15 pieces of fibers, length of 15 cm, total area of 0.01 m² were used; for flat sheet NF270 and RO membrane, 3 cm × 4 cm coupon was used. The procedures of extraction of foulants were similar to Section 4.2.3. The filtrate was tested by the LC-OCD. Microbial water analysis in the unfiltered filtrate was examined by the adenosine triphosphate (ATP) measurement, and the detailed protocol was described in the references (Holm - Hansen and Booth 1966, Luján-

Facundo, Fernández-Navarro et al. 2018). Unfiltered filtrate (1 mL) was examined by analyzing the sum of extracellular and intracellular ATP concentration using a luminometer (Hach, USA). CLSM analysis was performed on fouled membrane coupon (3 cm × 4 cm) and the biovolume of biofilm was calculated from the IMARIS software. The protocol was shown in **Section 3.4.5**. FE-SEM (**Section 3.4.11**) was performed on fouled membrane coupon (3 cm × 4 cm).

6.3. Results and Discussion

6.3.1 Performance of NF Membranes

6.3.1.1 NF Membrane Properties

Table 6.1 shows the membrane properties of NF270, NF1 and NF2. The pure water permeability of NF membranes was in the following order: NF1 > NF270 > NF2. It is interesting to note that NF1 showed higher permeability even with lower MWCO as compared to NF270, which was attributed to: (i) thinner active layer as confirmed by previous studies (Liu, Shi et al. 2015, Labban, Liu et al. 2018); and (ii) higher hydrophilicity as compared to NF270 (Liu, Shi et al. 2015) since NF1 has functional groups such as SO_3^- , which has high tendency to form hydrogen bonding (Qi, Li et al. 2012). In addition, NF2 (i.e., PSS+PAH+PSS+PAH+GA) exhibited lower permeability than NF1 (i.e., PSS+PAH+PSS+GA) due to additional polyelectrolyte layer that made it denser as confirmed by MWCO value.

Table 6.1 Properties of NF270, NF1 and NF2.

Membrane	Permeability (LMH/bar)		MWCO (Da)
	DI water	Seawater	
NF270	13.8 ± 1.2	3.5 ± 0.1	538 ± 33
NF1	15.3 ± 0.8	4.0 ± 0.3	275 ± 17
NF2	10.6 ± 0.5	1.9 ± 0.1	152 ± 26

6.3.1.2 Organic and Salt Rejection

Table 6.2 summarizes the water quality of raw seawater, UF and NF permeates. Only 27% of the large size biopolymers (BP) was removed by the UF with MWCO of 150 kDa, whereas humic substances (HS), building blocks (BB), and low molecular weight (LMW) compounds are not captured, thus became the potential foulants for the downstream RO process. In contrast, it is not surprising that the dissolved organic carbon (DOC) rejection of the NF was much higher than UF with the following order of NF2 (77%) > NF1 (71%) > NF270 (61%). In addition, the assimilable organic carbon (AOC) removal was in the order of NF2 > NF1 > NF270 > UF. UF was poor in AOC removal because majority of AOC in seawater was contributed by LMW, which was not captured by UF (*i.e.*, almost no removal of LMW). NF membranes was shown to remove >50% of AOC in seawater, thus could significantly reduce the biofouling potential of RO feed water.

In general, UF membrane did not remove any salts due to large pore size. The NF membranes showed relatively high rejection of Ca^{2+} , Mg^{2+} , and SO_4^{2-} with minimal rejection of Na^+ . As shown in **Table 6.2**, NF1 and NF2 membranes showed better multivalent rejection as compared to NF270, where NF2 removed ~75% of Ca^{2+} and ~90% of Mg^{2+} and SO_4^{2-} which was comparable to commercial NF90 which required much higher operating pressure (*i.e.*, > 30 bar) to achieve similar performance (Kaya, Sert et al. 2015). NF1 showed 66% of Ca^{2+} rejection and 80% of Mg^{2+} rejection, which was lower than that of NF2 but higher than NF270 whose Ca^{2+} and Mg^{2+} rejection were 41% and 32%, respectively. However, the rejection of SO_4^{2-} of NF1 (85%) was lower than that of NF270 (92%), owing to the surface charge where NF270 appeared more negative charge than NF1. The higher rejection of Mg^{2+} compared to Ca^{2+} can be described by the ionic diffusivity and Stoke radius of Mg^{2+} and Ca^{2+} (Wadekar and Vidic 2017). The higher rejection of SO_4^{2-} compared to Ca^{2+} can be explained by electrical interactions (Labban, Liu et al. 2017). The higher rejection properties of NF1 and NF2 towards Ca^{2+} and Mg^{2+} were due to electrostatic repulsion with the positively charged surface fabricated from layer-by-layer (LBL) polyelectrolyte deposition followed by the glutaraldehyde (GA) crosslinking, whereas NF270 was made from polyamides with negatively charged surface. In

