Polysaccharide Fouling in Reverse Osmosis and Forward Osmosis Desalination and Its Alleviation

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This thesis is presented for the degree of

Doctor of Philosophy

in Environmental Engineering

Murdoch University

2015
Declaration

I declare that, except where specific reference is made in the text to the work conducted by other authors, this thesis is my own account of my research and contains as its main content work that has not previously been submitted for a degree at any university.

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Date: 30/07/2015
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Date: ______________
Acknowledgement

I would like to acknowledge my supervisors Dr. Dan Li, Prof. Goen Ho, Dr. Lucy Skillman and Dr. Ralf Cord-Ruwisch for their long-term supervision.

I would like to thank Prof. Goen Ho. Without his help, I would not have attended Murdoch University. I would also like to thank him for the time he dedicated to supervising, both in group settings and individually.

I would like to acknowledge my principal supervisor Dr. Dan Li for her consistent care and concern about my research progress. I am grateful for her help during writing papers and the thesis.

I would like to express my appreciation to Dr. Lucy Skillman. I appreciate her support in providing necessary equipment and chemicals for my experiments and helping me with writings.

I am thankful to Dr. Ralf Cord-Ruwisch. The discussions between us generated some amazing ideas.

Many thanks are owed to Maedeh, Veena and Rabbani for their encouragement and support.

The financial support of Murdoch University and National Center of Excellence in Desalination made this research possible.
Abstract

Membrane separation processes, including forward osmosis (FO) and reverse osmosis (RO), for application in water desalination are plagued by membrane fouling. In particular, membrane biofouling is unpredictable in its nature and affected by numerous factors. One of the major contributors to biofouling is the extracellular polymeric substances (EPS) produced by bacteria, especially the polysaccharides that form a large part of EPS.

The objectives of this study are to understand the polysaccharide fouling mechanisms based on a comparison of polysaccharide fouling in FO and RO and to find suitable alleviating agents for polysaccharide fouling mitigation. Three major tasks were conducted in this study. Firstly, polysaccharide fouling in FO and RO were compared under identical solution chemistry and operational conditions to understand the respective fouling mechanisms in FO and RO. Secondly, some alleviating agents for mitigation of polysaccharide fouling in FO and RO were tested to demonstrate the fouling alleviation mechanism. Thirdly, a model of hydraulic resistances was developed to illustrate membrane fouling mechanisms based on analysis of the contribution of hydraulic resistances to permeate flux decline.

Major findings are:

1) Commercial polysaccharides and polysaccharides isolated from naturally adherent bacteria behaved differently in membrane fouling, which showed that alginate was not a typical model and it is important to select a proper model for polysaccharide fouling.

2) Under identical conditions, membrane fouling by both commercial and isolated polysaccharides was more severe in RO than FO, indicating the importance of pressure source in membrane fouling.
3) RO fouling was likely dominated by foulant – foulant interaction which was greatly affected by calcium ions, while FO fouling could be largely governed by foulant – membrane interaction, which was greatly influenced by solution viscosity.

4) Sodium nitroprusside (SNP) at a proper dose was found to be able to reduce membrane fouling, which could be explained by the electrostatic repulsion between polysaccharides and SNP.

5) Presence of calcium ions played a crucial role in polysaccharide fouling and its alleviation, with its presence leading to significant increase in cake resistance in RO fouling and reducing alleviation efficiency.
Symbols and abbreviations

<table>
<thead>
<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Water permeability coefficient of the membrane (m/(s·Pa))</td>
</tr>
<tr>
<td>$A_m$</td>
<td>Effective membrane area ($m^2$)</td>
</tr>
<tr>
<td>ASW</td>
<td>Artificial seawater</td>
</tr>
<tr>
<td>B</td>
<td>Solute permeability coefficient of the membrane (m/s)</td>
</tr>
<tr>
<td>BEOP</td>
<td>Biofilm-enhanced osmotic pressure</td>
</tr>
<tr>
<td>BSA</td>
<td>Bovine serum albumin</td>
</tr>
<tr>
<td>C</td>
<td>Concentration of solute (mol/L or M)</td>
</tr>
<tr>
<td>$C_{cp}$</td>
<td>Solution concentration of the salt on the membrane surface (mol/L or M)</td>
</tr>
<tr>
<td>$C_f$</td>
<td>Initial conductivity of the feed solution ($\mu$s)</td>
</tr>
<tr>
<td>CD</td>
<td>Charge density</td>
</tr>
<tr>
<td>CECP</td>
<td>Cake-enhanced concentration polarization</td>
</tr>
<tr>
<td>CEOP</td>
<td>Cake-enhanced osmotic pressure</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Conductivity of permeate ($\mu$s)</td>
</tr>
<tr>
<td>$C_{polymer}$</td>
<td>Concentration of the polymer (g/L)</td>
</tr>
<tr>
<td>CTA</td>
<td>Cellulose triacetate</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized (water)</td>
</tr>
<tr>
<td>DICP</td>
<td>Dilutive internal concentration polarization</td>
</tr>
<tr>
<td>DS</td>
<td>Draw solution</td>
</tr>
<tr>
<td>ECP</td>
<td>External concentration polarization</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>EPS</td>
<td>Extracellular polymeric substances</td>
</tr>
<tr>
<td>FO</td>
<td>Forward osmosis</td>
</tr>
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<tr>
<td>---------------------------</td>
<td></td>
</tr>
<tr>
<td>FS</td>
<td>Feed solution</td>
</tr>
<tr>
<td>HA</td>
<td>Humic acid</td>
</tr>
<tr>
<td>i</td>
<td>Van’t Hoff factor</td>
</tr>
<tr>
<td>ICP</td>
<td>Internal concentration polarization</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>J, J_w</td>
<td>Water permeate flux (LMH or m/s)</td>
</tr>
<tr>
<td>J_s</td>
<td>Solute flux (mole/(m²·h))</td>
</tr>
<tr>
<td>J_w0</td>
<td>Water permeate flux at time 0 (LMH or m/s)</td>
</tr>
<tr>
<td>J_wt, J_t</td>
<td>Water permeate flux at time t (LMH or m/s)</td>
</tr>
<tr>
<td>(J_t/J_0)_baseline</td>
<td>Normalized flux value in the absence of alleviating agents at time t (h)</td>
</tr>
<tr>
<td>(J_t/J_0)_alleviation</td>
<td>Normalized flux value in the presence of alleviating agents at time t (h)</td>
</tr>
<tr>
<td>KFCN</td>
<td>Potassium ferricyanide</td>
</tr>
<tr>
<td>M²⁺</td>
<td>Divalent cations</td>
</tr>
<tr>
<td>MWs</td>
<td>Molecular weights (kDa)</td>
</tr>
<tr>
<td>n</td>
<td>Van’t Hoff coefficient</td>
</tr>
<tr>
<td>NaDDC</td>
<td>Sodium dichloroisocyanurate</td>
</tr>
<tr>
<td>P</td>
<td>Pressure on the solution side (Pa)</td>
</tr>
<tr>
<td>PASP</td>
<td>Polyaspartic acid</td>
</tr>
<tr>
<td>PA TFC</td>
<td>Polyamide thin film composite</td>
</tr>
<tr>
<td>P₀</td>
<td>Pressure on the permeate side (Pa)</td>
</tr>
<tr>
<td>ΔP, ΔPₘ</td>
<td>Trans-membrane pressure difference (Pa)</td>
</tr>
<tr>
<td>R</td>
<td>Rejection coefficient</td>
</tr>
<tr>
<td>Rₜ</td>
<td>Blockage resistance (m⁻¹)</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_c$</td>
<td>Cake resistance ($m^{-1}$)</td>
</tr>
<tr>
<td>$R_{cp}$</td>
<td>Concentration polarization resistance ($m^{-1}$)</td>
</tr>
<tr>
<td>$R_{cpt}$</td>
<td>Concentration polarization resistance at time $t$ ($m^{-1}$)</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Cake resistance at time $t$ ($m^{-1}$)</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Universal gas constant ($R_g=0.0831 \text{ L-bar/(mol-K)}$)</td>
</tr>
<tr>
<td>$R_{if}$</td>
<td>Irreversible fouling resistance ($m^{-1}$)</td>
</tr>
<tr>
<td>$R_m$</td>
<td>Membrane resistance ($m^{-1}$)</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>$R_{rf}$</td>
<td>Reversible fouling resistance ($m^{-1}$)</td>
</tr>
<tr>
<td>$R_t$</td>
<td>Total hydraulic resistance ($m^{-1}$)</td>
</tr>
<tr>
<td>SAD</td>
<td>Surface area difference</td>
</tr>
<tr>
<td>SAMs</td>
<td>Self-assembled monolayers</td>
</tr>
<tr>
<td>SNP</td>
<td>Sodium nitroprusside</td>
</tr>
<tr>
<td>$t$</td>
<td>Time for collecting the permeate (s)</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature (K)</td>
</tr>
<tr>
<td>TRP</td>
<td>Thermo-responsive polymer</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume of the collected permeate (L)</td>
</tr>
<tr>
<td>$W_0$</td>
<td>Weight of the empty tube (g)</td>
</tr>
<tr>
<td>$W_1$</td>
<td>Weight of the tube with the dried polymer (g)</td>
</tr>
<tr>
<td>$W_d$</td>
<td>Weight of the fouled membrane after a fouling test (g)</td>
</tr>
<tr>
<td>$W_i$</td>
<td>Weight of the dried membrane after the baseline test (g)</td>
</tr>
<tr>
<td>$W_{foulant}$</td>
<td>Weight of polysaccharide deposited on the membrane surface after 24 h fouling test (g)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity of the permeate (Pa·s)</td>
</tr>
<tr>
<td>$\mu_{DI}$</td>
<td>Water viscosity (Pa·s)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------</td>
</tr>
<tr>
<td>$\pi$</td>
<td>Osmotic pressure of solution (Pa)</td>
</tr>
<tr>
<td>$\pi_{cp}$</td>
<td>Osmotic pressure of salt on the membrane surface (Pa)</td>
</tr>
<tr>
<td>$\pi_{feed}$</td>
<td>Osmotic pressure of the feed solution (Pa)</td>
</tr>
<tr>
<td>$\Delta \pi$</td>
<td>Trans-membrane osmotic pressure difference (Pa)</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Alleviation efficiency (%)</td>
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Chapter 1. Introduction

1.1 Background

1.1.1 Problem statements

Membrane desalination is widely applied to supply potable water. In particular, reverse osmosis (RO) desalination using hydraulic pressure as driving force dominates the worldwide desalination capacity installed [1]. Forward osmosis (FO) using an osmotic pressure gradient as driving force has attracted an increasing attention. However, comparison between FO and RO could only be conducted based on the corrected normalized flux due to the continuously diminished driving force in FO resulting from the continuous dilution of the draw solution [2, 3]. A new protocol maintaining a constant driving force in FO is necessary for a straightforward comparison with RO.

To date, biofouling remains a significant challenge in reverse osmosis (RO) and forward osmosis (FO). It is complex due to the synergistic effect of bacteria and the extracellular polymeric substances (EPS) they produce. EPS majorly composed of polysaccharides has been found to play an important role in biofouling [4], and polysaccharides are widely considered to be the major contributor. In previous studies [3, 5-9], alginate was commonly used as the model polysaccharide to study polysaccharide fouling in RO and FO, despite it being not a typical representative for polysaccharides. In addition, understanding on membrane fouling by polysaccharides isolated from bacteria naturally adherent in a seawater desalination plant remains superficial. It is also of importance how polysaccharides contribute to increase in hydraulic resistance.

There were studies aimed for biofouling control. Several methods have been developed including use of chemicals, pretreatment and use of spacers. In particular, some studies using chemicals, such as sodium nitroprusside (SNP),
were mostly focused on removal of biomass [10-17]. It is still unknown whether SNP can effectively alleviate polysaccharide fouling.

1.1.2 Research questions

Several research questions are presented:

1. How can a constant driving force in forward osmosis (FO) be maintained to better compare with reverse osmosis (RO)?
2. What are the differences in fouling behaviors between commercial polysaccharides and polysaccharides isolated from bacteria naturally adherent in a seawater desalination plant? Is there a better model polysaccharide compared to alginate?
3. How much do polysaccharides increase hydraulic resistance?
4. Can sodium nitroprusside (SNP) effectively alleviate polysaccharide fouling?

1.2 Research objectives

This study aimed to compare membrane fouling by different kinds of polysaccharides in forward osmosis (FO) and reverse osmosis (RO), and investigate polysaccharide fouling control using alleviating agents such that:

1. There is a straightforward comparison of polysaccharide fouling between FO and RO.
2. A better understanding on fouling behaviors of commercial polysaccharides and naturally produced polysaccharides in FO and RO can be achieved.
3. It is clear about the contribution of the hydraulic resistances to membrane fouling.
4. Polysaccharide fouling can be effectively mitigated by alleviating agents.
1.3 Thesis structure

This thesis consists of seven chapters and their brief descriptions are described as follows:

Chapter 1: Chapter One gives a brief background on the topic, lists the objectives of the research and outlines the thesis structure.

Chapter 2: Chapter Two reviews the recent literature in regard to investigation and comparison of membrane biofouling, especially by extracellular polysaccharides, in reverse osmosis (RO) and forward osmosis (FO), and methods for membrane biofouling control.

Chapter 3: Chapter Three describes some laboratory-scale systems and necessary experimental tests, as well as calculations conducted to verify the hypothesis.

Chapter 4: Chapter Four investigates and compares membrane fouling in RO and FO by commercial polysaccharides and polysaccharides isolated from naturally adherent bacteria in a seawater desalination plant, and discusses the experimental results.

Chapter 5: Chapter Five investigates alleviation of polysaccharide fouling in RO and FO using potential chemical compounds.

Chapter 6: Chapter Six describes a model of resistance in series developed to demonstrate the contribution of hydraulic resistances to permeate flux in the RO process.

Chapter 7: Chapter Seven contains the overall conclusion of this study as well as implications from the obtained results.


Chapter 2. Literature Review

2.1 Introduction to membrane desalination

With increasing water demand for increased human consumption, industries and agriculture, water supplies have become an unprecedented challenge for the world. While most of water covering the earth is seawater, amounting to 97% of the total water on earth, only less than 1% of the total water is naturally available fresh water. Therefore, the production of potable water has become a global concern, and solutions such as water desalination have been developed rapidly. Desalination refers to the process of removing salt from water to produce fresh water. In 2009, the total global desalination capacity has grown to around 50 million m$^3$ per day, and predicted to increase up to approximately 95 million m$^3$ per day by 2015 [18].

Desalination can be majorly divided into two categories, thermal desalination and membrane desalination. While thermal desalination remains primary technology of choice in the Middle East, membrane desalination processes have been rapidly developed [19]. Currently, membrane desalination has surpassed thermal desalination in new plant installation [19].

2.1.1 Reverse osmosis

In the last four decades, reverse osmosis (RO) membrane desalination has been widely considered as the primary choice for new desalination plant installations. RO desalination is conducted when the applied hydraulic pressure is greater than the osmotic pressure of the feed solution (Fig.2.1 a). The positive difference in pressure drives the water to permeate through the membrane, while the salts are retained and concentrated on the membrane surface.

The RO membranes are able to reject monovalent ions, such as sodium ions. To date, seawater RO membranes have achieved high salt rejection coefficient higher than 99%, some even achieved as high as 99.7 ~ 99.8% [19, 20].
Therefore, RO membrane desalination has the advantages as to high quality and capacity of drinking water production. Today, RO desalination accounts for 61.1% of the worldwide desalination capacity installed [1].

2.1.2 Forward osmosis

Forward osmosis (FO) is a membrane separation process in which water flows from a low-osmotic-pressure feed solution (FS) to a high-osmotic-pressure draw solution (DS) across a semi-permeable membrane (Fig. 2.1 b) [21, 22]. FO has become an increasingly interesting area of research and shown attractive potential in the field of desalination [23, 24]. Rather than the high hydraulic pressure required by pressure-driven membrane process, such as reverse osmosis (RO), the FO process instead utilizes an osmotic pressure gradient as driving force for separation; and could theoretically reduce energy consumption in desalination [25]. Although a high-osmotic-pressure DS is required and further separation of draw solute from water may be necessary in FO, FO has considerable advantages compared with pressure-driven processes, with regards to lower energy input [25], lower fouling propensity, easier fouling removal [2] and higher water recovery [26]. For example, previous study used fertilizer as the draw solute for low energy forward osmosis desalination and made fertilizer solution for fertigation [27]. In this case, the FO desalination process consumed
much less energy as there was no need to separate draw solute, the fertilizer, from water after the FO process.

2.2 Membrane fouling

Membrane fouling is a major obstacle to the development of membrane separation technologies. Membrane fouling occurs when the foulants in the feed solution are rejected by the membrane surface as the water in the feed solution permeates through the semi-permeable membrane, and block the membrane pores or accumulate on the membrane surface forming a cake layer, which increases concentration polarization and hydraulic resistance [3, 28, 29]. Membrane fouling causes flux reduction, increases energy consumption, reduces membrane lifespan, and increases operation cost [19, 28, 30]. Generally, membrane fouling is roughly categorized into four types based on the properties of the rejected contaminants [31]:

1) Inorganic fouling caused by scaling or salt precipitation of sparingly soluble salts);
2) Organic fouling resulted from mostly natural or effluent organic matters;
3) Colloidal fouling by accumulation of a colloidal cake layer on the membrane surface;
4) Biofouling caused by formation of biofilm.

In particular, biofouling caused by biofilm formation is more complex than fouling by any individual foulant, because biofilm consists of bacteria as well as bacteria produced extracellular polymeric substances (EPS), which provides structure for the biofilm and protects bacteria from environmental stresses [32]. Bacteria themselves play a key role in biofouling by growth and division. The polysaccharides produced by bacteria contribute greatly to biofouling by accumulation on the membrane surface, leading to increased hydraulic resistance and flux decline. Therefore, it is of great importance to improve the understanding of the contribution of EPS to membrane biofouling and develop effective control methods for membrane fouling.
2.2.1 Membrane biofouling by extracellular polymeric substances

Membrane biofouling is almost inevitable during membrane separation processes when microorganisms are present. Biofouling refers to biofilm formation which is caused by accumulation or growth of microorganisms on the membrane surface [8, 33-35]. Severe biofouling leads to deterioration of membrane performances during water treatment or desalination, such as flux decline, reduction of salt rejection and increase of energy consumption [33, 35, 36].

Most studies to date focus on the bacteria themselves rather than the EPS they produce. Extracellular polymeric substances (EPS) produced by bacteria are considered as the major components of biofilms, representing up to 95% of their biomass and can be considered the primary matrix material of the biofilms [37]. EPS is the largest identified fraction of organic matter in seawater, initiating formation of biofilms on the membranes and thus affecting the physical properties of biofilms (e.g. mechanical characteristics). Both attachment of microorganisms and cohesion of the biofouling layer are performed by the EPS. Previous studies attributed the significant decrease of membrane performance associated with biofouling to the presence of the EPS rather than microorganisms themselves [4, 31, 38]. Herzberg et al. [4] investigated the effect of isolated EPS on membrane biofouling and found that formation of the EPS fouling layer adversely affected flux by increasing the hydraulic resistance to permeate flow. During controlled experiments with isolated EPS, polysaccharides were more effectively adsorbed on the EPS fouling layer as compared to adsorption of proteins. The preferential adsorption of EPS was greatly promoted in the presence of calcium as a result of specific EPS – calcium interactions.

EPS vary considerably in their chemical and physical properties; but they are predominantly extracellular polysaccharides and proteins [33, 38, 39], from which the major hydraulic resistance offered by the biofilms is derived [31, 40, 41]. The molecular weights of most polysaccharides are large and
polysaccharide solutions would be accordingly viscous [42-44]. The heterogeneous components of EPS contain three main functional groups: carboxylic acids (COOH), phenolic alcohols (OH), and methoxycarbonyls (C = O) [38, 45]. The ionization of these groups results in electrostatic attraction and expansion of the biopolymers in the presence of other counter ions. The physiochemical characteristics of EPS, such as charges, conformation and hydrophobicity, which have great impacts on their fouling potential, could be affected by membrane properties, feed water chemistry (e.g. ionic strength and multivalent ions) and operating conditions (e.g. temperature, applied pressure and cross-flow velocity) [8, 38, 46, 47].

Membrane properties also play a crucial role in membrane biofouling. Membrane characteristics, such as roughness, surface charge and membrane hydrophilicity, affect the interaction between membrane and foulant in the feed solution. It has been reported that rougher membrane surface can promote attachment of foulants or bacteria onto the membrane [48]. Membrane with the same surface charge as that on EPS molecules can reduce deposition of EPS onto the membrane by electrostatic repulsion between the charges [49]. Hydrophilic membranes were found to suffer less fouling [50].

In addition to membrane properties, solution chemistry greatly affects membrane fouling. It is well known that seawater and wastewater contain a large amount of free ions. Ionic strength has a large impact on EPS fouling, for example, EPS fouling increases at higher ionic strength. Higher ionic strength could cause compression of electrical double layer (i.e., enhanced charge screening due to greater counter ion concentration), reducing electrostatic repulsion between EPS molecules and promoting deposition of EPS on membrane surface [46]. The deposited foulant layer in turn increases the osmotic pressure on the membrane surface by preventing back diffusion of ions [3, 29, 51-53].

The presence of divalent ions plays an important role on the interaction between adjacent negatively charged EPS macromolecules [54], and the
interaction between them and the membrane. Divalent cations such as Ca\(^{2+}\) ions and Mg\(^{2+}\) ions can form complexes with negatively charged functional groups, such as carboxylic groups (–COO\(^-\)) of macromolecules, and neutralize the negative charges on the macromolecules or bind them together via ion bridging. Membrane surface charges can be screened due to such charge neutralization effect. The consequently weakened electrostatic repulsion between foulants and membrane, as well as the formation of macrocomplexes, such as polysaccharide – Ca – membrane and polysaccharide – Ca – polysaccharide (Fig. 2.2), through ions interaction, promote the deposition of EPS on the membrane surface reducing permeate flux especially at high calcium concentrations [5, 43, 46, 47, 55].

![Fig.2.2 Schematic crosslinking of polysaccharides by calcium ions [56]](image)

Membrane fouling by EPS is dependent on operating conditions, including operational temperature, initial flux and cross-flow velocity. Temperature can affect the extent of EPS fouling perhaps through its impact on the viscosity of EPS inclusion feed water and permeate. In particular, temperature shows greater impact on FO process through the influence on osmotic pressure of draw solution. Elevated temperature results in reduced solution viscosity of both feed solution and water permeate/draw solution, and increased osmotic pressure of the solutions [57-59], resulting in increased permeate flux, according to the following equations [57, 60, 61]:

\[
\pi = iCR_gT \quad (2.1)
\]

\[
J = \Delta \pi / (\mu \cdot R_d) \quad (2.2)
\]
where $\pi$ is the solution osmotic pressure (bar), $i$ is the Van’t Hoff factor, $C$ is the concentration of the solute (mol/L or M), $R_g$ is the universal gas constant ($R_g=0.0831$ L·bar/(mol·K)), $T$ is the absolute temperature (K), $J$ is the water flux (LMH or m/s)), $\Delta\pi$ is the trans-membrane osmotic pressure difference (Pa), $\mu$ is the viscosity of water permeate (Pa·s), and $R_t$ is the total hydraulic resistance (m$^{-1}$).

It has been widely reported [32, 43, 62] that the initial flux obtained had a significant influence on membrane fouling. Faster buildup of foulants or biofilm was observed at higher initial flux, resulting in greater flux decline [32, 62]. Water flux resulting from applied pressure generates a convective drag force [43], which drives the EPS towards the membrane, thus leading to the attachment of EPS onto the membrane surface. Cross-flow velocity affects membrane fouling by generating a shear force which reduces the buildup of foulants and fouling layer on the membrane surface. In particular, in low fouling FO process, higher cross-flow velocity could be used as an effective way to control membrane fouling [3, 21, 32, 62, 63].

In summary, membrane fouling by EPS is complex. It is affected not only by membrane properties, but also by solution chemistry. Moreover, operating conditions play an important role in EPS fouling. In addition, the combined effect of these factors shows even greater impact on EPS fouling.

2.2.2 Mechanism to biofouling: Foulant – membrane interactions and foulant – foulant interactions

Two major stages can be considered in membrane fouling: foulant – membrane interactions and foulant – foulant interactions. The foulants in the feed solution firstly interact with the membrane material through functional groups and accumulate on the membrane surface under the convective flux. Afterwards, the foulants in the feed solution interact with the foulants that deposited on the membrane surface, and form macromolecules. This also applies in membrane biofouling [35]. Biofouling takes place by adhesion of microorganisms to the
membrane surface followed by growth of biofilm through growth/division and cohesion between the adhered microorganisms and the suspended microorganisms in the feed solution. Adhesive interactions between microorganisms, and microorganisms and membrane surfaces usually result from the sticky nature of the EPS, which help the cell to anchor on the membrane surface [35].

Foulant – membrane interactions are affected by membrane properties (i.e. roughness and charges), foulant properties (i.e. charges) and solution chemistry (i.e. ionic strength and divalent ions), while foulant – foulant interactions are also affected by operational conditions (i.e. initial flux and cross flow). Specifically, divalent cations (M$^{2+}$) play a critical role in membrane fouling by EPS. They may promote not only foulant – membrane interactions through forming bridges between EPS macromolecules and the membrane surface, but also foulant – foulant interactions, forming bridges between EPS macromolecules. The resultant bridging between EPS and membrane surface promotes further deposition of EPS onto the membrane surface. Further accumulation of EPS due to the formation of EPS–M–EPS complexes, as divalent ions bridge EPS in the feed solution and the EPS deposited on the membrane surface, lead to increased fouling resistance and permeate flux decline.

2.3 Overview of reverse osmosis fouling

Despite the fact that reverse osmosis (RO) desalination has been widely used for water supply, membrane fouling, especially biofouling, remains one of the most difficult challenges in RO separation processes. RO membranes suffer from biofouling caused by a large diversity of bacteria including *Mycobacterium, Flavobacterium, Pseudomonas* and other species [33, 64]. EPS produced by such bacteria also contribute to biofouling by providing support to bacteria, enabling bacteria to anchor on the membrane surface, and protecting bacteria from dispersal by chemical agents. A number of studies have been conducted to investigate RO membrane fouling by EPS, with some focusing on
the effect of physical and chemical factors and demonstration of the mechanisms that govern RO membrane fouling by EPS, especially by polysaccharides [6, 8, 47, 65, 66].

Under the effect of hydrodynamic forces resulting from convective and diffusive natures of water flow, the EPS are carried to the membrane surface [6, 31, 38]. Membrane fouling by EPS then occurs in two stages – adhesion of the foulants and cohesion of the foulants. The membrane – foulant interactions and foulant – foulant interactions in association with adhesion and cohesion of the foulants are affected by a number of factors described below.

2.3.1 The influential factors of foulant – membrane interactions

The interactions between foulants in the feed solution and membrane can be affected by a number of individual or synergistic factors:

1) Membrane properties and foulant characteristics.

2) Solution chemistry.

3) Hydrodynamic forces.

Membrane properties (i.e. roughness, charges and hydrophilicity) and foulant characteristics (i.e. molecular size and charge) play a crucial role in membrane fouling, especially on the initial attachment of foulants on the membrane surface [50, 67, 68].

A major factor affecting the membrane – foulant interactions was the membrane surface properties. For example, the membranes with higher hydrophobicity and less surface charge exhibited stronger membrane – foulant adhesion forces [68]. Li et al. [49] found that membrane fouling was dominated by the electrostatic interactions between the organic compounds and the membrane surface. Nguyen et al. [67] correlated initial flux decline rate with membrane properties, such as membrane permeability and roughness, and alginate – membrane interfacial free energy. The fouling layer’s porosity was
found to be greatly influenced by the contact angle and surface area difference (SAD) of the membrane, which also greatly affected fouling layer mass and thickness, respectively. Contreras et al. [50] correlated alginate adsorption on self-assembled monolayers (SAMs) with water contact angle, where –CH₃ and –OPh showed the highest adsorption, while the lowest adsorption was observed on the most hydrophilic surfaces (–OH and –CONH₂). Pedersen et al. [69] correlated RO membrane fouling with polymer charge density (CD) and membrane surface charge, and found that more severe fouling was found in the presence of the lower CD polymers than that of the medium CD polymers. Highly negatively charged membrane surfaces were more susceptible to irreversible fouling.

In addition, specific interactions between functional groups on the foulant molecules and the membrane surface promote the adherence of foulants to the membrane surface [50]. Wu et al. [65] reported that –COOH on the SAMs of the membrane resulted in greater initial attachment and adsorption of alginate than other functional groups in the presence of calcium ions. Calcium ions affect adherence of alginate to membrane surfaces. Addition of calcium ions can lead to decrease in the free energy of adhesion between alginate and RO membranes, increasing alginate adsorption [50]. The presence of calcium ions can also reduce the negative charges on both the alginate and the membrane surface, which results in the reduction in the repulsion between the them, ultimately leading to adhesion of more alginate onto the membrane surface [66]. Calcium ions can make the polyamide composite RO membranes and alginate more hydrophobic, and thus increased the rate of flux decline [5].

Feed solution chemistry, such as the foulant concentration, pH and ionic strength, also affects adhesion of foulants to the membrane surface. During the first stage of fouling, conditioning the RO membrane surface is mainly caused by organic compounds and is dominated by their concentration in the feed solution [70]. Foulant – membrane interactions are greatly affected by feed solution pH through protonation and deprotonation of the functional groups on
the foulant molecules and the membrane surface, which greatly affect the adsorption of foulants on the membrane surface. Protonation occurs when pH is above the isoelectric point (IEP). The increased pH may result in the decrease in the zeta potential of the foulants and the membrane surface, making them more negative, and cause strong electrostatic repulsion between them [71] and less attachment of foulants on the membrane surface [8, 66]. Conversely, when pH value is between the IEPs of foulants and the membrane surface, adsorption of foulants on the membrane would be promoted [8, 66]. In some circumstances, the effect of pH could be masked. Yu et al. [72] reported elevated pH resulted in the reduction of electrostatic repulsion between the foulants and the membrane surfaces at a low ionic strength, promoting accumulation of foulants on the membrane surfaces; but negligible effect on membrane fouling at seawater level ionic strength was observed. Higher ionic strength of the feed solution showed great impact the adsorption of foulants on the membrane surface. High ionic strength caused significant charge screening and compression of electrostatic double layer for the foulants as well as the membrane surfaces, enhancing the hydrophobic interactions between them and leading to great fouling rate [8]. It was found that at high pH the zeta potential of the membrane surface was less negative at lower ionic strength compared to higher ionic strength, while at low pH the zeta potential of the membrane surface was less positive at lower ionic strength [71]. This indicated the increase in ionic strength showed negligible influence on the IEP of the membrane surface, but caused electrical double layer compression or charge screening by the increase in counter ions.

Adhesion of foulants on the membrane is also greatly affected by the hydrodynamic forces, such as flux and cross-flow velocity. Initial flux decline rate in the RO process of organic foulants was found to be increased with elevated operating pressures [73]. The higher initial permeate flux or applied pressure generated higher permeation drag, which accelerated foulant deposits on the membrane and the initial permeate flux decline [74]. The shear rate generated by the cross-flow velocity could also affect the loading rate of
organic compounds, which were the main nutrients supply in the feed solution, and adherence properties of EPS [70]. It was found that the increased shear rate led to reduction in the deposition of alginate and calcium ions on the membrane surface, lessening alginate fouling [8].

2.3.2 The influential factors of foulant – foulant interactions

After the deposition of the foulants onto the membrane surface, a thin layer of the foulants forms. The deposited foulants change the physicochemical characteristics of the surface, including surface roughness, surface hydrophobicity and surface charges, which then affect adsorption of the foulants in the aqueous feed solution [38]. The cohesion of foulants takes place by the interactions between the deposited foulants on the membrane surface and the foulants in the feed solution, which is dominated by the foulant characteristics and affected by individual or synergistic factors, such as:

1) Solution chemistry.
2) Hydrodynamic forces.

Feed solution chemistry including pH, ionic strength and specific ions greatly affects foulant characteristics, especially charge. As mentioned above, pH affects foulant charges through protonation (below isoelectric point or IEP) and deprotonation (above IEP) of the functional groups of the foulant molecules, and therefore alters the electrostatic repulsion between the foulant molecules [68, 71, 75].

The foulant charges are also affected by ionic strength. Higher ionic strength results in charge screening of the foulant molecules or double layer compression, accelerating the hydrophobic interactions among the neighbor molecules. For example, during alginate fouling, increase in ionic strength caused compression of electric double layer around charged alginate molecules, which led to reduction in electrostatic repulsion between adjacent alginate molecules in the feed solution [8, 75]. With the reduced interchain electrostatic repulsion, alginate molecules become more coiled and the intermolecular
adhesion between adjacent alginate molecules increased, leading to formation of a thicker and more compact alginate fouling layer on the membrane surface and increment of hydraulic resistance to the permeate flow through the membrane, and thus flux decline [8, 75].

Specific counter ions in the feed solution, such as calcium ions, can act as a bridge between the negatively charged functional groups of the foulant molecules, promoting the formation of compact fouling layers. The impact of calcium ions on membrane fouling by alginate has been widely studied [5, 8, 66, 75]. Severe alginate fouling was observed in the presence of calcium ions and attributed to the complexation of calcium ions with the carboxylic groups of the alginate molecules [5, 8, 65, 66, 75]. The bridging effect of calcium ions between adjacent alginate molecules resulted in an egg-box-shaped gel network, leading to dense and compact fouling layer [5, 8, 66, 75].

Hydrodynamic forces including initial flux (applied pressure) and shear force generated from cross-flow velocity plays an important role in formation of fouling layers. Higher fluxes under higher applied hydraulic pressure resulted in an increased flux decline and fouling rate [8, 73, 76]. The elevated operating pressure resulted in significant increase in steady-state permeate flux at the end of filtration, which demonstrated a pressure-dependent permeate flux [73]. During alginate fouling, alginate fouling layer was more compressed at higher initial flux (or trans-membrane pressure), leading to increase in hydraulic resistance to permeate flow [8]. Shear force generated from the linear flow velocity was found to affect EPS chemical composition, which led to changes in EPS cohesion and elasticity [70]. EPS elasticity increased at higher shear rate, likely to induce compactness of biofilm and enhance flux decline rate. Higher shear rate could result in a lower amount of biomass at lower TOC concentration probably through the combination of reduced CP, reduced cell attachment rate, extended biomass detachment rate and lower substrate concentration for biofilm growth. Mattaraj et al. [73] reported the increase in cross-flow velocity did not have a significant effect on the initial flux, but
enhanced flux for longer period of filtration, which was attributed to the decrease in specific cake resistance.

2.3.3 Subsequential effect of foulant adsorption on membrane fouling

As foulants in the feed solution accumulate on the membrane surface, fouling layers form and accelerate the flux decline rate largely through the increase of cake resistance, and cake- and biofilm-enhanced osmotic pressure (CEOP and BEOP).

In 2002, Hoek et al. [77] for the first time proposed the model combining cake filtration theory and the CEOP effect. The CEOP effect occurs when the formation of fouling layer on the membrane surface hinders the back-diffusion of salt to the feed solution which results in increase of salt concentration near the membrane surface. It was found to be more significant in thicker fouling layer than thinner fouling layers that formed on the seawater membranes [6], and strongly enhanced by the flux [76]. Herzberg and Elimelech [31] proposed a BEOP effect governing the decline in RO membrane performance through increase in both trans-membrane osmotic pressure and hydraulic resistance. During biofouling, bacterial cells enhanced osmotic pressure on the membrane surface through the effect of BEOP and the EPS contributed to the flux decline by increasing the hydraulic resistance to permeate flow [4, 31].