addition, previous results in term of rejection of divalent ions showed marginal relationship with membrane charge (Wadekar and Vidic 2017) and thickness (Labban, Liu et al. 2017). Therefore, higher rejection of divalent ions observed in NF2 compared to NF1 was mainly attributed to the MWCOs (Labban, Liu et al. 2017, Labban, Liu et al. 2018).

Table 6.4 shows the organic rejection of UF and NF membranes as a function of recovery. All NF membranes showed stable organic rejection at all recoveries and not affected by elevated salt condition (i.e., divalent ions) since size exclusion was the main separation mechanism.

The cation and anion rejection properties as a function of recovery of NF membranes are listed in **Table 6.4** and **Table 6.5**. The rejection of Ca^{2+} and Mg^{2+} slightly decreased with increasing recovery, while the rejection of Na^+ was relatively stable. The divalent ions (i.e., Ca^{2+} and Mg^{2+}) were concentrated in the bulk solution which promoted the diffusion of divalent ions across the membrane. Therefore, relatively low rejection ratio of divalent ions was observed with the increase in recovery. **Table 6.5** displays a negative rejection of Cl^- in NF270, which probably was attributed to the charge electroneutrality (Yaroshchuk 2008). NF270 retained averagely 90% of the SO_4^{2-} but only ~40% of the Ca^{2+} and Mg^{2+} , indicating that more mobile Cl^- may be captured from retentate to permeate to neutralize the positive charge ions (Ca^{2+} and Mg^{2+}).

Overall, based on the inorganic rejection properties, the permeates of NF1 and NF2 showed lower scaling potential of CaSO_4 which has been reported as the critical scalant in SWRO process (Song, Gao et al. 2013) compared to permeate of NF270.

Table 6.2 Water quality of raw seawater and permeate from UF and UF-NF pretreatment.

	Feed	Permeate (Rejection)			
	Raw seawater	UF	NF270	NF1	NF2
Turbidity (NTU)	9.27 ± 0.4	0.02 ± 0.1 (100%)	N.D (100%)	N.D (100%)	N.D (100%)
DOC (µg-C/L)	1233 ± 42	1169 ± 101 (5%)	484 ± 42 (61%)	363 ± 22 (71%)	288 ± 11 (77%)
Biopolymers (µg-C/L)	109 ± 28	80 ± 25 (27%)	11 ± 6 (90%)	8 ± 3 (93%)	4 ± 1 (96%)
Humic substances (µg-C/L)	617 ± 65	532 ± 43 (14%)	N.D (100%)	N.D (100%)	N.D (100%)
Building blocks (µg-C/L)	124 ± 35	125 ± 35 (2%)	39 ± 9 (69%)	16 ± 5 (87%)	N.D (100%)
LMW neutrals (µg-C/L)	335 ± 59	328 ± 44 (2%)	268 ± 23 (20%)	263 ± 14 (21%)	155 ± 18 (54%)
AOC (µg-C/L) (n=3)	212 ± 54	182 ± 28 (14%)	98 ± 24 (54%)	73 ± 12 (66%)	57 ± 11 (73%)
Ca ²⁺ (mg/L)	329 ± 1	318 ± 4 (3%)	195 ± 7 (41%)	112 ± 5 (66%)	83 ± 2 (75%)
Mg ²⁺ (mg/L)	1602 ± 7	1578 ± 8 (1%)	1090 ± 2 (32%)	313 ± 9 (80%)	118 ± 4 (93%)
Na ⁺ (mg/L)	10800 ± 97	10769 ± 36 (0%)	11014 ± 63 (-2%)	11026 ± 86 (-2%)	10496 ± 67 (3%)
Cl ⁻ (mg/L)	16654 ± 101	16783 ± 84 (-1%)	16878 ± 37 (-1%)	15008 ± 44 (10%)	14878 ± 32 (11%)
SO ₄ ²⁻ (mg/L)	2384 ± 6	2302 ± 8 (3%)	202 ± 4 (92%)	364 ± 3 (85%)	167 ± 3 (93%)

N.D: non-detectable

Table 6.3 Organic rejection by UF and NF membranes against recovery (measurements were obtained from cross-flow filtration at 1 bar for UF and 4 bars for NF membranes).