2.3.4 Hydraulic resistances

Hydraulic resistance is an alternative way to describe the extent of fouling. Generally, total hydraulic resistance consists of membrane resistance \( R_m \), resistance due to blockage \( R_b \), resistance due to concentration polarization \( R_{cp} \) and resistance due to cake formation \( R_c \) [78]. In the reverse osmosis (RO) process, the membranes e.g. polyamide thin film composite (BW30), have small pore sizes, with a 180 Da molecular weight cut-off [79]. As a result, the effect of pore blockage by EPS is considered negligible in RO, and so is the resistance which results from blockage.
However, the fouling mechanism is often complicated because of the interplay between the accumulated salt during concentration polarization and the growing foulant layer or cake formation on the membrane surface which increases cake resistance [76]. Concentration polarization is a universal phenomenon in membrane separation process when the feed solution contains salt solutes. A build-up of solutes forms on the membrane surface as the salt solutes in the feed solution are carried toward the membrane under the convective flux and rejected by the membrane. Subsequently, concentration polarization increases the osmotic pressure near the membrane surface and reduces the effective driving force, which results in reduction in permeate flux. Cake formation refers to the build-up of fouling layers by the accumulation or deposit of foulants, such as polysaccharides, to the membrane surface from the bulk feed solution. The fouling layers add cake resistance to the convective flow towards the membrane and therefore reduce the permeate flux.

The presence of salt promotes the accumulation of polymer foulants by compression of electrical double layers, whilst the accumulated polymer enhances cake-enhanced osmotic pressure (CEOP) or cake-enhanced concentration polarization (CECP), which occurs when the build-up of the cake layer on the membrane surface hinders the back-diffusion of salt ions to the bulk solution that leads to an elevated salt concentration near the membrane surface [29, 31, 76]. Herzberg and Elimelech [31] attributed deterioration of membrane performance to the elevated trans-membrane osmotic pressure, which resulted from bacterial cells on the membrane hindering the back diffusion of salt and increasing in hydraulic resistance of the EPS to the permeate flow. Therefore, contribution of resistance due to concentration polarization ($R_{cp}$) and resistance due to cake formation ($R_c$) to membrane fouling vary during the membrane separation processes.

Some models of the resistance in series based on Darcy’s Law were developed to quantify effect of hydraulic resistance on membrane fouling [67, 80-82]. Some literature subdivided non-membrane resistances based on the cleaning
effect into the reversible fouling resistance ($R_{rf}$) and the irreversible fouling resistance ($R_{if}$) [83]. Rare studies included $R_{cp}$ in the total hydraulic resistance and demonstrated the relationship between $R_{cp}$ and elevated osmotic pressure on the membrane surface. It would be interesting to develop a model to illustrate the effect of concentration polarization on membrane fouling based on analysis of hydraulic resistances.

2.4 Overview of forward osmosis fouling

Forward osmosis (FO) has been extensively studied due to its great application potential in desalination [23, 24]. However, questions and challenges regarding production efficiency in association with membrane property, draw solution and membrane fouling remain. Despite a lower fouling propensity in FO observed in previous studies [3, 9, 28, 43, 47, 52, 62], membrane fouling in FO is a more complicated phenomenon compared to the pressure-driven membrane processes. In addition to the factors affecting fouling in RO (membrane property, feed solution chemistry and operating conditions) additional factors derived from the draw solution side need to be considered in FO, which include membrane substrate [43, 47, 84-87], draw solute type as well as draw solution concentration [63, 88, 89] and draw solution temperature [57, 90, 91]. This section will review two aspects of FO fouling: the active membrane layer on the feed solution side; and effect on the draw solution side.

2.4.1 Factors in the feed solution side that affect forward osmosis fouling

Similar to RO fouling, forward osmosis (FO) fouling experiences two stages of fouling: foulant – membrane interactions and foulant – foulant interactions. As FO has a low fouling propensity, it is considered to be dominated by the interaction between foulants and the membrane surface, which is associated with membrane properties and solution chemistry.
1) Membrane properties

Membrane properties, such as surface roughness, surface hydrophilicity and surface charges, strongly affect the interactions of foulants with the membrane surface. Smoother and more hydrophilic membrane are less likely to cause foulant adhesion and accumulation on the membrane surface. A recent study by Lu et al. [48] demonstrated that membrane surface roughness was the most important factor in determining membrane fouling propensities using alginate as the model polysaccharide. A greater fouling propensity was observed using polyamide thin film composite (PA TFC) membranes compared to that of cellulose triacetate (CTA) membranes, due to its greater surface roughness [92]. The PA TFC membrane surface was more susceptible than the CTA membrane to alginate absorption as indicated by its slightly faster initial fouling rate [2].

Several studies [43, 47, 84-86] evaluated organic fouling behavior of CTA FO membrane by operating in forward osmosis (FO) mode (active layer facing the feed solution) and pressure retarded osmosis (PRO) mode (support layer facing feed water) of the membrane by altering membrane orientation. The active layer is more likely to prevent the adhesion and accumulation of foulants on the membrane surface, especially under a higher hydrodynamic shear force, while the support layer suffers more significant deposition of the foulants cannot easily be removed by the hydrodynamic shear rate. The active layer is denser, smoother and tighter than the support layer, and therefore less susceptible to fouling.

2) Solution chemistry

Solution chemistry is of great importance in FO fouling, especially the interactions between the foulants in the feed solution and the membrane surface. Specifically, the presence of divalent cation ions (i.e. calcium ions) has great influence on the foulant – membrane interactions in the FO process [47, 48, 63, 84, 93]. Calcium can interact with the negatively charged functional groups, such as carboxyl groups on the foulant molecules and membrane surface. This
leads to a reduction in the hydrophilicity of the membrane and the foulant, and decreases the electrostatic repulsion between the foulants and the membrane. A previous study [47] evaluated the effect of calcium ions on the interfacial free energy of alginate adhesion to membrane, and found the presence of calcium increased the negative value of alginate-membrane interfacial free energy of adhesion, which indicated the presence of calcium ions resulted in greater alginate – membrane attraction. Therefore, calcium ions facilitate bridging between the foulant molecules and membrane surface, resulting in the accelerated adsorption of foulants on the membrane surface.

2.4.2 The draw solution plays an important role in forward osmosis fouling

The forward osmosis (FO) process utilizes an osmotic pressure gradient of the draw solution as driving force. Therefore, the type and concentration of draw solution play an important role in the FO process. And FO fouling is greatly influenced by draw solution through permeate flux, which is generated by the osmotic pressure of draw solution, and interactions of foulants in the feed solution with draw solutes, which reversely diffused from the draw solution to the feed solution.

1) Draw solution affects FO fouling through initial flux

Generally, FO fouling is more severe at higher initial flux generated by a higher osmotic pressure [63, 86, 88, 89]. Draw solutes of different types at the same solution concentration have different osmotic pressures [63]. As a result, in order to achieve the same initial flux, the draw solution concentration varied according to the types of draw solutes [88, 89]. For example, Achilli and co-workers [89] found that to achieve the same osmotic pressures, the required mass concentrations of different solutes were different (Fig.2.3).
Fig. 2.3 Relationship between solution osmotic pressure and solution concentration of different draw solutions [89].

Fig. 2.4 Water Flux generated using different concentrations of NaCl draw solution [86].

The draw solution concentration greatly affects the diluted internal concentration polarization (ICP) on the draw solution side, which in turn has a great influence on initial flux. Although the initial flux is dependent on the concentration of draw solution, the relationship is indeed non-linear (Fig. 2.4) [63, 85, 86]. The reduced effectiveness of draw solution concentration is attributed to the ICP [53, 63, 85-88, 94], which is caused by the accumulation of the solutes from the feed solution retained by the rejection layer of the membrane and more importantly the hindered diffusion of solutes in the porous
support layer from the draw solution [63, 85]. As a result of the accumulated solutes on the two sides of the membrane rejection layer, the effective driving force of the FO process (i.e. the difference in the concentration across the membrane rejection layer) is much lower than the apparent driving force (i.e. the difference between the draw solution concentration and feed solution concentration). Therefore, at higher draw solution concentration, the ICP is more severe due to the higher water flux level, and the water flux enhancement with the increase in draw solution concentration becomes marginal [63, 85].

2) Draw solution affects FO fouling through reverse diffusion of draw solute

In FO, membrane fouling is greatly promoted by accelerated cake-enhanced osmotic pressure (CEOP). The cake fouling layer in the feed solution hinders reverse diffusion of draw solutes from the draw solution side and causes an increase in osmotic pressure near the membrane surface [3, 51-53]. The reverse diffusion of draw solutes is influenced largely by the type and concentration of draw solution. Different types of draw solutes reversely diffuse at different rates [88], change the feed solution composition and may potentially interact with foulants in the feed solution. Greater FO membrane fouling can be observed when divalent ions are used as draw solutes [63, 88].

The reverse diffusion rate (solute flux) is dependent on the water flux, as described in the Equation (2.3) [48, 88, 95]:

\[ J_s = J_w \frac{B}{A n R_g T} \]

where \( J_s \) is the solute flux (mole/(m\(^2\)·h)), \( J_w \) is the water flux (LMH or m/s), \( A \) is the water permeability coefficient of the membrane (m/(s·Pa)), \( B \) is the solute permeability coefficient of the membrane (m/s), \( n \) is the van’t Hoff coefficient, \( R_g \) is the universal gas constant (\( R_g = 0.0831 \) L·bar/(mol·K)) and \( T \) is the absolute temperature (K).

Therefore, decrease in the draw solution reduces the water flux and the solute flux. In addition, the decrease in the draw solution results in reduction of ICP.
However, most studies [2, 3, 9, 48, 62, 63] on FO fouling recirculated the diluted draw solution to the draw solution bank, which prevented constant operational conditions being attained. Thus, to better control the experimental operation, it is necessary to explore better methods to maintain a constant draw solution concentration.

2.5 Comparison of fouling in reverse osmosis and forward osmosis

Rare studies have been carried out to compare polysaccharide fouling in forward osmosis (FO) and reverse osmosis (RO) [2, 3]. In 2010, Lee and co-workers [3] compared FO and RO fouling behaviors performed under identical physicochemical conditions for the first time; in which 5.0 M NaCl solution was used as draw solution in FO and alginate was used as one of model foulants to represent common polysaccharide. Their results, based on comparison of alginate fouling in FO and RO, elucidated that the key mechanism of flux decline in FO was rather accelerated cake-enhanced osmotic pressure (CEOP) due to reverse salt diffusion from the draw solution to the feed solution hindered by the fouling layer than increased fouling layer resistance; and the fouling layer was loose and able to be removed by physical cleaning in FO, demonstrating the high reversibility of FO fouling. Meanwhile, Mi and Elimelech explored fouling and cleaning mechanisms with the use of 4.0 M NaCl solution as draw solution in FO and alginate as the model foulant by comparing membrane separation performances in FO and RO [2].

Both of the studies used corrected normalized flux due to continuous decrease in driving force resulting from the dilution of non-saturated NaCl draw solution in FO. As the water was continuously driven from the feed solution side to the draw solution side, the draw solution was correspondingly diluted. It was found in both of the studies that alginate caused more severe or similar fouling and permeate flux decline in FO compared to RO under identical experimental conditions (Table.2.1) [2, 3].
Table 2.1 Comparison of alginate fouling in RO and FO in two previous studies

<table>
<thead>
<tr>
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<tbody>
<tr>
<td><strong>RO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial flux</td>
<td>7.0 μm/s (25.2 L/m²·h)</td>
<td>8.1 μm/s (29.2 L/m²·h)</td>
</tr>
<tr>
<td>Driving force</td>
<td>450 psi</td>
<td>400 psi</td>
</tr>
<tr>
<td>5.0 M NaCl</td>
<td></td>
<td>4.0 M NaCl</td>
</tr>
<tr>
<td>Flux after 500 min</td>
<td>~5.0 μm/s</td>
<td>~4.5 μm/s</td>
</tr>
<tr>
<td>Flux decline after 500 min</td>
<td>~29%</td>
<td>~44%</td>
</tr>
</tbody>
</table>

As discussed in Section 2.3.2, dilution of draw solution causes reduction in osmotic pressure of draw solution and affects internal concentration polarization (ICP) in the supporting layer of the membrane. Therefore, the FO performance test was recommended to be conducted with either a large volume of draw solution or a control system to maintain constant draw solution concentration [58], which may not be feasible. Thus it is important to develop a new method to effectively maintain constant driving force in FO. For research, the use of constantly saturated draw solution could be a promising method to maintain constant driving force in FO, enabling a better comparison of membrane fouling in FO and RO. Detailed information on design of constantly saturated draw solution can be found in Section 3.5. It will be of interest to compare membrane fouling in RO with that in FO under identical solution chemistry (i.e. ionic strength, Ca²⁺ concentration and foulant concentration) and operating conditions (i.e. temperature, initial flux, cross-flow velocity) except that the pressure source in FO being osmotic pressure and hydraulic pressure in RO, and elucidate polysaccharide fouling mechanisms under different pressure sources.

Similar with fouling in the RO process, alginate was also commonly selected as the only model to study membrane fouling by polysaccharides. However, alginate is atypical to represent polysaccharides produced by most species of bacteria. It is very important to investigate polysaccharide fouling mechanisms...
in FO and RO using different kinds of polysaccharides as foulants. Rare studies [4, 38] have been conducted on membrane fouling by EPS isolated from bacteria, demonstrating rather a synergistic fouling effect of polysaccharides and proteins in the EPS than the effect of individual foulants. Therefore, a better understanding on fouling behaviors of polysaccharides in both RO and FO is essential.

2.6 Membrane fouling control

Although membrane fouling is an inevitable phenomenon during membrane separation process, it can be controlled or alleviated by a number of strategies. These strategies included operation under elevated cross-flow velocity, physical washing, chemical cleaning, membrane modification, pre-treatment of feed and use of spacers. Due to the inherent differences in the formation of fouling in reverse osmosis (RO) and forward osmosis (FO) processes, fouling control methods vary significantly. Mostly, operation under elevated cross-flow velocity and physical washing are useful in the FO process, as FO process is a low fouling process and fouling is reversible. However, neither method can completely remove foulants from the membrane surface in RO because of the compactness of the foulant layer under high hydraulic pressure [96-98]. As a result, RO fouling mitigation was usually achieved by other methods, one of which is chemical cleaning compounds. This section reviews mitigation of membrane fouling by chemical compounds during the RO process and briefly introduces other strategies for membrane fouling control in RO.

2.6.1 Membrane fouling mitigation by chemical compounds during the RO process

Irreversible fouling is the strong attachment of foulants, which cannot be removed by physical cleaning. However, control of irreversible membrane fouling could be achieved by correct dosing of chemical compounds during the fouling process. Table.2.2 summarizes the effect of commonly used chemical
compounds for membrane fouling mitigation during the reverse osmosis (RO) process.

Table 2.2 Commonly used chemical compounds for membrane fouling mitigation

<table>
<thead>
<tr>
<th>Chemical compounds</th>
<th>Chemical concentration</th>
<th>exposure time</th>
<th>Solution pH</th>
<th>Fouling control efficiency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA</td>
<td>1 mM</td>
<td>–</td>
<td>7</td>
<td>54% inhibition efficiency</td>
<td>[99]</td>
</tr>
<tr>
<td>PASP</td>
<td>10 mg/L</td>
<td>–</td>
<td>7</td>
<td>91% inhibition efficiency</td>
<td>[99]</td>
</tr>
<tr>
<td>PASP</td>
<td>10 mg/L</td>
<td>–</td>
<td>7</td>
<td>95% inhibition efficiency</td>
<td>[100]</td>
</tr>
<tr>
<td>LB-0100</td>
<td>5 mg/L</td>
<td>–</td>
<td>7</td>
<td>65% inhibition efficiency</td>
<td>[100]</td>
</tr>
<tr>
<td>NaDCC</td>
<td>10 mg/L as TAC</td>
<td>–</td>
<td>7.2</td>
<td>~2.0 log cells reduction</td>
<td>[101]</td>
</tr>
<tr>
<td>NaOCl</td>
<td>10 mg/L as TAC</td>
<td>–</td>
<td>7.2</td>
<td>~1.6 log cells reduction</td>
<td>[101]</td>
</tr>
<tr>
<td>SNP</td>
<td>80 μmol/L</td>
<td>12 h</td>
<td>7.4</td>
<td>38% biovolume reduction</td>
<td>[10]</td>
</tr>
<tr>
<td>MAHMA NONOate</td>
<td>20 μmol/L</td>
<td>2 h</td>
<td>7.4</td>
<td>40% biovolume reduction</td>
<td>[10]</td>
</tr>
<tr>
<td>PROLI NONOate</td>
<td>40 μmol/L</td>
<td>1 h</td>
<td>7.4</td>
<td>30% biovolume reduction</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Antiscalants are widely used in control of membrane scaling during desalination. Their effects on other kinds of membrane fouling, such as organic fouling and biofouling, have also been studied [99, 100, 102]. Polyaspartic acid (PASP), as an antiscalant, was effective in inhibiting membrane fouling by protein and humic acid (HA) if properly dosed, likely through the formation of stable water-soluble complex through Ca^{2+} ions bridging the antiscalant and the foulants [99, 100]. In spite of its effectiveness in mitigating protein fouling and humic acid fouling, antiscalant enhanced biofilm formation on RO membranes by either altering the membrane properties, such as hydrophobicity and surface charge, or serving as a phosphorous source of nutrients for microorganisms [102].

Some new disinfectants were also explored to mitigate biofouling in RO desalination [17, 101]. For instance, sodium dichloroisocyanurate (NaDCC) exhibited a better inactivation effect on biofilm (Pseudomonas aeruginosa
PAO1 GFP) than chlorine under the same total available chlorine concentration, showing promises for biofouling control in the RO process [101]. Vanillin was found to be able to suppress biofilm formation on the membrane, revealed by the reduction in average thickness, total biomass and the total protein content of the biofilm [17].

Nitric oxide (NO) donor compounds are able to alleviate bacterial adhesion, induce dispersal of biofilm on the membrane surface and reduce biofouling [10-16]. The addition of NO at low, nontoxic concentrations led to the dispersal of microbial biofilm. For example, NO donors at picomolar and low nanomolar levels resulted in reduction of total biofilm surface, with an average reduction rate of 63% [14]. NO at a flux of 30 pmol/(cm²·s) led to reduction in adhesion of *Staphylococcus aureus*, *Staphylococcus epidermidis*, and *Escherichia coli*, with a reduction rate of 96%, 48% and 88%, respectively [12]. However these bacteria species are not typical in seawater environments. One kind of NO donor, SNP, at the low, sublethal concentrations of 25 to 500 nM induced dispersal of *Pseudomonas aeruginosa* biofilm [13]. Various NO donors dispersed not only single species biofilms of some microorganisms, but have also been effective at removing multi-species biofilms from water treatment and purification systems such as membrane bioreactor and reverse osmosis [10, 14].

Optimal efficiency of biofilm dispersal could be achieved by optimizing NO donor concentration and exposure times. NO donors with short half-lives would disperse biofilms at short exposure times [10]. Biofilm dispersal involved a reduction of both EPS and bacteria cells. For example, a 29% reduction in EPS was observed corresponded to a 38% reduction in live cells in the samples that were treated with the NO donor, MAHMA NONOate, probably due to the lower live cell numbers resulting in a lower production of EPS [10]. A study on NO treatment for the control of RO membrane biofouling revealed that a 92% reduction in the rate of RO membrane biofouling (pressure rise over a given period) was achieved with NO treatment by adding 40 μM PROLI NONOate at 24-h intervals [16]. It was also observed that PROLI NONOate treatment
reduced polysaccharides, proteins and microbial cells, with a reduction rate of 48%, 66% and 29%, respectively [16]. However, biofilm dispersal could be less effective when alginate is produced. NO induced dispersal of PAO1 biofilm was found to be inhibited, which could be due to inactivation of NO by the thickly coated alginate layer on the cells preventing NO from initiating the cascade of events resulting in dispersal of biofilm [11]. Although alginate was considered to protect bacteria from induced dispersal, effect of NO on alginate fouling in the absence of cell is still unknown. It is of great interest to investigate the effect of NO on control of membrane fouling by EPS, such as alginate.

2.6.2 Other strategies for membrane fouling control

1) Chemical cleaning after fouling runs

Generally, irreversible membrane fouling can also be mostly removed by short time (i.e. 30 min) chemical cleaning after the membrane fouling runs using chemical solutions in the absence of foulants. Aqueous solutions with low concentration of chemical compounds, such as ethylenediaminetetraacetic acid (EDTA) [5, 96, 98], NaCl [98], SDS [98] and thermo-responsive polymer (TRP) [97], have been found to be effective during fouled membrane cleaning.

2) Operation under elevated cross-flow velocity

Operating at higher cross-flow velocity can reduce membrane fouling in FO by generating a greater shear force, which reduces external concentration polarization (ECP) [21, 32, 63] and hinders foulant accumulation on the membrane surface [3, 62].

3) Physical washing

Based on foulant strength of attachment to the membrane surface, membrane fouling can be divided into reversible and irreversible fouling [103]. Reversible fouling can be removed using physical cleaning. When the fouling layer is loose and sparse, the fouling layer can be broken into small patches and
removed by backwashing or cross flow. As FO is a low fouling process with low fouling propensity, physical cleaning, for example, periodic rinses with water at a same or an elevated cross-flow velocity, is commonly used an effective strategy to mitigate FO fouling [2, 9, 34, 47, 104-106].

4) Use of spacer

Spacers placed alongside the membrane are able to create turbulence, reduce external concentration polarization (ECP) and membrane fouling [28, 62, 94, 107-109]. In FO, a spacer in the draw solution side also effectively reduced dilutive internal concentration polarization (DICP) [107]. Inserting a spacer in the feed channel improves mass transfer in the boundary layer near the membrane surface [62]. Using thicker spacer greatly reduced flux decline during FO biofouling [36]. Modifying the polymer of the feed spacer with organo-selenium led to reduction of biomass concentration and biofilm thickness [108]. Altman’s study [110] indicated that spacers had a more significant influence on alleviating permeate flux decline, but had greater bacteria concentrations.

5) Pretreatment

Pretreatment is a practical method for reduction of fouling during membrane separation processes, such as RO, especially spiral-wound design membrane systems which allow only one-way flow through the system and cannot be recovered by backwashing. Pretreatment is normally designed to remove some constituents, such as sediment, micro-pollutants and microbes, which would otherwise increase fouling resistance and reduce mass transport [33, 111]. In general, a RO membrane pretreatment system consists of one or more the of operations [111], such as coagulation/flocculation [112, 113], ion exchange [114, 115] and filtration (i.e. MF and UF) [115-117]. Since FO is a low fouling membrane process, it’s unnecessary to carry out pretreatment prior to FO. Instead, due to its low fouling propensity and high reversibility, FO can be used as an advanced pretreatment strategy prior to other desalination processes [22, 28, 118, 119].
6) Modification of membrane surface

Membrane biofouling can be mitigated by modification of membrane surface properties, such as roughness, surface charge and membrane hydrophilicity. As the more severe fouling mostly occurs on rougher membrane surfaces, smoothing membrane surfaces can reduce the adhesion of microorganisms and biofouling. Roughness of membrane surface can be reduced using physical coating with polymers or surfactants [80, 120-127]. Since most EPS produced by bacteria are negatively charged in the aqueous solution, correctly altering the charge on membrane surface can increase the electrostatic repulsion between the membrane and EPS, and consequently reduce membrane fouling [80, 122, 128, 129]. Increasing membrane hydrophilicity is another method to decrease deposition of foulants on the membrane surface [80, 120-122, 124, 125, 127-130].

As FO is a low fouling process, rare studies were performed to reduce membrane fouling in the FO process by modification of membrane through improvement of fouling resistance to organic fouling or biofouling [127, 128, 130]. Sometimes, the improvement of membrane anti-fouling properties was achieved at the cost membrane performance, such as permeate flux [80, 120, 121, 126, 131, 132] and salt rejection [80, 121].

2.7 Concluding remarks

Polysaccharides are considered to play a major role during membrane biofouling in membrane desalination. Previous studies [3, 5, 43, 47, 57, 130] commonly selected alginate as a model polysaccharide during the study of polysaccharide fouling although it is atypical of the bacterial polysaccharides produced by most species of bacteria in a seawater environment [84]. This means that there is a scope for better understanding the contribution that polysaccharides have on membrane fouling with regards to the best models to use and the major factors that influence fouling propensity. These could be achieved by investigation of polysaccharide fouling behaviors using
polysaccharides isolated from bacteria naturally adherent in a seawater desalination plant.

To date, only a few studies compared polysaccharide fouling in forward osmosis (FO) and reverse osmosis (RO), where a constant driving force cannot be achieved in FO because of the continuous dilution of draw solution. The constant driving force can be achieved by using constantly saturated draw solution in FO, based on which a series of study including better comparison of membrane performance between FO and RO can be carried on.

Control of membrane biofouling mostly focused on the removal of bacteria in terms of biovolume using chemical compounds. There is interest in using the chemical compounds to remove the polysaccharides produced by bacteria.
Chapter 3. Materials and Methods

3.1 Membrane

A commercial forward osmosis (FO) pouch membrane, supplied by Hydration Technologies Inc. (HTI, Albany, USA), was used in both of forward osmosis (FO) and reverse osmosis (RO) experiments. This type of membrane is made of cellulose triacetate and cast onto a non-woven backing consisting of polyethylene-coated polyester fibers. Prior to use, the membrane was cut into pieces based on the dimension of the FO and RO cells, and stored in deionized (DI) water overnight prior to use.

3.2 Polysaccharides

Alginate has been commonly selected as the model polysaccharide to investigate fouling in reverse osmosis (RO) and forward osmosis (FO). However, use of sole alginate as the model polysaccharide to study polysaccharide fouling cannot yield sufficient information on fouling behavior of polysaccharides. Moreover, as discussed in Section 2.1.1, alginate is not a typical representative of bacteria polysaccharides in the seawater. It has been reported [133] that most of the EPS were produced by prevalent bacteria, such as Achromobacter and Xanthomonas in the desalination plants. Therefore, xanthan, a more typical bacterial polysaccharide secreted by Xanthomonas, was selected in fouling tests and compared with the most commonly tested model polysaccharide, alginate.

The literature has revealed that alginate forms a gel layer with a network structure on the membrane surface in the presence of calcium ions, due to the preferential binding between calcium and carboxylate groups of alginate. A third polysaccharide, pullulan which lacks carboxylic functional groups, was also selected for comparison to provide a better understanding of the
importance of selecting suitable polysaccharide models in FO and RO fouling tests.

Therefore, three kinds of polysaccharides, alginate, xanthan and pullulan were selected for the study of polysaccharide fouling in RO and FO in this study. Their chemical molecular structures are shown in fig.3.1.

Alginate:

Pullulan:

Xanthan:

Fig.3.1 Chemical molecular structures of alginate, pullulan and xanthan

1) Alginate

Alginate is a commonly used model microbial polysaccharide in membrane fouling research, and consists of a linear co polymer of (1,4)-linked β-D-mannuronate and α-L-guluronate in varying proportions and combinations [134]. Alginate is unusual compared to other polysaccharides as it is composed solely of uronic acid residues with no neutral monosaccharides [134].
2) Pullulan

Pullulan is a linear polysaccharide produced from starch by the fungus Aureobasidium pullulans. It consists of maltotriose units with three glucose units connected by a $\alpha$-1,4 glycosidic bond and consecutive maltotriose units connected to each other by $\alpha$-1,6 glycosidic bond [135, 136].

3) Xanthan

Xanthan is a heteropolysaccharide produced by bacteria of the genus *Xanthomonas*. Its molecule possesses pentasacchaide repeating units consisting of D-glucose, D-mannose and glucuronic acid units linked through the $\beta$-1, 4 position, its linear backbone is similar to cellulose [137]. Typically its backbone also contains carboxylic functional groups.

The above three polysaccharides were purchased from Sigma-Aldrich (USA). All of them are macromolecules and do not have an exact but a range of molecular weight. According to the manufacturer’s information, the molecular weights (MWs) of sodium alginate, xanthan gum and pullulan are 200 kDa, 1,000 kDa ~ 50,000 kDa and 75 kDa, respectively.

3.3 Alleviating agents

Two kinds of alleviating agents, sodium nitroprusside (SNP) and potassium ferricyanide (abbreviated KFCN in this study), were used to investigate membrane fouling control. Their chemical molecular structures are presented in Fig.3.2. SNP is an inorganic compound with the formula Na$_2$[Fe(CN)$_5$NO]. It has five cyanide ligands (—CN) and one linear nitric oxide ligand (—NO). Therefore, SNP is a well-characterized NO donor and it has a half-life of approximately 2 min in aqueous solutions at neutral pH [16]. SNP used in this study was ACS reagent grade (Sigma-Aldrich, AU).

KFCN is another inorganic compound with the formula K$_3$[Fe(CN)$_6$]. It has a similar molecular structure as SNP. Compared with SNP, it has one more cyanide ligands but no oxide ligand. It does not produce NO radical and can be
considered as a control for NO radical. KFCN, was AR grade (Ajax finechem Pty. Ltd, AU).

\[
\text{SNP:}
\]

\[
\text{KFCN:}
\]

Fig. 3.2 Chemical molecular structures of SNP and KFCN.

### 3.4 Chemicals and feed solutions

Salts, NaCl and CaCl₂, used to prepare feed and draw solutions were AR and LR grade (Chem-Supply Pty. Ltd, AU), respectively. Artificial seawater (ASW) was prepared using the following salts in addition to NaCl and CaCl₂: MgCl₂ and KCl were AR grade (Chem-Supply Pty. Ltd, AU); NaHCO₃ and NaSiO₃ were AR and LR grade (BDH chemicals Pty. Ltd, AU), respectively; KBr, H₃BO₃ and SrCl₂ were LR grades (AJAX chemicals, AU); NH₄Cl was AR grade (MERCK Pty. Ltd, AU); and NaF was AR grade (Ajax finechem Pty. Ltd, AU).

The artificial seawater was prepared based on ZoBell's recipe (ZoBell, 1946), shown in Table 3.1.
Table 3.1 Ingredients of artificial seawater and their concentrations

<table>
<thead>
<tr>
<th>Salt</th>
<th>NaCl</th>
<th>MgCl₂</th>
<th>CaCl₂</th>
<th>KCl</th>
<th>NaHCO₃</th>
<th>KBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (g/L)</td>
<td>24.32</td>
<td>5.14</td>
<td>1.14</td>
<td>0.69</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Salt</th>
<th>H₃BO₃</th>
<th>SrCl₂</th>
<th>NH₄Cl</th>
<th>NaF</th>
<th>NaSiO₃</th>
<th>FePO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (g/L)</td>
<td>0.027</td>
<td>0.026</td>
<td>0.0064</td>
<td>0.003</td>
<td>0.002</td>
<td>0.001</td>
</tr>
</tbody>
</table>

3.5 Polymer preparation

Extracellular polysaccharides (EPS) were purified from four bacterial species isolated from seawater in Western Australia. The strains were from raw seawater (RSW 8, RSW 12 and RSW 14) and filtered seawater (FSW 6). According to the research results of Nagaveena Nagajara, another PhD candidate, these polymers were identified by several methods including 16S sequencing [138]. RSW 8 was identified as a *Marinomonas* species. This is one genera in the *Oceanospirillales* family (order *Oceanospirillales*, class *Gammaproteobacteria*). These species are evident in the RO membrane biofouling community (at 0.8% of the total population). RSW 14 was identified as *Pseudomonas brenneri/moraviensis*. FSW 6 was identified as a *Pseudomonas* species. *Pseudomonas* species represented 9% of the total fouling community.

Sugar analyses of the monosaccharides of some isolated polymers (FSW 6 and RSW 14) as well as the commercial polysaccharides (alginate, xanthan and pullulan) were conducted using chromatography following acid hydrolysis [138]. The results of the sugar analyses are presented in Fig. 3.3. Alginate is majorly composed of glucuronic acid and galacturonic acid; pullulan is solely glucose; and xanthan contains glucuronic acid, glucose and mannose; while FSW 6 and RSW 14 are composed of more sugars.
Fig. 3.3 Sugar analysis of commercial polysaccharides and polysaccharides isolated from bacteria [138].

The EPS were isolated from large volumes of liquid cultures. The cultures were grown in commercially available media, Marine Broth or Marine Agar (Becton Dickinson, USA), which is similar to seawater with some additional nutrients. Another richer media, Trypticase Soy Broth (Becton Dickinson, USA), was more effective for the RSW 8 strain.

The protocol used for EPS preparation was modified from a method in previous study [139]. The bacteria were grown on the liquid media on an orbital shaker at 160 rpm for >3 days. The cultures were then centrifuged at 14,000 rpm for 30 min; after which the supernatant was collected, followed by the addition of Trichloroacetic acid [140], which was ACS reagent grade (Sigma-Aldrich, USA), with a weight concentration of 20g/100mL to precipitate proteins in the solution by centrifugation and decanting the supernatant. The collected supernatant was then added to cold acetone with the volume ratio of 3:1 between acetone and supernatant to precipitate the polymers. The acetone/supernatant mixture was stored at -20 °C to improve precipitation if necessary. The precipitated polymers were collected again by centrifugation at 14,000 rpm for 30 min. To remove all traces of acetone and salt, the polymers were dissolved in a small amount of distilled water, and dialyzed in dialysis tubing against water for 48 h.
3.6 Bench-scale reverse osmosis and forward osmosis systems

Fig. 3.4 Schematic diagram of bench-scale (a) reverse osmosis (RO) and (b) forward osmosis (FO) systems

The membrane fouling behaviors of polysaccharides were investigated in bench-scale RO and FO cross-flow systems (Fig. 3.4). Fig. 3.4a shows a schematic diagram of bench-scale RO system; in which a Sterlitech CF042
cross-flow RO cell (9.207 cm in length, 4.572 cm in width, and 0.23 cm in depth) with an effective membrane area of 42 cm$^2$ was used. No spacer was used in the RO cell. The membrane coupon was housed in the RO cell with the active layer facing downwards against the feed solution. The feed solution was transported by using a hydra-cell pump (B Line Pumps Pty. Ltd, AU). The cross-flow velocity of the solution was monitored by a flow meter (GEC-Elliott Process Instruments Ltd, Croydon, UK). The temperature of the feed solution was maintained at 25 ± 1 °C by passing it through a coil in a refrigerated water bath (Thermoline Scientific, Pty. Ltd, AU). The permeate produced during the RO process was collected in a container on a digital balance (A & D Australasia Pty. Ltd, AU); weight change was monitored and recorded by a laboratory computer. In order to match the gradual increase in the feed solution concentration which occurred in FO, the permeate in the RO process was not recycled back to the feed [3].

Fig.3.4b shows a schematic diagram of the bench-scale FO system; a similar system had been used in other studies [43]. The cross-flow FO cell had the same dimensions as the RO cell, but with two symmetrical channels on both sides of the membrane for co-current flows of feed and draw solutions. Similarly, no spacer was used in the FO cell. For better comparison with RO process, the membrane was placed with the active layer downwards against the feed solution. Two Masterflex peristaltic pumps (Cole-Parmer, USA) were used to transport and adjust the cross-flow of the feed and draw solutions. The temperatures in both feed and draw solutions were controlled by passing them through coils in a refrigerated water bath (Thermoline Scientific, Pty. Ltd, AU). The draw solution tank was placed on a digital balance (A & D Australasia Pty. Ltd, AU); weight change was continuously recorded by a laboratory computer. We adopted a novel, new design for the FO test; that the draw solution tank contained constantly saturated NaCl draw solution, as shown in Fig.3.5. This enabled vastly superior comparisons of the FO and RO systems and is crucial to the development of the new mathematical models to describe polysaccharide membrane fouling. The input tube withdrew constantly saturated draw solution
with a filter preventing solid salt entering the system. During the FO process, saturated draw solution was diluted by water permeate and then returned to the draw solution tank via the output tube. A separator made from polyethylene, which has outstanding resistance to salt corrosion, was used to make sure the diluted draw solution flowed down along the tank bottom, contacting the solid salt at the bottom and then dissolved the salt to become saturated again (shown as the arrow in Fig.3.5).

The draw solution was assumed to be constantly saturated. In the experiments, the cross-flow velocity was 8.5 cm/s, equivalent to about 8.93 mL/s as the flow rate of draw solution over 1.05 cm$^2$ cross section area of the membrane cell. On the other hand, the permeate flux is about 9.5 L/(m$^2$·h) through the effective membrane area 42 cm$^2$, that is 0.011 mL/s of water was driven to the draw solution. As a result in every second, only 0.011 mL water is added into 8.93 mL saturated draw solution. Such instant dilution could be negligible. Moreover, the negligibly diluted draw solution constantly contacts solid salt. Herein we assumed the solution to become saturated afterwards.