	Recovery				
	10%	20%	30%	40%	50%
UF	33%±2	35%±2	35%±1	34%±3	36%±2
NF1	80%±4	81%±5	82%±4	81%±3	80%±4
NF2	84%±5	85%±4	86%±5	84%±3	85%±5
NF270	72%±3	74%±3	71%±3	72%±4	70%±3

6.3.1.3 Membrane Fouling in NF

It was found that the amount of extracted foulants on NF membranes was in the order of NF270 > NF2 > NF1 (**Appendix B, Figure B.1**) while flux decline was in the order of NF2 > NF270 > NF1 (**Appendix B, Figure B.2**). In general, membrane fouling is governed by the interplay among water chemistries, membrane properties and operating parameters. In this case, all three factors varied simultaneously because the NF membranes used have different permeabilities and rejection properties that increased the degree of complexity. Thus, a clear explanation of the fouling mechanism and trend observed between the three NF membranes could not be established. This is beyond the scope of this study and further work is required. Nonetheless, the quality of the treated seawater or RO feed is the focus in this study.

Table 6.4 Cation rejections of NF membranes against recovery (measurements were obtained from cross-flow filtration at 4 bars).

	Recovery														
	10%			20%			30%			40%			50%		
	Ca ²⁺	Mg ²⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Na ⁺
NF1	68%±2	84%±2	1%±0	65%±2	82%±2	2%±0	62%±2	80%±2	2%±0	60%±2	79%±1	1%±0	59%±2	78%±1	2%±0
NF2	88%±4	95%±2	3%±0	88%±3	95%±2	1%±0	86%±4	94%±3	1%±0	82%±4	91%±2	0%±0	81%±4	91%±3	1%±0
NF270	46%±2	44%±2	2%±0	39%±2	34%±2	1%±0	38%±2	34%±1	2%±0	37%±2	32%±1	2%±0	36%±1	31%±2	1%±0

Table 6.5 Anion rejections of NF membranes against recovery (measurements were obtained from cross-flow filtration at 4 bars).

	Recovery									
	10%		20%		30%		40%		50%	
	SO ₄ ²⁻	Cl ⁻	SO ₄ ²⁻	Cl ⁻	SO ₄ ²⁻	Cl ⁻	SO ₄ ²⁻	Cl ⁻	SO ₄ ²⁻	Cl ⁻
NF1	85%±4	10%±1	85%±5	9%±1	84%±5	9%±1	84%±4	10%±1	83%±5	12%±1
NF2	93%±2	14%±1	93%±3	14%±1	93%±3	10%±1	92%±3	12%±1	92%±3	10%±1
NF270	92%±3	0%±0	92%±4	-4%±1	92%±5	-7%±1	91%±4	-14%±1	90%±3	-10%±2

6.3.2 Performance of RO

6.3.2.1 Permeate Flux

The RO flux decline profile of UF and NF pretreated RO feed waters is shown in **Figure 6.2**. Most severe fouling was observed for UF pretreated RO feed water, where the flux decline rate was ~20% after 6 days. This was caused by biofilm formation on membrane surface due to high AOC concentration in feed water as well as scaling of sparingly soluble salts. In contrast, least RO fouling was observed for NF2 pretreated water, where the flux decline rate was only 3% after 6 days. This corresponded to the lowest AOC concentration in **Table 6.2**. The flux decline of NF1 and NF270 had similar trend in the first 2 days, while with a long-term operation, NF1 presented more stable flux than that of NF270, and the normalized flux was maintained above 90% until the end of the experiment. This could be attributed to the lower organic components and AOC amount in the permeate of NF1 compared to NF270 (**Table 6.2**).

Figure 6.2 Flux decline profile of RO system fed with permeate from UF and UF-NF pretreatment.