To evaluate FO using constantly saturated NaCl draw solution, the baseline experiment (denoted as FO baseline-S) was carried out and compared with that in RO (denoted as RO baseline) operated under the same conditions, including temperature, initial water flux and cross-flow velocity and feed water chemistry (see 2.3.1 for details). For comparison, another FO baseline test (denoted as FO baseline-I) was conducted using the same FO setup (Fig.3.5 and Fig.3.4b) without the addition of excess solid salt in the draw solution tank; but using initially saturated NaCl solution as the draw solution. During FO, the draw solution was continuously diluted by the water transported through the membrane (permeate) from the feed to the draw solution.
3.7 Fouling and Alleviation tests

The operational conditions (i.e. temperature, initial water flux and cross-flow velocity) and feed water composition (i.e. feed volume, ionic strength and calcium concentration) during FO and RO fouling tests were kept identical for comparing fouling behaviors. In a typical FO or RO fouling test, the cross-flow velocity and temperature of solution were set at 8.5 cm/s and maintained at 25 ± 1 °C. In FO, the use of constantly saturated NaCl solution as draw solution generated an initial flux of ~9.5 L/(m²·h). On the other side, to achieve a similar initial flux, the hydraulic pressure of 400 psi (2757.9 kPa) was utilized in RO fouling test. When effect of hydraulic pressure on membrane fouling in RO was investigated, the pressure varied from 400 psi to 500 psi (3447.4 kPa). 10 L feed solution, containing 1 mM Ca²⁺ ions when effect of Ca²⁺ ions on membrane fouling was investigated, was adjusted to 50 mM total ionic strength by adding NaCl [3]. The polysaccharide solution was firstly prepared by dissolving 2 g polysaccharide compound in 200 mL water through vigorous stirring without further purification prior to fouling tests. The concentration of polysaccharides (e.g. alginate, xanthan or pullulan) tested in all FO and RO experiments was 0.2 g/L or 0.5 g/L. The concentration of isolated polymer solution was set at 0.2 g/L.
Before RO or FO fouling test, the membrane was firstly compacted with DI water for 2 h, followed by 2 h stabilization and equilibration with the use of foulant-free electrolyte solution, which had 1 mM Ca\(^{2+}\) ions and 50 mM ionic strength. After a stable permeate flux was observed, the foulant was added into the feed solution. During the alleviation of polysaccharide fouling, the alleviating agent (SNP or KFCN) was added to the feed water supplemented with polysaccharide when the tests were initiated, and its concentration was set at 0.1 mM or 1 mM. Unless specified, all the experiments lasted for 24 h.

Herein, the RO or FO baseline (control) test followed the same protocol as that in the fouling experiments, except that there was no polysaccharide foulant in the feed solution. The difference in flux decline between the baseline test (control) and corresponding fouling test represents the permeate reduction caused by polysaccharide fouling.

### 3.8 Characterization and Calculation

#### 3.8.1 Water flux and permeability of membrane

Typically, good membrane presents high water permeability (A value) which represents the water flux that the membrane can achieve under certain pressure. It is dependent on the membrane material and structure.

Water permeability of the membrane (A value) was measured using the following equation [81, 141]:

\[
A = \frac{J_w}{\Delta P} \tag{3.1}
\]

Where \(A\) is the water permeability coefficient of membrane \([\text{m/(s·Pa)}]\), \(J_w\) is the water flux (LMH), and \(\Delta P\) is the transmembrane pressure difference (Pa).

It can be seen from the above equation that permeate flux is determined by \(A\) and \(\Delta P\). Generally, the volume changes of permeate as a function of time are used to calculate permeate fluxes; this was adopted in our study as well [80, 81, 129, 142]:

---

43
\[ J_t = \frac{1}{A_m} \frac{dV}{dt} \]  

(3.2)

Where \( J_t \) is the water flux (LMH) at time \( t(h) \), \( A_m \) is the effective membrane area (m\(^2\), 0.0042 m\(^2\) in this study), \( V \) is the volume of the collected permeate (L), and \( t \) is the time for collecting the permeate (s).

In this study, the \( A \) value is \( 9 \times 10^{-13} \) m/s·Pa based on flux versus applied pressure using DI water as the feed solution, as can be seen in Fig.3.6.

As variation exists among different membranes, the normalized flux \( J_t/J_0 \) calculated based on the ratio between \( J_t \) and \( J_0 \), was also used to evaluate the membrane fouling extent; \( J_0 \) was obtained after the stabilization and equilibration finished in the fouling test.

![Fig.3.6 membrane permeability A value based on flux versus applied pressure](image)

3.8.2 Rejection coefficient by membrane

A good membrane also presents high solute rejection coefficient (R) of salt (NaCl in this study) [67]. Solute rejection coefficient by the membrane was calculated using Equation (3.3) [29, 80, 124, 143]:

\[ R = (1 - \frac{C_p}{C_f}) \times 100\% \]  

(3.3)
Where $C_p$ and $C_f$ were the conductivity of permeate and the initial conductivity of the feed solution, respectively (μs). In this study, the lowest rejection coefficient of NaCl by the membrane tested so far was 98.8%.

In this study, $R$ based on $C_p$ and $C_f$ was measured before and after fouling tests to check membrane’s intactness.

3.8.3 Determination of polymer solution concentration

Concentration of the collected polymer solutions was measured. The weight of an empty little tube was measured and recorded as $W_0$. 1 mL polymer solution was extracted and put into the tube. The liquid was evaporated in Savant speed vac concentrator (Thermo Fisher Scientific, Inc, AU) to dry the polymer for over 4 h. After the polymer was dried, the weight of the tube with the dried polymer was measured, and recorded as $W_1$. The weight difference between $W_0$ and $W_1$ is the weight of the polymer. And the concentration of the polymer ($C_{\text{polymer}}$) was then calculated:

$$C_{\text{polymer}} = \frac{(W_1 - W_0)}{\text{mL}} \quad (3.4)$$

The concentration of the polymer solution was obtained as an average concentration of six samples.

3.8.4 Foulant Deposit Weight

The weight of polysaccharide deposited on the membrane surface after 24 h fouling test, $W_{\text{foulant}}$, was calculated based on Equation (3.5):

$$W_{\text{foulant}} = W_d - W_i \quad (3.5)$$

where $W_d$ is the weight of the fouled membrane after a fouling test, which was dried at 54.0 °C in a Contherm Digital Series incubator (Thermo Fisher Scientific, Inc, AU); whilst $W_i$ is the weight of the dried membrane after the baseline test.
3.8.5 Hydraulic Resistance

Total hydraulic resistance \( R_t \) directly reflects the extent and causes of membrane fouling. Total hydraulic resistance includes 4 kinds of resistances: membrane resistance \( R_m \), blockage resistance \( R_b \), resistance caused by concentration polarization \( R_{cp} \) and resistance caused by cake deposition \( R_c \). During the membrane fouling tests in this study, as FO membrane with small molecular weight cut-off was used, blockage of membrane \( R_b \) was not included.

\[
R_t = R_m + R_{cp} + R_c \quad (3.6)
\]

Total hydraulic resistance has a relationship with transmembrane pressure difference, permeate viscosity and permeate flux, and can be calculated based on the following equations [67, 80-82]:

\[
J_w = \frac{\Delta P}{\mu \cdot R_t} \quad (3.7)
\]

\[
R_t = \frac{\Delta P}{\mu \cdot J_w} \quad (3.8)
\]

where \( \mu \), the solution viscosity of the permeate (Pa·s), was measured with Gilmont® Instruments falling-ball viscometer model GV-2200 (glass ball size #3, GF-1332-P) (Thermoline Scientific Pty. Ltd, AU); \( R_t \) is the hydraulic resistance (m\(^{-1}\)).

3.8.6 Fouling alleviation efficiency

The alleviation efficiency \( \psi \) was calculated based on the following equation [99, 100]:

\[
\psi = \frac{(J_t/J_0)_{\text{alleviation}} - (J_t/J_0)_{\text{baseline}}}{1 - (J_t/J_0)_{\text{baseline}}} \times 100\% \quad (3.9)
\]

where \((J_t/J_0)_{\text{baseline}}\) and \((J_t/J_0)_{\text{alleviation}}\) are the normalized flux values in the absence and presence of alleviating agents at time \( t \) (h), respectively. The value of \( \psi \) is in the range of 0–100% when \((J_t/J_0)_{\text{inhibition}}\) changes from \((J_t/J_0)_{\text{baseline}}\) to 1.
A negative value of $\psi$ means that the addition of alleviating agent enhances polysaccharide fouling.
Chapter 4. Polysaccharide fouling in reverse osmosis and forward osmosis

This chapter investigates and compares the membrane fouling by model polysaccharides and polysaccharides isolated from naturally adherent bacteria in a seawater desalination plant in forward osmosis (FO) and reverse osmosis (RO). A constantly saturated draw solution was applied in FO to maintain a constant driving force to compare with the applied hydraulic pressure in RO. Three kinds of model polysaccharides (alginate, xanthan and pullulan) were selected and four species of polysaccharides were isolated from naturally adherent bacteria in a seawater desalination plant for membrane fouling tests in FO and RO.

4.1 A novel approach for maintaining a constant osmotic pressure in forward osmosis

Fig. 4.1 Comparison of normalized flux versus operation time in forward osmosis (FO) and reverse osmosis (RO) baseline experiments. RO test (RO baseline) was conducted with a hydraulic pressure of 400 psi (2757.9 kPa); whilst FO test was carried out by using constantly (FO baseline-S) or initially (FO baseline-I) saturated NaCl solutions as draw solutions. All runs were performed under identical conditions: initial flux of
9.5 L/(m²·h); cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; feed solution consisting of 1 mM Ca²⁺ ions and 50 mM total ionic strength by adding NaCl.

In the baseline experiments above (Fig.4.1) the normalized flux versus operation time obtained during the RO and FO are presented. Only NaCl and CaCl₂ were utilized as solutes in the feed solution in the absence of polysaccharide foulants [3]. Either NaCl draw solution (FO) or a hydraulic pressure of 400 psi (equivalent to 2757.9 kPa) (RO) was utilized to generate sufficient driving force for water to permeate through the semipermeable FO membrane. The initial flux was adjusted to 9.5 L/(m²·h) for the baseline and subsequent polysaccharide fouling tests. The fluxes in RO baseline test remained almost constant throughout the 24 h operation with a slight decrease of ~5.6% (Fig.4.1). This is attributed to the continuous recycling of concentrated feed solution back to the feed tank, subsequently increasing the osmotic pressure of the feed solution during the experiment [3]. Further membrane structure compaction under hydraulic pressure could also contribute to the decline of normalized flux versus operation time in RO.

In order to better compare the polysaccharide fouling behaviors in our FO and RO tests, we adopted a new protocol for carrying out FO fouling experiments. Instead of using the common approach of a high concentration draw solution e.g. 5.0 M NaCl [3], which is continuously diluted during separation, a constantly saturated NaCl draw solution was used, outlined in Fig.3.5. The flux observed using constantly saturated draw solution was stable (FO baseline-S in Fig.4.1) and was only moderately reduced to 93.9% of the initial flux after 24 h. It declined slightly as the osmotic pressure of feed solution increased when using constantly saturated draw solution, due to the semipermeable FO membrane allowing water to transport through from the feed to the draw solution side but rejecting salts. Moreover, the reverse solute diffusion from the constantly saturated draw solution to the feed solution could also contribute to the higher osmotic pressure of the feed. As the osmotic pressure of the continuously saturated NaCl draw solution remained unchanged, the increased
osmotic pressure of the feed would eventually lead to lower transmembrane osmotic pressure difference ($\Delta \pi$) and in turn declined flux [3, 88, 95, 144, 145]. The slight decrease of flux using constantly saturated feed solution in the FO process (Fig. 4.1) strongly resembled the slight decline also observed in the RO baseline test, which began at a similar initial flux of 9.5 L/(m²·h). By contrast, when using only initially saturated NaCl draw solution (FO baseline-I in Fig. 4.1), a much larger flux decline (~25%) was observed over 24 h, due to the gradual dilution of the draw solution and the increase of osmotic pressure of the feed solution. Therefore, the utilization of constantly saturated NaCl solution, which minimized membrane flux decline, enabled a much better direct comparison between FO and RO operating conditions.

### 4.2 Polysaccharide fouling in reverse osmosis

#### 4.2.1 Effect of polysaccharide concentration on fouling

![Graph showing normalized flux vs. time for varying polysaccharide concentrations](image)

(a)
Fig.4.2 Effect of polysaccharide type and concentration on membrane fouling in reverse osmosis (RO) process for 24 h: (a) alginate fouling; (b) xanthan fouling and (c) pullulan fouling. A hydraulic pressure of 400 psi (2757.9 kPa) was applied. Other experimental conditions included: initial flux of 9.5 L/(m²·h); cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; feed solution consisting of 1 mM Ca²⁺ ions and 50 mM total ionic strength by adding NaCl; polysaccharide concentration of 0.2 g/L or 0.5 g/L.

The impact of polysaccharide concentration on membrane fouling in the RO process was investigated (Fig.4.2). Alginate and xanthan at the concentration of 0.2 g/L caused significant flux decline after 24 h, accounting for ~25% and ~21%, respectively, while pullulan did not cause a significant flux decline. The effect of polysaccharide concentration on membrane fouling varied according to type of polysaccharide. With alginate, flux declined more as concentration
was increased from 0.2 g/L to 0.5 g/L, while the difference in flux decline between 0.20 and 0.5 g/L with xanthan was minimal.

The addition of alginate at 0.2 g/L caused ~25% flux decline after 24 h as compared to the baseline experiment, indicating alginate caused severe membrane fouling under the RO experimental conditions. Alginate is a macromolecule with a large amount of carboxylic functional groups (shown in Fig.3.1) [146] that Ca\(^{2+}\) ions can bind to them [7, 147]; and form bridges between neighboring alginate macromolecules and subsequently form a crosslinked gel network [43, 75, 98]. In the RO test, with a relatively high hydraulic pressure utilized as the driving force, there is a dramatically increased concentration of alginate macromolecules and Ca\(^{2+}\) ions on the membrane surface [3], which results in formation of a densely crosslinked Ca-alginate gel layer and an increase in membrane hydraulic resistance, reducing water fluxes in the RO process. Membrane fouling by Ca-alginate gels was stated to be irreversible [56]. At a concentration of 0.5 g/L, alginate caused a flux decline of ~33% after 24 h fouling test, which was about 8% lower than flux decline using 0.2 g/L alginate. Again, this could be attributed to the formation of Ca-alginate gels. The difference in flux decline between 0 and 0.2 g/L (25%) was greater than that between 0.20 and 0.5 g/L (8%), perhaps as Ca\(^{2+}\) concentration in the feed solution decreased as Ca-alginate gels formed.

Flux decline during xanthan fouling tests (Fig.4.2b) showed 0.2 g/L xanthan also caused significant flux decline (21%) after 24 h. Similar to alginate, xanthan molecule also contains carboxylic functional groups. Therefore, there could be interactions between the carboxylic groups and Ca\(^{2+}\) ions during RO fouling, generating a crosslinked macromolecular network, increasing membrane hydraulic resistance, and reducing water permeation. Further increase in xanthan concentration from 0.2 g/L to 0.5 g/L had a negligible impact on flux behavior. Compared to alginate, the density of carboxylic functional groups along xanthan macromolecules is much lower (Fig.3.1), possibly leading to less xanthan accumulation on the membrane surface.
forming a looser layer through bridging by Ca\(^{2+}\) ions. The loose Ca-xanthan layer could be sloughed off by the cross flow. As a result, no additional xanthan could accumulate even if concentration increased.

The normalized fluxes obtained using pullulan as foulant (Fig.4.2c) fluctuated around 1 throughout the whole RO test irrespective of pullulan’s concentration (0.20 or 0.5 g/L). This was an interesting finding and may suggest further clues as to why some types of polysaccharides foul membranes and others do not. Pullulan lacks carboxylic functional groups (Fig.4.2c) and cannot form densely crosslinked macrocomplex layers. This may explain why no flux decline was observed for pullulan even in the presence of Ca\(^{2+}\) ions. Surprisingly, the use of pullulan even seems to slightly enhance permeate flux (Fig.4.2c). The gradual increase in permeate flux for pullulan at 0.2 g/L (0 to 10 h) could be due to the improved hydrophilicity and smoothness of the resulting membrane surface, caused by the deposition of hydrophilic pullulan on the membrane during filtration [148]. A similar phenomenon has also been reported in the literature when utilizing hydrophilic polymer, e.g. polyvinyl alcohol, to modify membrane surface [149]. After 10 h, the normalized flux slightly decreased, likely due to enhanced osmotic pressure as some ions from the feed solution were captured by pullulan on the membrane surface. This was supported by the decreased salt rejection from 99.35% to 98.80%. As pullulan deposited on the membrane surface under the effect of flux, it was likely to capture the ions from the feed solution to the membrane. As a result, the osmotic pressure on the membrane surface increased leading to decrease in flux which eventually overcame the small increase in flux evident between 0 and 10 h. When a higher concentration of pullulan was used (0.5 g/L), flux began increasing sooner (5.5 h), indicating more ions were captured at a higher concentration.
4.2.2 Comparison of fouling in reverse osmosis by model polysaccharides and polysaccharide isolated from naturally adherent bacteria in a seawater desalination plant

Fig. 4.3 Comparison of membrane fouling by model polysaccharides and polysaccharide isolated from naturally adherent bacteria in a seawater desalination plant. A hydraulic pressure of 400 psi (2757.9 kPa) was applied. Other experimental conditions included: initial flux of 9.5 L/(m²·h); cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; feed solution consisting of 1 mM Ca²⁺ ions and 50 mM total ionic strength by adding NaCl; all polysaccharide concentration of 0.2 g/L.