Table 6.6 lists the amount and distribution of foulants on fouled RO membranes. It can be seen that BP were observed as the major organic foulants, followed by LMW compounds. It is worth noting that the high amount of BP mainly comes from the excreta of the microorganism in the forms of extracellular polymeric substances (EPS) (**Chapter 5**) and not from indigenous BP since NF pretreatment has removed most

of the large MW organics such as BP in seawater (**Table 6.2**). The EPS produced by bacteria contains polysaccharides and proteins with carboxyl functional groups that can interact strongly with membrane surface in the presence of Ca^{2+} under seawater condition, resulting in the increase in hydraulic resistance and biofilm-enhanced osmotic pressure (BEOP) effect (Li, Winters et al. 2015). In addition, permeate from conventional UF pretreatment showed a severe SWRO biofouling as evidenced by the autopsy results of ATP and biovolume (**Table 6.6**). The amount of ATP and biovolume dramatically reduced at least 3 times using the permeate from NF pretreatment, indicating a significant biofouling reduction. The more AOC rejected by the NF membrane; the less biological activity appeared on RO membrane. This result supports that prolonging flux decline should focus more on the effective removal of LMW compounds which hardly rejected by conventional UF pretreatment, and NF2 performed the best potential in fouling prevention.

Table 6.6 Foulant analysis on RO membranes using permeate from UF and NF pretreatments.

	Foulant on RO membrane			
	UF+RO	NF270+RO	NF1+RO	NF2+RO
DOC (mg-C/m ²)	46.98	17.42	6.85	4.31
Biopolymers (mg-C/m ²)	33.96	8.52	1.67	0.83
Humic substances (mg-C/m ²)	N.D.	N.D.	N.D.	N.D.
Building blocks (mg-C/m ²)	5.79	1.63	0.48	0.56
LMW neutrals (mg-C/m ²)	5.92	1.83	1.58	0.88
ATP (pg/m ²)	4421.39±52.29	1610.66±71.57	1289.55±56.86	1010.95±10.77
Biovolume (μm ³ /μm ²)	6.81±1.1	6.12±1.8	5.37±0.8	3.54±1.5

N.D: not detectable

Figure 6.3 shows the morphology of fouled RO membrane with different pretreated feed waters. A dense fouling layer of organic/inorganic foulants can be clearly observed on fouled RO membrane with UF pretreated feed water. Since UF pretreated feed water has the poorest water quality and highest biofouling potential, a thick biofilm was first formed on the membrane surface that subsequently hindered the solute back-diffusion, thus caused an accumulation of scaling species (Ca^{2+} , SO_4^{2-}) which eventually exceeded the solubility limit and formed precipitate on the membrane surface. In contrast, no crystallization was observed on RO membrane

surface by using NF permeate, suggesting that NF pretreatment effectively mitigated scaling. In addition, the amount of foulants on RO membrane surface was in the order of NF270+RO > NF1+RO > NF2+RO, which agreed well with the flux profile (**Figure 6.2**) and foulant analysis (**Table 6.6**).

Figure 6.3 Morphology of RO membrane surface fed with (a) UF permeate, (b) NF270 permeate, (c) NF1 permeate and (d) NF2 permeate under a magnitude of $\times 10,000$.

In summary, NF pretreatment produced a better water quality for subsequent RO process, which greatly reduced RO fouling. However, a balance between permeability, rejection and fouling should be considered when selecting the membrane for seawater pretreatment. NF270 has been used for seawater pretreatment (Llenas, Ribera et al. 2013, Zhou, Zhu et al. 2015). In this study, it was demonstrated that NF1, which showed higher permeability and lower RO fouling than NF270, can be potentially applied for seawater pretreatment. In addition, reduction in RO fouling shall not be accompanied by ‘transferring’ the fouling issue to upstream pretreatment process, i.e., NF pretreatment in this case, thus further study to understand NF fouling is needed.

6.4 Conclusion

LMW compounds are difficult to be removed by conventional pretreatment process. In this study, the feasibility of NF membranes (i.e., NF1, NF2, and NF270) for seawater pretreatment was studied. Conventional UF pretreatment was used as comparison. Organic/inorganic rejection rate was measured and permeate was collected for further study of SWRO fouling process. Conclusions are drawn:

- (i) Organic (in term of LMW) rejection of NF membranes were in the order of NF2 (54%) > NF1 (22%) > NF270 (20%) > UF (2%);
- (ii) While the rate of RO fouling was in the order of NF2 (3%) < NF1 (10%) < NF270 (16%) < UF (20%). The results were supported by membrane autopsy results;
- (iii) Although NF pretreatment showed greater performance on fouling reduction compared with UF pretreatment, economical factor needs to be considered. The results suggested that NF membrane can be optimized to achieve excellent removal of LMW, but a balance between permeability, rejection and fouling shall be considered when selecting the membrane for seawater pretreatment. For instance, NF2 membrane with the lowest permeability (~1.9 LMH/bar) was less competitive even though it showed the lowest SWRO fouling (i.e., flux decline ~3%) as compared to NF 1 (permeability of 4.0 LMH/bar, flux decline ~10%).

CHAPTER 7 Conclusions and Future Works

7.1 Overall Conclusions

Reverse osmosis (RO) membrane is currently the most commonly used technology for producing high quality water from seawater. However, organic and biofouling as well as the interplay between them are still the major challenge in SWRO desalination process. This thesis mainly focused on the membrane fouling in seawater reverse osmosis (SWRO) desalination process. The overall contributions of this thesis is shown below:

Chapter 7

Organic compositions of seawater

AOC/DOC ratio

Chapter 2 focused on the literature review of RO fouling. Organic matters have a close relationship with biofouling due to organic matters not only cause fouling, but also contribute to biofouling as the nutrients. It is necessary to understand the fouling mechanism in RO process. However, model foulants with well-known structure are always chosen to understand the fouling mechanism in many previous studies, which may not be representative for the nature situation since nature organics are the complex of materials with various characteristics. Therefore, in this thesis, in order to understand the role of organic material in organic fouling and biofouling in RO process, nature seawater organics has been selected.

Chapter 3 summarized the materials and methods that were applied in this thesis.

Chapter 4 presented the organic fouling mechanism in seawater reverse osmosis (SWRO) process. In this chapter, dissolved organic matter (DOM) in seawater was fractionated and concentrated by membrane technique into three major fractions, namely, F.BP, F.HS&BB, F.LMW. Overall recovery of >80% was attained. Results showed that biopolymer in seawater was mainly made up of polysaccharides-like and protein-like compounds, the HS&BB showed smaller MW, all isolated organic fractions showed lower fluorescence intensities, and had lower fouling potentials than common model foulants used in SWRO fouling studies. Initial fouling (i.e., foulant-membrane interaction) was the main driver in SWRO organic fouling with biopolymer fraction as the major contributor followed by low molecular weight fraction. In addition, divalent ions were found to enhance the RO fouling by increasing the adhesion and cohesion forces between foulant-membrane and foulant-foulant.

Chapter 5 studied the SWRO biofouling mechanism by using the isolated organic fractions. The AOC/DOC ratio was in the order of F.LMW (~35%) > F.BP (~19%) > F.HS&BB (~8%); AOC/DOC of seawater was ~20%; organic compositions of seawater were BP ~6%, HS&BB ~52% and LMW ~42%; thus LMW accounted for >70% of AOC in seawater. In SWRO biofouling study, F.LMW caused the most severe flux decline (30%), followed by F.BP (20%), while insignificant effect in F.HS&BB (<10%). In F.BP as RO feed, the BP preferentially formed a conditioning layer on the RO membrane due to strong interaction of BP-membrane, followed by the deposition of bacteria due to greater interaction of bacteria-BP than bacteria-membrane. The BP was then biodegraded to LMW, which could be easily assimilated by bacteria for proliferation. BP and LMW was generated as SMP and EPS. On the other hand, in F.LMW as RO feed, due to weaker interaction of LMW-membrane, the deposition of LMW onto membrane was not favourable. But bacteria consumed LMW and produced BP as a by-product, which could then form a conditioning layer on the membrane surface. This process was slower than the direct deposition of BP in F.BP, thus slower flux decline rate was observed in F.LMW as compared to F.BP during the initial stage of biofouling. However, due to continuous supply of LMW in F.LMW, in which the amount was much higher than the amount of LMW generated

through biodegradation of BP in F.BP, rapid microbial growth and generation of SMP and EPS were observed, thus biofouling rate in F.LMW surpassed F.BP at the later stage of biofouling process. The large amount of BP and LMW presence (i.e., HS&BB was insignificant) in the foulants of biofouled membranes in F.BP and F.LMW as RO feed were not from the deposition of indigenous BP and LMW from the bulk feed solution, but rather from the generation of BP and LMW during microbial growth on the membrane surface through biodegradation of BP in F.BP and production of SMP and EPS in both F.BP and F.LMW. The accumulation of bacteria cells embedded in matrix of SMP and EPS (i.e., in particular BP) formed a biofilm that caused an increase in hydraulic resistance and biofilm-enhanced osmotic pressure effect, thus decline in flux.