Membrane fouling in reverse osmosis (RO) by model polysaccharides (alginate, xanthan and pullulan) and two polysaccharides isolated from adherent bacteria in a desalination plant (RSW 8 and RSW 12) were compared over 4 h at a concentration of 0.2 g/L (Fig. 4.3). Alginate caused greatest flux decline and the most severe fouling likely due to formation of Ca-alginate gels. Pullulan did not cause flux decline. Both the naturally occurring polysaccharides, RSW 8 and RSW 12, caused fouling, suggesting these polymers accumulated on membrane surface. The findings are the first to compare the types of polysaccharides which are naturally occurring with model polysaccharides and demonstrate they do contribute to biofouling in RO and may explain a large proportion of the flux decline observed in desalination plants worldwide. Alleviation of biofouling may be achieved by the reduction of polymer accumulation on the membrane surface.
However, the extent of fouling by the two isolated polymers also differed. RSW 12 caused more severe fouling than RSW 8, but its fouling extent was still lower than that of alginate (Fig. 4.3). This indicates that alginate is an atypical model membrane fouling and this should be considered in experimental design.

4.2.3 Effect of applied pressure on polysaccharide fouling in reverse osmosis

Fig. 4.4 Effect of applied pressure on membrane fouling by model polysaccharides for 24 h in reverse osmosis (RO). A hydraulic pressure of 400 psi (2757.9 kPa) or 500 psi (3447.4 kPa) was applied. Accordingly, the initial fluxes were 9.5 L/(m²·h) and 13.0 L/(m²·h), respectively; Other experimental conditions included: cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; feed solution consisting of 1 mM Ca²⁺ ions and 50 mM total ionic strength by adding NaCl; polysaccharide concentration of 0.2 g/L.

The effect of applied hydraulic pressure on polysaccharide fouling was investigated by comparing 400 psi (2757.9 kPa) and 500 psi (3447.4 kPa). As expected, the higher applied pressure resulted in greater initial permeate flux. In the absence of polysaccharide, flux decline was not significantly different between 400 and 500 psi. Normalized flux decline was greater for alginate and xanthan under the higher applied pressure (Fig. 4.4). This is supported by previous studies [32, 46, 73] which suggest higher initial flux result in more severe membrane fouling. As applied pressure increased from 400 psi to 500 psi, the normalized flux declined from 0.70 to 0.46 for alginate fouling and
from 0.73 to 0.54 for xanthan fouling. This could be explained by the effect of applied pressure on the foulant-foulant interactions. As discussed in Section 4.2.1, alginate and xanthan can be bridged by Ca$^{2+}$ ions and form macrocomplex layers under the applied pressure (400 psi), leading to increase in hydraulic resistance and reduction in permeate flux. An increase in the applied pressure from 400 psi to 500 psi may result in the accumulation of more Ca$^{2+}$ ions and polysaccharides on the deposited macrocomplex layer on the membrane surface. Bridged by Ca$^{2+}$ ions, the polysaccharides may interact with the deposited polysaccharides, leading to formation of more macrocomplex layers. Under the compression of increased hydraulic pressure, the macrocomplex layers would become compacted, which could significantly increase the membrane hydraulic resistance and reduce the permeate flux. Compared to 400 psi, the higher applied pressure (500 psi) caused a 24% flux decline for alginate and a 19% flux decline for xanthan, indicating alginate fouling was affected to a greater extent. This could be explained by the denser Ca-alginate macrocomplex layer.

4.2.4 Effect of calcium ions on membrane fouling in reverse osmosis under the applied hydraulic pressure of 500 psi

The impact of Ca$^{2+}$ ions on polysaccharide fouling in reverse osmosis (RO) under the applied hydraulic pressure of 500 psi was investigated (Fig. 4.5). In the absence of polysaccharides (alginate and xanthan), Ca$^{2+}$ ions exerted negligible effect on permeate flux. As indicated in the baseline experiments, Ca$^{2+}$ ions themselves do not cause fouling. In the absence of Ca$^{2+}$ ions the flux declined to 68.8% and 73.7% for alginate and xanthan fouling tests, respectively. However, in the presence of Ca$^{2+}$ ions the flux declined further to 46.0% and 54.5%, respectively, indicating the contribution of Ca$^{2+}$ ions to membrane fouling. This agrees with previous studies [7, 43, 46, 75, 98, 147] showing Ca$^{2+}$ ions could promote severe membrane fouling by forming macrocomplex with carboxylic functional groups of the organic foulants and subsequently form a crosslinked network or gel. In this study, both alginate and
xanthan molecules contain carboxylic functional groups, and are able to form macrocomplex in the presence of Ca\(^{2+}\) ions. Specifically, alginate formed compact thin gels by interaction with Ca\(^{2+}\) ions, and resulted in more severe fouling.

![Graph showing Effect of Ca\(^{2+}\) ions on membrane fouling in RO by model polysaccharides](image)

Fig. 4.5 Effect of Ca\(^{2+}\) ions on membrane fouling in RO by model polysaccharides under the applied hydraulic pressure of 500 psi for 24 h. A hydraulic pressure of 500 psi (3447.4 kPa) was applied. Other experimental conditions included: initial flux of 13.0 L/(m\(^2\)·h); cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; feed solution consisting of 50 mM total ionic strength in the absence or presence of 1 mM Ca\(^{2+}\) ions; polysaccharide concentration of 0.2 g/L.

### 4.3 Polysaccharide fouling in forward osmosis

#### 4.3.1 Effect of feed solution on polysaccharide fouling in forward osmosis

Initially, the effect of feed solution was investigated comparing polysaccharide fouling in forward osmosis (FO) using alginate, xanthan and pullulan as foulants and comparing artificial seawater (ASW) and DI feed solution (DI water which included 1 mM Ca\(^{2+}\) ions and 50 mM total ionic strength). When ASW feed solution was used, the initial permeate flux was at about 7.4 LMH; while an initial flux of about 9.5 LMH could be achieved using DI feed solution (graphs not shown).
Fig. 4.6 Effect of feed solution on polysaccharide fouling in FO by alginate, xanthan and pullulan. Constantly saturated NaCl solution was used as draw solution. Other experimental conditions included: polysaccharide concentration of 0.2 g/L; initial flux of 9.5 L/(m²·h) using DI water as feed solution containing 1 mM Ca²⁺ ions and 50 mM total ionic strength by adding NaCl, or 7.4 L/(m²·h) using ASW as feed solution; cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C.

Fig. 4.7 Viscosity of polysaccharide solutions e.g. alginate, xanthan, and pullulan (0.2 g/L).
Using DI feed solution, pullulan caused only marginal fouling compared to the baseline in FO. Interestingly, xanthan caused the most severe fouling with a significant final flux decline of 14.5% after 24 h; whilst only ~ 8.5% of flux reduction is observed in the presence of alginate. Solution viscosity may be the most critical factor governing the different fouling behaviors of polysaccharides in FO. Viscosities of polysaccharide solutions follow the order of xanthan > alginate > pullulan (Fig.4.7). This is consistent with previous studies that indicate polysaccharides of larger MWs induce higher solution viscosities [42, 150]. The relationship between weight of polysaccharide deposit and normalized flux after 24 h FO shows that the weight of xanthan foulant is greatest, followed by alginate and then pullulan (Fig.4.8). This further supports the argument that xanthan, which has largest MW (1000 kDa ~ 50,000 kDa) and highest viscosity in solution, causes most severe flux reduction in the FO test. The use of polysaccharides with high MW in the feed solution may reduce the shear force generated by the cross-flow velocity and promote polymer accumulation, resulting in greater fouling [73, 98]. In particular, as xanthan accumulates on the membrane, its concentration near the surface increases and consequently increases viscosity. Polymer deposition accumulates, making the fouling more pronounced and reducing water permeation. After 20 h in FO, relatively constant fluxes were observed in both alginate and xanthan fouling

Fig.4.8 Relationship between the weight of polysaccharide deposit and normalized flux after 24 h FO.
tests, suggesting further accumulation of polysaccharide was limited by the shear force [151].

By contrast, when ASW was used as feed solution, the three polysaccharides behaved differently (Fig.4.6). Alginate caused the most fouling, xanthan had negligible impact on fouling and pullulan slightly improved the membrane performance. Compared to the DI feed solution, ASW contains a much higher salt concentration, which generates high osmotic pressure on the feed solution side and thus can significantly reduce permeate flux. As a high salt concentration in the feed solution caused a severe flux decline, the additional impact of polysaccharides was much reduced. This is consistent with the results in previous study which also reported a great reduction in flux decline at seawater-level ionic strengths [68]. Nevertheless, as ASW contains a large amount of Ca$^{2+}$ ions (10.37 mM, Table.3.1), alginate could form compact Ca-alginate gels by crosslinking with Ca$^{2+}$ ions. This may explain why alginate still resulted in flux decline in FO fouling using ASW as feed solution, even though the flux decline was only half that observed when DI feed solution was used. The Mg$^{2+}$ ions in ASW are also known to increase macrocomplexes by alginate and may compete for binding sites on the carboxylic acid functional groups of alginate. A previous study compared the effect of Mg$^{2+}$ and Ca$^{2+}$ ions on alginate fouling in RO, and observed a dramatic flux decline in the presence of Ca$^{2+}$ ions but not Mg$^{2+}$ ions [8]. In the presence of Ca$^{2+}$ ions, compact Ca-alginate gels formed on the membrane surface while no gel layers was visible in the presence of Mg$^{2+}$ ions. In our study, ASW feed solution contained a higher concentration of Mg$^{2+}$ (54.1 mM) than Ca$^{2+}$ ions (10.37 mM) (See in Table.3.1), and may play a more significant role than in previous studies. Although alginate caused moderate flux decline and membrane fouling, the competition for binding sites between Ca$^{2+}$ and Mg$^{2+}$ ions may partially explain why the extent of membrane fouling was reduced.

Unlike alginate, xanthan cannot form compact gels in the presence of Ca$^{2+}$ or Mg$^{2+}$ ions. In DI feed solution with low ionic strength (50 mM), xanthan caused
most severe fouling likely due to high viscosity in solution which could reduce the shear force by the cross-flow velocity. By contrast, in the ASW feed solution, the high osmotic pressure became the dominating contributor to the flux decline and xanthan presented negligible impact on flux decline. While alginate promoted flux decline and xanthan showed negligible impact in the ASW feed solution, the presence of pullulan slightly improved membrane performance with an increase in flux of 3.7%. As discussed in Section 4.2.1, the accumulation of hydrophilic pullulan could improve hydrophilicity and smoothness of the membrane surface, and thus improve membrane performance. Similarly, using ASW feed solution, pullulan presented a positive effect on membrane performance.

4.3.2 Comparison of forward osmosis fouling by model polysaccharides and polysaccharides isolated from naturally adherent bacteria in a seawater desalination plant

![Graph showing comparison of forward osmosis fouling](image)

Fig.4.9 Comparison of forward osmosis (FO) fouling by model polysaccharides and polysaccharides isolated from naturally adherent bacteria in a seawater desalination plant. Three kinds of model polysaccharides, alginate, xanthan and pullulan, and three species of polysaccharides isolated from naturally adherent bacteria, FSW 6, RSW 8 and RSW 14, were used as foulants. Constantly saturated NaCl solution was used as draw solution. Other experimental conditions included: polysaccharide concentration of 0.2 g/L; initial flux of 9.5 L/(m²·h); cross-flow velocity of 8.5 cm/s; solution
temperature of 25 ± 1 °C; feed solution consisting of 1 mM Ca\(^{2+}\) ions and 50 mM total ionic strength.

In FO, all three model polysaccharides caused some fouling, while the three isolated polymers did not cause fouling (Fig.4.9). In these short-term fouling tests (4 h), alginate caused the most severe fouling among the three model polysaccharides. Again, this could be explained by the bridging and gel formation by Ca\(^{2+}\) ions. Compared to xanthan and pullulan, alginate possessed the most negatively charged carboxylic functional groups, which may have enabled alginate to quickly accumulate on the membrane surface. By contrast, pullulan molecules are neutral (Fig.3.1), perhaps explaining their minimum fouling effect. Interestingly, all the isolated polymers did not cause fouling in the FO process. FSW 6 and RSW 14 caused an increase in permeate flux, compared to the baseline with model polysaccharides added, indicating some polymers could improve membrane performance. The difference in flux behaviors between model polysaccharide fouling and isolated polymer fouling in FO once again demonstrates that alginate is an atypical polymer model in FO fouling. It is important to select appropriate polysaccharide models for membrane fouling research.

4.4 Comparison of fouling in reverse osmosis and forward osmosis

4.4.1 Comparison of membrane fouling in reverse osmosis and forward osmosis by model polysaccharides

The normalized flux declines in forward osmosis (FO) and reverse osmosis (RO) polysaccharide fouling tests are compared after 24 h (Fig.4.10a), while the weight of polysaccharide deposited on the membrane are presented in Fig.4.10b. Deposit weight of both alginate and xanthan were higher in RO than FO (Fig.4.10b). The deposit weight of pullulan was negligible in both FO and RO. The results are consistent with the fluxes obtained in the polysaccharide fouling tests (Fig.4.10a). Hence, the weight of foulant deposit is suggested as an
indicator of membrane fouling in both FO and RO; if more deposit is present, membrane fouling is more severe. The use of pullulan with negligible deposit weight caused almost no fouling during separation.

This finding conflicts with some previous reports [2, 3]. For instance, Lee and co-workers found higher flux decline for alginate in the FO process compared to the RO process; which was attributed to cake-enhanced osmotic pressure (CEOP) [3, 29, 31]. In their work, using continuously diluted 5 M NaCl as the draw solution, the reverse diffusion of salt from the draw solution to feed solution was hindered by the fouling layer, elevating osmotic pressure near the active layer of the membrane surface and subsequently reducing the driving force across the membrane. However, in this study, normalized flux decline was 16% greater in RO than in the FO process (Fig. 4.10a). This could be explained by our newly developed FO separation protocol which uses constantly saturated NaCl solution as a draw solution. Undoubtedly, the salt reversely passes through the semi-permeable membrane from the draw solution side to the feed solution side; which is trapped within the fouling (gel) layer. However, due to the high osmotic pressure generated by the constantly saturated NaCl solution, despite a build-up of salts near the membrane surface and CEOP occurring, the substantial drop in the net osmotic pressure difference is greatly minimized and flux decline in FO alginate fouling test is moderated. Moreover, because of using the osmotic pressure gradient as driving force, it is believed that alginate fouling (gel) layer formed on the membrane active surface during the FO process is looser and thicker, compared with that observed in the RO process. This loose and thick layer was found to be reversible by changing cross-flow velocity [2, 3]. Therefore, some of the alginate fouling layer, especially on the top is loose and sparse at the surface and likely to be scraped away by shear force arising from flow. Thus, FO fouling by alginate is largely governed by foulant – membrane interaction. By contrast, this effect is not evident in the RO process, in which hydraulic pressure works as the driving force and the Ca-alginate gel layer is irreversible [56]. This is further supported by comparing the weight of alginate deposit on
the membrane surface after FO and RO tests (Fig. 4.10b); the RO-induced foulant weight is more than doubled, compared to FO. Therefore, the compact and cohesive fouling layer formed during the RO fouling process reduces permeate flux more significantly, which is coupled with the CEOP effect. Hence, RO fouling by alginate is by contrast largely governed by foulant – foulant interaction. This mechanism may also be used to explain the similar normalized flux decline in fouling caused by xanthan in both RO and FO processes.

![Fig. 4.10](image)

Fig. 4.10 Comparison of (a) normalized flux decline and (b) weight of polysaccharide deposit after 24 h FO and RO fouling tests.
Despite alginate frequently being selected as a representative model for organic membrane fouling, our study suggests it is atypical of bacteria polysaccharides, causing more severe fouling and the impact of ions in seawater such as Ca\(^{2+}\) ions may play a larger role in alginate fouling than other polysaccharides. Therefore, alginate is not a suitable model for investigation of membrane fouling, fouling alleviation or the development of antifouling membranes in the field of desalination.

With our superior experimental set up using over saturated FO draw solution, identical operational conditions and solution chemistry, we were able to better compare fouling in FO and RO processes. We could directly determine the effect of pressure type on membrane fouling in membrane separation processes. Our experimental results revealed that more severe fouling occurred under applied pressure (RO) than under equivalent osmotic pressure (FO) based on the initial flux they generated. To the best of our knowledge, it is the first time that pressure source alone has been proved to plays a key role in membrane fouling during membrane separation processes.

4.4.2 Comparison of membrane fouling in reverse osmosis and forward osmosis by polysaccharides isolated from naturally adherent bacteria in a seawater desalination plant

Membrane fouling in forward osmosis (FO) and reverse osmosis (RO) using the polysaccharide isolated from naturally adherent bacteria, RSW 8, as the foulant were compared (Fig.4.11). The addition of RSW 8 caused fouling in RO but not in FO. These results and those presented above (Fig.4.10a) suggest the fouling behaviors of polymers in FO and RO under identical operating conditions and feed water chemistry vary. The pressure source (applied hydraulic pressure or osmotic pressure) also plays an important role in the extent of fouling in membrane separation processes.

As the membrane fouling in both of FO and RO varies according type of polysaccharide, it is very important to select representative polysaccharide
foulant models for each process. This study provides the first insight into this fundamental research area; and more work is continuing using mixtures of different polysaccharides, which may better simulate fouling in the field.

Fig. 4.11 Comparison of membrane fouling in reverse osmosis and forward osmosis by polysaccharides isolated from naturally adherent bacteria RSW 8. RO fouling tests were conducted with a hydraulic pressure of 400 psi; whilst FO tests were carried out by using constantly saturated NaCl solutions as draw solutions. All runs were performed under identical conditions: initial flux of 9.5 L/(m²·h); cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; feed solution consisting of 1 mM Ca²⁺ ions and 50 mM total ionic strength; polymer concentration of 0.2 g/L.

4.5 Summary

Investigation and comparison of polysaccharide fouling in forward osmosis (FO) and reverse osmosis (RO) have been conducted by using model polysaccharides (alginate, xanthan and pullulan) and polysaccharides (FSW 6, RSW 8, RSW 12 and RSW 14) isolated from naturally adherent bacteria in a seawater desalination plant. The major findings are as follows:

Firstly, the use of constantly saturated draw solution maintained a constant driving force in FO and enabled a better comparison of polysaccharide fouling in FO and RO.

Secondly, some findings from RO fouling tests are:
1) Both alginate and xanthan caused membrane fouling; while pullulan enhanced permeate flux. As the polysaccharide concentration increased from 0.2 g/L to 0.5 g/L, the membrane fouling was aggravated for alginate, and negligible further fouling was observed for xanthan.

2) Comparison of model polysaccharides (alginate, xanthan and pullulan) and polysaccharides (RSW 8 and RSW 12) showed that the polysaccharides behaved differently in membrane fouling. The results also indicate alginate is not a typical model for polysaccharide in membrane fouling. More work is necessary to explore the most representative polysaccharides for membrane fouling study.

3) Increased applied hydraulic pressure and addition of Ca$^{2+}$ ions could cause more severe alginate and xanthan fouling.

Thirdly, some findings from FO fouling tests are:

1) Using DI water feed solution in FO, solution viscosity could be the major factor governing polysaccharide (alginate, xanthan and pullulan) fouling; while using artificial seawater feed solution, osmotic pressure was the major contributor to flux decline in polysaccharide fouling tests.

2) Comparison of FO fouling by model polysaccharides (alginate, xanthan and pullulan) and polysaccharides (FSW 6, RSW 8 and RSW 14) isolated from naturally adherent bacteria in a seawater desalination showed that all the model polysaccharides caused flux decline, while all the isolated polysaccharides improved permeate flux, indicating that some polymers could improve membrane performance.

Fourthly, it was found from comparison of membrane fouling in RO and FO that xanthan and alginate caused more severe fouling in RO than in FO, and RSW 8 caused membrane fouling in RO but improve permeate flux in FO. These results indicated that the pressure source alone plays an important role in polysaccharide fouling during the membrane separation.
Chapter 5. Alleviation of polysaccharide fouling in reverse osmosis and forward osmosis

This chapter investigates and compares alleviation efficiency of sodium nitroprusside (SNP) and potassium ferricyanide (KFCN) in alleviating membrane fouling by alginate and xanthan in forward osmosis (FO) and reverse osmosis (RO). In a typical experiment on polysaccharide fouling alleviation, the alleviating agent was added with the polysaccharide foulant after 2 h membrane compaction with DI water and 2 h membrane stabilization using foulant-free electrolyte solution (DI water containing 1 mM Ca$^{2+}$ ions and 50 mM ionic strength by adding NaCl). As mentioned in Section 3.3, SNP molecule contains five cyanide ligands (-CN) and one linear nitric oxide ligand (-NO) and can produce NO radical; while KFCN has six cyanide ligands but no oxide ligand. Therefore, KFCN can be used to compare with SNP in regard to production of NO radical and its effect in polysaccharide fouling alleviation. Both SNP and KFCN are toxic when their cyanide ligands are released under certain circumstances. However, effect of the two alleviating agents was tested at a nontoxic or sublethal concentration in this study. In addition, the membrane used in this study has a high rejection coefficient and can retain most of SNP and KFCN from the feed solution. As a result, it is safe to use these agents to mitigate membrane fouling.

5.1 Alleviation of polysaccharide fouling in reverse osmosis

5.1.1 Effect of alleviating agent type on polysaccharide fouling alleviation in reverse osmosis

The alleviating efficiencies of sodium nitroprusside (SNP) and potassium ferricyanide (KFCN) on polysaccharide fouling in reverse osmosis (RO) were compared (Fig.5.1). In the baseline experiment that the feed solution contained
only NaCl, permeate flux decreased nearly 4.5% after 24 h experiment (Fig. 5.1a). This was likely due to concentration of the feed water as the water in the feed water continuously permeated through the membrane, subsequently increasing the osmotic pressure of the feed water [3]. Negligible flux decline was observed when SNP and KFCN at the concentration of 0.1 mM was added to the NaCl feed solution (Fig. 5.1a). This could be due to the enhancement of osmotic pressure as the addition of SNP and KFCN increased the feed concentration as well as the osmotic pressure. This is consistent with the change in solution conductivity. When the feed solution contained only NaCl, its solution conductivity was 3.345 ms; while the conductivities negligibly increased to 3.375 ms and 3.445 ms, respectively, when SNP (0.1mM) and KFCN (0.1mM) were added. The results indicate SNP and KFCN do not significantly change permeate flux.
Fig. 5.1 Alleviating effect of SNP/KFCN on polysaccharide fouling: (a) normalized flux after 24 h; (b) alleviation efficiency. A hydraulic pressure of 500 psi (3447.4 kPa) was applied, generating an initial flux of 13.0 L/(m²·h). The concentration of SNP/KFCN was 0.1 mM. Other experimental conditions included: polysaccharide concentration of 0.2 g/L; cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; total ionic strength of 50 mM.

Alginate caused membrane fouling which resulted in 27% permeate flux decline while xanthan caused 22% flux decline (Fig. 5.1a). Such fouling behavior can be attributed to accumulation of polysaccharide on the membrane surface under high hydraulic pressure and cake-enhanced osmotic pressure. Accumulation of polysaccharide occurs through two steps: the attachment of polysaccharide on the membrane surface, followed by interaction between polysaccharide on the membrane surface and polysaccharide in the feed water [55, 152]. Polysaccharide in the feed water firstly interacts with the membrane material through some chemical functional groups, such as carboxyl groups in alginate and xanthan molecules. Polysaccharide in the feed water then interacts with the polysaccharide deposited on the membrane surface. Under the constantly high hydraulic pressure, the accumulation of polysaccharide can be promoted, leading to an increase in total hydraulic resistance. Meanwhile, accumulation of polysaccharide on the membrane surface can contribute to cake-enhanced osmotic pressure by entrapping the dissolved solute in the feed water and hindering the back diffusion of salt ions [3], which results in an increase in osmotic pressure of the feed water near the membrane surface. Therefore, the accumulation of polysaccharide increasing hydraulic resistance, together with sequential enhanced osmotic pressure on the membrane surface, resulted in significant flux decline.

When SNP and KFCN were present, both normalized fluxes for alginate and xanthan fouling were improved (Fig. 5.1a). The flux for alginate fouling was 68.8%, and improved to 76.9% and 70.8% by SNP and KFCN, respectively. Similarly with xanthan as the polysaccharide foulant, flux decline was improved from 73.7% to 80.6% by SNP and 81.3% by KFCN. As to fouling
alleviation efficiency ($\psi$) SNP accounted for 26% improvement in alginate fouling, KFCN 7% (Fig.5.1b). For xanthan fouling, 26% improvement was achieved in the presence of SNP; 29% in the presence of KFCN. Both SNP and KFCN can alleviate polysaccharide fouling (Fig.5.1). This could be explained by rather the electrostatic repulsion between polysaccharides and alleviating agents than reduced solution viscosity, as the addition of SNP and KFCN increased viscosity of alginate solution and xanthan solution (Fig.5.2). Previous studies [71, 100] attributed the reduction of BSA fouling in RO in the presence of $\text{Ca}^{2+}$ ions to the strong electrostatic repulsion as both BSA and BSA-absorbed membrane surface bore negative charges. In this study, alginate and xanthan contained negatively charged –COO- functional groups, while SNP and KFCN were also negatively charged $\left[\text{Fe(CN)}_5\text{NO}\right]^{2-}$ and $\left[\text{Fe(CN)}_6\right]^{3-}$, respectively. As the alleviating agents and the polysaccharide foulants accumulated on the membrane surface, strong electrostatic repulsion could occur and significantly lead to less compact fouling layer on the membrane surface, which would be washed off under the shear force of the cross-flow velocity [32].

Fig.5.2 Viscosity of polysaccharide solutions in the absence and presence of alleviating agents. The solution contains 50 mM NaCl, 0.2 g/L alginate or xanthan, and 0.1 mM SNP or KFCN if added.
While KFCN was as effective as SNP in alleviating xanthan fouling, SNP reduced alginate fouling more efficiently than KFCN. The higher efficiency of SNP could be due to effect of nitric oxide (NO) as a free radical released from SNP on alginate dispersal, whereas KFCN does not release an NO radical, which was in good agreement with previous study [153] that NO could depolymerize polysaccharides. While one study has recognized the potential of alginate to inactivate the NO free radical, reducing cell dispersal from biofilms [11], we have demonstrated that through direct interaction with polysaccharides, NO can alleviate polysaccharide membrane fouling (Fig.5.1).

5.1.2 Effect of calcium ions on polysaccharide fouling and its alleviation by sodium nitroprusside/potassium ferricyanide in reverse osmosis
Fig. 5.3 Effect of Ca\textsuperscript{2+} ions on alginate and xanthan fouling and their alleviation by sodium nitroprusside (SNP) and potassium ferricyanide (KFCN) in reverse osmosis (RO). (a) fouling by Ca\textsuperscript{2+} ions; (b) effect of Ca\textsuperscript{2+} ions on alginate fouling and its alleviation by SNP; (c) effect of Ca\textsuperscript{2+} ions on alginate fouling and its alleviation by
KFCN; (d) effect of Ca$^{2+}$ ions on xanthan fouling and its alleviation by SNP; and (e) effect of Ca$^{2+}$ ions on xanthan fouling and its alleviation by KFCN. A hydraulic pressure of 500 psi (3447.4 kPa) was applied, generating an initial flux of 13.0 L/(m$^2$·h). The concentration of SNP/KFCN was 0.1 mM. Ca$^{2+}$ concentration was 1 mM if added to the feed water. Other experimental conditions included: polysaccharide concentration of 0.2 g/L; cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; total ionic strength 50 mM.

Table 5.1 Alleviation efficiency $\psi$ (%) of SNP and KFCN on alginate and xanthan fouling in the absence and presence of Ca$^{2+}$ ions

<table>
<thead>
<tr>
<th></th>
<th>Alleviation of alginate fouling</th>
<th>Alleviation of xanthan fouling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>by SNP</td>
<td>by KFCN</td>
</tr>
<tr>
<td>Without CaCl$_2$</td>
<td>26.0</td>
<td>6.6</td>
</tr>
<tr>
<td>With CaCl$_2$</td>
<td>11.0</td>
<td>5.8</td>
</tr>
</tbody>
</table>

In the absence of Ca$^{2+}$ ions, both SNP and KFCN reduced polysaccharide fouling (Section 5.1.1). In the absence of polysaccharide foulants, Ca$^{2+}$ ions had a negligible impact on flux behaviour, indicating interactions between Ca$^{2+}$ ions with negatively charged functional groups of SNP and KFCN did not contribute to membrane fouling (Fig. 5.3a). However, in the presence of polysaccharide foulants, Ca$^{2+}$ ions had a significant impact on polysaccharide fouling and alleviation by SNP and KFCN (Fig. 5.3b-e). In the absence of SNP and KFCN, Ca$^{2+}$ ions caused more severe flux decline during alginate and xanthan fouling tests by 23% and 19%, respectively. The effect of Ca$^{2+}$ ions on polysaccharide fouling has been discussed in Section 4.2.4. The Ca$^{2+}$ ions also significantly reduced the efficiency ($\psi$) of SNP and KFCN in alleviating alginate fouling (Table 5.1). In the feed water supplemented with both alginate and alleviating agent, Ca$^{2+}$ ions preferentially interact with $-\text{COO}^-$ functional groups of alginate, leading to the formation of Ca-alginate gels [75], which was found to be irreversible [56] and would prevent interaction between alleviating agents.
and alginate. As a result, the efficiency of SNP and KFCN in alginate fouling greatly decreased in the presence of Ca\(^{2+}\) ions. Compared to KFCN in the absence and presence of Ca\(^{2+}\) ions, SNP presented higher efficiency in alleviating alginate fouling (Table 5.1). This further confirms that the NO moiety released by SNP could alleviate alginate fouling.

On the other hand, Ca\(^{2+}\) ions showed great impact on alleviation of xanthan fouling by KFCN that the alleviation efficiency (ψ) was found to be negative (Table 5.1), indicating that xanthan fouling was aggravated by Ca\(^{2+}\) ions even in the presence of KFCN. This phenomenon could be attributed to the interaction among KFCN, Ca\(^{2+}\) ions and xanthan. Ca\(^{2+}\) ions could play a role in bridging between negatively charged functional groups carboxylic functional groups(-COO\(^-\)) on xanthan molecules and –CN of KFCN, which led to formation of xanthan-Ca-KFCN macrocomplexes network and significant reduction of the electrostatic repulsion between polysaccharides and alleviating agents. Under high hydraulic pressure, the macrocomplexes would become compact, which could significantly increase the hydraulic resistance and reduce the permeate flux. In addition, the capture of KFCN by xanthan may add to osmotic pressure near the membrane surface, which leads to further decline in permeate flux. While KFCN showed negative efficiency in alleviating xanthan fouling in the presence of Ca\(^{2+}\) ions, alleviation efficiency of SNP in xanthan fouling maintained at a slightly higher level in the presence of Ca\(^{2+}\) ions compared to that in the absence of Ca\(^{2+}\) ions.

Generally, the presence of Ca\(^{2+}\) ions aggravated polysaccharide fouling and reduced the alleviation efficiency (ψ) of SNP and KFCN. SNP appeared to alleviate polysaccharide fouling to a greater extent than KFCN, likely due to the NO free radical spontaneously released.
5.1.3 Effect of alleviating agent concentration on polysaccharide fouling alleviation in reverse osmosis

Two concentrations of alleviating agents (SNP and KFCN) were used to compare their effect on alginate and xanthan fouling in reverse osmosis (RO) in the presence of Ca$^{2+}$ ions (Fig. 5.4). SNP showed more alginate and xanthan fouling alleviation than KFCN, again likely due to the release of NO (Fig. 5.4). Alleviation of alginate fouling increased with increasing SNP/KFCN concentration. The high concentration of SNP caused less xanthan fouling alleviation than the low concentration, while KFCN did not appear to improve permeate flux at all (Fig. 5.4).

![Fig. 5.4](image_url)

Fig. 5.4 Effect of alleviating agent concentration on alleviation of polysaccharide fouling in RO in the presence of Ca$^{2+}$ ions: (a) normalized flux after 24 h; (b) alleviation efficiency. A hydraulic pressure of 500 psi (3447.4 kPa) was applied,
generating an initial flux of 13.0 L/(m$^2$·h). The concentration of sodium nitroprusside/potassium ferricyanide (SNP/KFCN) was 0.1 mM or 1 mM. Ca$^{2+}$ concentration was 1 mM. Other experimental conditions included: polysaccharide concentration of 0.2 g/L; cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 ℃; total ionic strength 50 mM.

During alleviation of alginate fouling, SNP and KFCN at high concentration (1 mM) could compete against carboxylic functional groups (-COO$^-$) of alginate in interaction with Ca$^{2+}$ ions, to some degree prevent the interaction between Ca$^{2+}$ ions and alginate and thus reduce the formation of Ca-alginate gels, leading to decrease in total hydraulic resistance. The fact that the efficiency on alleviation of alginate fouling is nonlinear with increased concentration of alleviating agent could be attributed to the preferential interaction between carboxylic functional groups (-COO$^-$) of alginate and Ca$^{2+}$ ions rather than between functional groups and SNP and KFCN.

Alleviation of xanthan fouling decreased with increased alleviating agent concentration could be due to the over-dosage of SNP and KFCN. Compared to alginate, xanthan has less –COO$^-$ functional groups and could interact with less SNP and KFCN. The remaining SNP and KFCN in the feed water could react with Ca$^{2+}$ ions and be captured by xanthan fouling layer, resulting in an increase in osmotic pressure of the feed water near the membrane surface. The results indicate the importance of proper dosage of the compounds in alleviating polysaccharide fouling.

5.1.4 Effect of applied hydraulic pressure on alleviation of polysaccharide fouling using sodium nitroprusside in the presence of calcium ions

To understand the influence of applied hydraulic pressure on fouling alleviation, alginate and xanthan were added in the presence of Ca$^{2+}$ ions using sodium nitroprusside (SNP) as the alleviating agent (0.1 mM) (Fig.5.5). Under the applied hydraulic pressure of 400 psi and 500 psi, initial fluxes of ~9.5 and ~13.0 L/(m$^2$·h) were respectively achieved. It has been widely reported that membrane suffers more severe fouling with increased initial flux [32, 55, 154].
In this study, with an applied hydraulic pressure of 500 psi alginate fouling caused a 54% flux decline (Fig. 5.5a); xanthan fouling caused 48% flux decline (Fig. 5.5b). When a lower applied hydraulic pressure of 400 psi was applied, less membrane fouling was observed, with 30% (alginate) and 28% (xanthan) flux declines observed (Fig. 5.5a and b).
Fig. 5.5 Effect of applied pressure on alleviation of polysaccharide fouling using SNP in the presence of Ca\(^{2+}\) ions: (a) alginate fouling in absence and presence of SNP; (b) xanthan fouling in absence and presence of SNP; and (c) alleviation efficiency of SNP on alginate and xanthan fouling. Hydraulic pressure of 400 psi (2757.9 kPa) and 500 psi (3447.4 kPa) were applied, generating an initial flux of 9.5 L/(m\(^2\)·h) and 13.0 L/(m\(^2\)·h), respectively. The concentration of SNP was 0.1 mM. Ca\(^{2+}\) concentration was 1 mM. Other experimental conditions included: polysaccharide concentration of 0.2 g/L; cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; total ionic strength 50 mM.

In addition to the increased membrane fouling evident at higher hydraulic pressure, the alleviation of fouling by SNP was also more effective at higher hydraulic pressure (Fig. 5.5c). At 400 psi, xanthan fouling alleviation efficiency (\(\psi\)) was calculated as ~5%, at 500 psi alleviation was 29%. The lower alleviation efficiency under the lower applied hydraulic pressure could be explained by the negligible interaction between SNP and xanthan. With the reduced applied hydraulic pressure, the xanthan fouling layer became less compact under less compression, and much less SNP could accumulate on the membrane surface. As a result, the chances for the interaction between SNP and xanthan were reduced significantly, and thus led to negligible alleviation of xanthan fouling.