Chapter 6 focused on the LMW removal by using low-pressure NF pretreatment process and the subsequent impact on SWRO fouling. Three different membranes were evaluated: NF270 was a commercial membrane based on polyamide thin film composite, NF1 and NF2 were glutaraldehyde cross-linked layer-by-layer polyelectrolyte membranes. The organic/inorganic rejection of NF membranes followed the order of $NF2 > NF1 > NF270$ while pure water permeability (PWP) was in the order of $NF1 > NF270 > NF2$. Meanwhile the degree of RO fouling in term of flux decline and foulant amount was in the order of $NF270 > NF1 > NF2$. In addition, the results suggested that NF membrane can be optimized to achieve excellent removal of LMW, but a balance between permeability, rejection and fouling shall be considered when selecting the membrane for seawater pretreatment.

7.2 Recommendations for Future Works

Potential works in the future are listed below:

- (i) It is necessary to continue the improvement of the fractionation process on extracting organic matters, especially for LMW compounds. LMW compounds failed to be isolated due to high salt concentration. Therefore, future study should integrate forward osmosis (FO) and electrodialysis (ED) techniques to concentrate and desalt the LMW organics;

- (ii) Natural organic matter is a complex mixture of compounds. However, organic compositions have not been well understood. Fractionation process has huge potential to be applied to other type of water (e.g., surface water, wastewater, etc.) and the organic fractions can further be analyzed in terms of their seasonal change and impact of fouling. In addition, organic characterization can offer a helpful information and principle to select suitable pretreatment methods;
- (iii) In practice, fouling is a result of the interplay of various foulant with different characteristics, including the interaction among different foulants and the interaction between different foulants and membranes. Future study can investigate the interplay between different organic fractions, understanding the synergistic effect on the RO membrane;
- (iv) NF pretreatment can significantly reduce RO fouling, but NF membrane itself still faces the challenge of fouling. Due to different fabrication materials of NF membrane, the fouling mechanism is also different. Therefore, understanding the fouling mechanism of NF membrane is important for the future study.

Appendix A

A.1 Electrodialysis (ED) Setup

The electrodialysis stack (PCCell, GmbH, Germany) consisted of 25 cell pairs assembled with standard cation exchange membrane (PC-SK), and standard anion exchange membrane (PC-SA). The electrodes were equipped with anode (Pt/Ir-MMO coated Ti-stretched metal) and cathode (stainless steel). The membrane size was 12.5 × 26 cm with an active membrane area of 0.02 m². The spacer type was 0.35 mm of silicone/polyester. The power supply had 3.5 digits display of voltage and current. The range of output voltage was 1-60 V, and the range of output amperage was 0-15 A. Different voltages (i.e., 10 V, 30 V, 60 V) was applied to study the transport efficiency in ED process.

The diluate solution was prepared by using different organic solutions (with volume of 5 L), i.e., 0.2 µm filtered seawater, humic acids (HA) solution with 5 mg-C/L, F.HS&BB solution with 5 mg-C/L from the fractionation process, sucrose solution (Sigma Aldrich, USA) with 5 mg-C/L, and algal organic matter with MW of <350 Da (labelled as AOM.LMW) with 100 mg-C/L at voltage of 60V. AOM.LMW was extracted from *Thalassiosira Pseudonana*. The protocol of incubation of *Thalassiosira Pseudonana* was reported in previous work (Sim, Suwarno et al. 2019). To extract the AOM.LMW, the culture solution was first filtered by a 0.2 µm cartridge filter to remove the suspended particles/algae, followed by a 500 Da membrane to separate the LMW compound. The organic matter was detected by the LC-OCD. The concentrate solution (5 L) was prepared by mixing 3.5 g NaCl with 1 L DI water. The diluate and concentrate was recirculated back to each original container. The electrolyte was prepared by using 0.1 M of sulfamic acid monosodium salt (NaNH₂SO₃, BOC Science, USA). Samples from diluate and concentrate were collected and analyzed by LC-OCD with interval of 10 mins.

A.2 Performance of Electrodialysis (ED) in Desalting Seawater

Due to the low organic concentration in F.LMW, in this section, different feed water was selected to amplify the extent of organic transfer in ED process.

➤ Salt transfer in ED process

Figure A.1 shows the conductivity profile when using MF filtered seawater as diluate at applied voltage of 10, 30, and 60 V. There was a rapid drop in conductivity at high voltage of 60 V, where more than 90% removal of salt was achieved in 20 mins. The time required increased with decreasing applied voltage. Desalting rate was high at the beginning of the process and gradually slower afterwards, which was because every unit of the membrane surface was initially in contact with large amount of salt ions while it becomes less with the decrease of salt concentration in diluate. In addition, low conductivity in the concentrate tends to attract more salt from the diluate (Han, Galier et al. 2017). Therefore, refreshing the concentrate frequently can increase the desalting rate.

Figure A.1 Conductivity profile of MF filtered seawater in diluate during the ED process at applied voltage of 10, 30, and 60 V.

➤ Organic transfer in ED process

(1) Seawater organics

Figure A.2 shows the organic transfer by using MF filtered seawater as diluate. Diluate 0 and concentrate 0 represented the original status of the solution. It can be

seen that seawater organics decreased in the diluate with the salt, while the organic amount in concentrate kept increasing, indicating that organics transferred with the salt from diluate to concentrate. In addition, it is interesting to note that BP, HS&BB, and LMW compounds seemed all could pass through the ion exchange membrane as all these organic fractions were detected in concentrate. Moreover, slightly higher concentration of BB than that of HS was observed in concentrate indicating that organics with smaller MW could transfer easily than those organics with higher MW. Similar finding of organic transfer can also be found in previous studies (Vetter, Perdue et al. 2007, Zhang, Pinoy et al. 2011). However, it shall be noted that ion exchange membrane as a dense membrane is not supposed to transport large molecular weight such as BP and HS&BB. So far there is no study have observed such phenomenon by using LC-OCD in the literature. Due to ED application was not the focus in this thesis, only basic measurement and analysis were involved here.

Figure A.2 MF filtered seawater organic transfer in diluate and concentrate during ED process at voltage of 60V.

(2) HA & F.HS&BB

In addition to seawater organics, other organic types were also analyzed in the ED process. **Figure A.3** shows the comparison of humic acids and F.HS&BB on organic transfer in diluate and concentrate. Significant difference can be observed by using different type of organic compounds. **Figure A.3a** shows that there is no significant organic transfer by using humic acid in the ED process while **Figure A.3b** shows significant organic transfer when using F.HS&BB. Due to there is no relevant study

discussing such phenomenon, the possible explanation may because of the different characteristic of the organic matters. Such phenomenon also implied that model organic compounds may not be representable for the natural organics. It is necessary to explore more information in terms of the natural organic matters.

Figure A.3 Comparison of (a) humic acids, and (b) F.HS&BB on organic transfer in diluate and concentrate during ED process at voltage of 60V.

(3) Sucrose & AOM.LMW

In order to simply investigate the LMW organic transfer in ion exchange membrane, uniform organics such as sucrose with neutral charge and AOM.LMW were studied. As shown in the **Figure A.4a**, it surprisingly shows that sucrose tends to retain in the diluate and only salt transfers to the concentrate, indicating that sucrose is successfully separated from the salt. In contrast, **Figure A.4b** shows AOM.LMW still

Appendix A

can transfer with the salt. Due to extremely high amount of the AOM.LMW can be obtained from the AOM incubation process, small amount of the AOM.LMW with negligible salt can still be collected at the end of the process, which could be treated as the LMW surrogate for the fouling study.

Figure A.4 Comparison of (a) sucrose, and (b) AOM.LMW on organic transfer in diluate and concentrate during ED process at voltage of 60V.

Appendix B

B.1 Permeate Flux of NF Membranes:

Figure B.1 Flux decline of (a) NF1, NF2, and NF270 against recovery and (b) extended operating time (right) fed with raw seawater.

Figure B.2 Foulant analysis on NF membranes (a) fed with raw seawater and (b) UF filtered seawater.

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