Applied hydraulic pressure had less impact on alleviation of alginate fouling by SNP with alleviation of 8% (400 psi) and 11% (500 psi) (Fig. 5.5c). This is consistent with the findings in previous literature [99]. Yang [99] reported higher flux decline under higher trans-membrane pressure during membrane fouling by bovine serum albumin (BSA) in the absence and presence of antiscalant polyaspartic acid (PASP), but the alleviation efficiency of PASP under higher trans-membrane pressure was similar to that under lower trans-membrane pressure. In this study, the similarity of \(\psi\) of SNP under different applied hydraulic pressure could be due to the formation of crosslinked Ca-alginate gels. The fouling layer caused by formation of crosslinked
Ca-alginate gel network is irreversible [56], and was therefore independent of cross-flow velocity and nonresponsive to the hydraulic pressure variation.

5.2 Alleviation of polysaccharide fouling in forward osmosis

5.2.1 Effect of alleviating agent type on alleviation of polysaccharide fouling in forward osmosis

![Normalized flux after 24 h forward osmosis (FO) fouling tests by alginate and xanthan in the absence and presence of alleviating agents, sodium nitroprusside (SNP) and potassium ferricyanide (KFCN). Constantly saturated NaCl solution was used as draw solution. Other experimental conditions included: polysaccharide concentration of 0.2 g/L; initial flux of 9.5 L/(m²·h) using DI water containing 1 mM Ca²⁺ ions and 50 mM total ionic strength; cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; feed solution using artificial seawater or DI water containing 1 mM Ca²⁺ ions and 50 mM total ionic strength; alleviating agents’ (SNP and KFCN) concentration of 0.1 mM.

The effects of different alleviating agents were compared (Fig.5.6). Normalized permeate flux after 24 h for alginate fouling in the absence of alleviating agents was 0.86. Flux improved to nearly 0.90 in the presence of SNP, and 0.89 in the presence of KFCN (Fig.5.6). For xanthan, the normalized flux was reduced to 0.80 after 24 h xanthan fouling, but alleviation was evident using SNP (0.91) and KFCN (0.88) (Fig.5.6).
As discussed in Section 4.3.1, solution viscosity could be the major factor governing polysaccharide fouling in FO, and therefore xanthan solution with higher viscosity caused more severe fouling compared to alginate solution. Polysaccharide fouling could be alleviated by reducing feed solution viscosity and thus the interaction between polysaccharides and membrane material. However, as shown in Fig.5.7, the addition of alleviating agents into polysaccharide solution slightly increased solution viscosity, indicating that reduction of alginate fouling and xanthan fouling was not resulted from the reduced viscosity. Alleviation of alginate fouling and xanthan fouling by SNP and KFCN could be explained by the electrostatic repulsion between polysaccharides (alginate and xanthan) and alleviating agents (SNP and KFCN). As discussed in Section 5.1.1, alginate and xanthan molecules contain negatively charged –COO⁻ functional groups, and SNP and KFCN have [Fe(CN)₅NO]²⁻ and [Fe(CN)₆]³⁻, respectively. The negative charges on polysaccharides and alleviating agents led to strong electrostatic repulsion between them, reducing interaction between polysaccharides and membrane. Therefore, less polysaccharide accumulated on the membrane surface in the presence of the alleviating agents.

![Graph showing viscosity changes](image)

**Fig.5.7** Viscosity of polysaccharide solutions in the absence and presence of alleviating agents. The solution contains 1 mM Ca²⁺ ions, 50 mM ionic strength by adding NaCl, 0.2 g/L alginate or xanthan, and 0.1 mM SNP or KFCN if added.
Alleviation efficiency ($\psi$) of SNP and KFCN on alginate and xanthan fouling in the presence of Ca$^{2+}$ ions was presented in Table 5.2. As can be seen, 26.9% and 18.3% of alleviation efficiency on alginate fouling were achieved by SNP and KFCN, respectively. On the other hand, SNP and KFCN present high alleviation efficiency during xanthan fouling, with 55.4% and 40.9%, respectively. Compared to KFCN, SNP presented higher efficiency for both alginate and xanthan fouling, which could be due to its –NO functional groups dispersing polysaccharides and enhancing alleviation efficiency. The results demonstrate that SNP could be a better alleviating agent to reduce polysaccharide fouling.

Table 5.2 Alleviation efficiency $\psi$ (%) of SNP and KFCN on alginate and xanthan fouling in the presence of Ca$^{2+}$ ions.

<table>
<thead>
<tr>
<th></th>
<th>SNP (0.1 mM)</th>
<th>KFCN (0.1 mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl+CaCl$_2$+alginate</td>
<td>26.9</td>
<td>18.3</td>
</tr>
<tr>
<td>NaCl+CaCl$_2$+xanthan</td>
<td>55.4</td>
<td>40.9</td>
</tr>
</tbody>
</table>

5.2.2 Effect of sodium nitroprusside concentration on alleviation of polysaccharide fouling in forward osmosis

![Graph showing normalized flux vs NaCl+CaCl$_2$+alginate and NaCl+CaCl$_2$+xanthan](image)
Fig. 5.8 Effect of sodium nitroprusside (SNP) concentration on alleviation of polysaccharide fouling in forward osmosis (FO) in the presence of Ca²⁺ ions: (a) normalized flux after 24 h; (b) alleviation efficiency. Constantly saturated NaCl solution was used as draw solution. Other experimental conditions included: polysaccharide concentration of 0.2 g/L; initial flux of 9.5 L/(m²·h) using DI water containing 1 mM Ca²⁺ ions and 50 mM total ionic strength; cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; feed solution using DI water containing 1 mM Ca²⁺ ions and 50 mM total ionic strength; SNP concentration of 0.1 mM and 0.01 mM.

In Section 5.2.2, SNP was found to be a better alleviating agent compared to KFCN for both alginate and xanthan fouling. Therefore, SNP was selected as the alleviating agent to investigate the effect of concentration (0.1 mM and 0.01 mM) on polysaccharide fouling alleviation in the presence of Ca²⁺ ions. As the concentration of SNP increased from 0.01 mM to 0.1 mM, alleviation efficiency (ψ) decreased for alginate fouling but increased for xanthan fouling (Fig. 5.8). The normalized flux after 24 h alginate fouling (0.86) was improved to 0.96 when 0.01 mM SNP was added, equivalent to an alleviation efficiency of 70.2% (Fig. 5.8b). With increased SNP concentration (0.1 mM), the normalized flux was 0.90, equivalent to an alleviation efficiency of 26.9% (Fig. 5.8b). The results show that high concentration of SNP could reduce their effectiveness on fouling alleviation. With xanthan fouling, in the absence of SNP, the normalized flux after 24 h was 0.80. SNP improved the flux to 0.88.
(0.01 mM) and 0.91 (0.1 mM). Alleviation efficiency therefore increased with concentration from 38.2% (0.01 mM) and 55.4% (0.1 mM).

The difference in the alleviating efficiency of SNP on alginate and xanthan fouling could be explained by the different extents of fouling caused by alginate and xanthan. In the absence of SNP, alginate caused less severe fouling compared to xanthan. As a result, less SNP was needed to alleviate alginate fouling. Over-dosage of SNP introduced more ions than necessary, which might aggravate cake-enhanced osmotic pressure as the SNP captured by the alginate deposited on the membrane surface or compression of electrical double layer because of higher ionic strength. Compared to alginate, xanthan caused more severe fouling, and thus needed more alleviating agents to reduce membrane fouling. The experimental results indicate proper dosage of SNP based on fouling extent by different kinds of polysaccharides can effectively reduce membrane fouling.

5.3 Comparison of efficiency of sodium nitroprusside in alleviating polysaccharide fouling between forward osmosis and reverse osmosis
Fig. 5.9 Comparison of efficiency of sodium nitroprusside (SNP) in alleviating polysaccharide fouling between forward osmosis (FO) and reverse osmosis (RO). (a) alleviation of alginate fouling in FO and RO; (b) alleviation of xanthan fouling in FO and RO; and (c) alleviation efficiency of SNP on alginate and xanthan fouling in FO and RO. RO fouling tests were conducted with a hydraulic pressure of 400 psi; whilst FO tests were carried out by using constantly saturated NaCl solutions as draw solutions. All runs were performed under identical conditions: initial flux of 9.5 L/(m²·h); cross-flow velocity of 8.5 cm/s; solution temperature of 25 ± 1 °C; feed solution consisting of 1 mM Ca²⁺ ions and 50 mM total ionic strength; polymer concentration of 0.2 g/L; SNP concentration of 0.1 mM.

A direct comparison of polysaccharide fouling alleviation by SNP (0.1 mM) in FO and RO is presented (Fig. 5.9). All operational conditions were the same including temperature, initial permeate flux, cross-flow velocity, and feed water
chemistry such as ionic strength, calcium concentration and polysaccharide concentration. The only difference was applied pressure, with applied hydraulic pressure in RO and chemical osmotic pressure in FO. In Section 4.4.1, it was found that alginate and xanthan caused more severe fouling in RO than in FO.

Both alginate and xanthan fouling in both FO and RO processes were alleviated by SNP (Fig.5.9), indicating the potential of SNP to alleviate polysaccharide fouling at the correct dose. Normalized fluxes after 24 h alginate and xanthan fouling in the presence of SNP were much higher in FO than in RO (Fig.5.9a and b). SNP alleviated fouling to a greater extent in FO than in RO for both alginate and xanthan (Fig.5.9c). For example, for alginate fouling, SNP alleviation efficiency was 27.0% (FO) and 7.6% (RO) and with xanthan 55.4% (FO) and 4.5% (RO). In RO, as hydraulic pressure was applied, membrane fouling could be largely attributed to the foulant – foulant interaction; while foulant – membrane interaction was likely the major mechanism governing FO fouling. The addition of SNP in FO caused electrostatic repulsion between membrane and the polysaccharides due to the negative charges on both SNP and the polysaccharides, less accumulation of polysaccharides on the membrane surface, and thus alleviated polysaccharide fouling. In RO, electrostatic repulsion between SNP and polysaccharides became negligible as alginate and xanthan formed compact macrocomplex networks or gels in the presence of Ca^{2+} ions, which were promoted under hydraulic pressure in RO. Therefore, the foulant – foulant interaction governing membrane fouling in RO was less affected by SNP. The results demonstrate the importance of pressure resources during the membrane separation processes.

### 5.4 Summary

Alleviation of polysaccharide (alginate and xanthan) fouling in reverse osmosis (RO) and forward osmosis (FO) was investigated using sodium nitroprusside (SNP) and potassium ferricyanide (KFCN) as alleviating agents.

Firstly, the findings in RO are as follows:
1) SNP and KFCN both alleviated both alginate and xanthan fouling in the absence of Ca\(^{2+}\) ions.

2) In the presence of Ca\(^{2+}\) ions, SNP (0.1mM) alleviated both alginate and xanthan fouling; KFCN (0.1mM) alleviated alginate fouling but aggravated xanthan fouling.

3) In the presence of Ca\(^{2+}\) ions, as the concentration of SNP and KFCN increased from 0.1 to 1 mM, their efficiency increased in alleviating alginate fouling, but decreased in alleviating xanthan fouling.

4) In the presence of Ca\(^{2+}\) ions, elevated applied hydraulic pressure improved alleviation efficiency of SNP in alginate and xanthan fouling.

Secondly, the findings in FO in the presence of Ca\(^{2+}\) ions are as follows:

1) Both SNP and KFCN alleviated polysaccharide (alginate and xanthan) fouling in FO, likely due to the electrostatic repulsion between them and the polysaccharides.

2) The alleviation efficiency increased with SNP concentration for xanthan fouling, but decreased for alginate fouling. The results indicate that it is important to properly dose the alleviating agent for polysaccharide fouling alleviation.

Thirdly, it was found that SNP (0.1 mM) presented higher efficiency in alleviating polysaccharide (alginate and xanthan) fouling in the presence of Ca\(^{2+}\) ions in FO than in RO, suggesting the pressure source plays an important role in polysaccharide fouling alleviation.
Chapter 6. Modeling hydraulic resistances to permeate flux in RO membrane separation

In this chapter, we developed a resistance in series model to study the contributions of membrane resistance and non-membrane resistance (resistances due to concentration polarization and cake formation) to the permeate flux decline during the RO separation process. The model was verified by conducting experiments of RO membrane fouling by two model polysaccharides, alginate and xanthan. Separate experiments were conducted to determine membrane resistance, the effect of concentration polarization in the absence of polymers, cake resistance in the absence of salts and the effect of adding NaCl. Effects of calcium ions and applied hydraulic pressure were also investigated. Based on resistance analysis data, the relationship between the concentration polarization resistance and the elevated osmotic pressure was demonstrated; the coupled effect of concentration polarization and cake formation was illustrated; and some possible methods to improve membrane permeate flux was suggested.

6.1 Description of the model of hydraulic resistances

Based on the different causes of fouling, some studies incorporated $R_{cp}$ and $R_c$ into non-membrane resistances [73, 155]. Some studies that treated the concentrated salt solution on the membrane surface as elevated osmotic pressure did not incorporate $R_{cp}$ in the total hydraulic resistance [76, 156]; while some used it as concentration polarization resistance rather than the increase in the osmotic pressure [82, 155]. This study synthesizes both characteristics (concentration polarization and the increase in the osmotic pressure) and yields the relationship between them.
The model is based on the following assumptions:

1) The membrane resistance is constant during the separation process. The interaction between the membrane surface and foulants in the feed solution is considered to contribute only to non-membrane resistances, without affecting membrane resistance.

2) The effect of pore blockage by foulants is negligible as the pore sizes of the membranes are small [79].

3) The osmotic pressure by polysaccharides in the feed solution is negligible as it is extraordinarily small compared to that by salt in the feed solution.

The three kinds of resistances were calculated based on the following equations.

Fig. 6.1 Schematic diagram of the hydraulic resistance model for explaining the calculation of different resistance components: (a) membrane resistance using DI water; (b) concentration polarization resistance using salty water; (c) cake resistance using polymer solution; (d) Combined concentration polarization resistance and cake resistance using polymer inclusion salty water.
1. Membrane resistance ($R_m$)

The membrane resistance ($R_m$) was obtained during the RO process using DI water as the feed solution (shown in Fig. 6.1a). The experiment started with compaction of the membrane using DI water for 2 h. Afterwards, the baseline experiment was conducted with DI water remaining the only component of the feed solution. As no foulants such as ions and polymers existed in the feed, the hydraulic resistance solely consisted of $R_m$.

$$R_m = R_t = \frac{\Delta P_m}{\mu_{DI} J_w} = \frac{(P - P_0)}{(\mu_{DI} J_w)} \quad (6.1)$$

where $R_m$ and $R_t$ are the membrane resistance and total hydraulic resistance, respectively (m$^{-1}$); $\Delta P_m$ is the trans-membrane pressure difference (Pa); $\mu_{DI}$ is the water viscosity (Pa·s); $J_w$ is the water permeate flux (m/s); $P$ and $P_0$ are the pressures on the solution side and the permeate side, respectively (Pa), and the value of $P - P_0$ can be directly read from the pressure gauge.

2. Concentration polarization resistance ($R_{cp}$)

To measure concentration polarization resistance ($R_{cp}$), solution containing salt ions was used as the feed solution (shown in Fig. 6.1b). The experiment started with compaction of the membrane using DI water for 2 h, followed by another 2 h stabilization and equilibration of membrane using background electrolyte solution. Afterwards the fouling test was conducted and investigated. During the membrane separation process, only water passed through the membrane. The ions were rejected and concentrated on the membrane surface under the hydraulic pressure, and forms a “salt layer”, and the “salt layer” can be represented as either $R_{cp}$ or elevated osmotic pressure ($\pi_{cp}$). When the “salt layer” is viewed as $R_{cp}$,

$$R_t = \frac{\Delta P_m}{\mu_{DI} J_w} = \frac{(P - P_0 - \pi_{feed})}{(\mu_{DI} J_w)} \quad (6.2)$$

$$R_{cp} = R_t - R_m = \frac{(P - P_0 - \pi_{feed})}{(\mu_{DI} J_w)} - R_m \quad (6.3)$$
where $\pi_{\text{feed}}$ is the osmotic pressure of the feed solution (Pa), $R_{\text{cp}}$ is concentration polarization resistance ($m^{-1}$).

When the “salt layer” serves as $\pi_{\text{cp}}$, the pressure difference between the two sides of the membrane can be expressed in Eq. (6.4) and $J_w$ can be calculated using Eq. (6.5).

$$\Delta P_m = P - P_0 - \pi_{\text{cp}} \tag{6.4}$$

$$J_w = (P - P_0 - \pi_{\text{cp}}) / (\mu_{\text{DI}} R_m) \tag{6.5}$$

where $\pi_{\text{cp}}$ is the osmotic pressure of salt on the membrane surface (Pa).

Based on the calculation of $R_{\text{cp}}$ in Eq. (6.3) and $\pi_{\text{cp}}$ in Eq. (6.5), the relationship between them could be deduced, as shown in Eq. (6.6).

$$\pi_{\text{cp}} - \pi_{\text{feed}} = \mu_{\text{DI}} J_w R_{\text{cp}} \tag{6.6}$$

Then, the concentration of the salt accumulated on the membrane surface can be calculated based on the van’t Hoff equation [60, 61] as long as it is not relatively high, as can be seen in Eq. (6.7).

$$C_{\text{cp}} = \pi_{\text{cp}} / i R_g T \tag{6.7}$$

where $i$ is the Van’t Hoff factor, $C_{\text{cp}}$ is the solution concentration of the salt on the membrane surface (mol/L or M), $R_g$ is the universal gas constant ($R_g=0.0831 \text{ L}\cdot\text{bar/(mol}\cdot\text{K})$), and $T$ is the absolute temperature (K).

3. Cake resistance ($R_c$)

Similar to the calculation of $R_{\text{cp}}$, calculation of $R_c$ was carried out using polymer solution as the feed solution (shown in Fig.6.1c). The experiment started with compaction of the membrane using DI water for 2 h. Then polysaccharides were added to the DI water and the fouling test was conducted and investigated. During the fouling tests, the polymers were rejected and accumulated on the membrane surface, forming a cake layer and increasing hydraulic resistance.
\[ R_c = R_t - R_m = (P - P_0 - \pi_{\text{feed}})/(\mu_{\text{DI}} \cdot J_w) - R_m \]  \hspace{1cm} (6.8)

where the \( R_c \) is the cake resistance (m\(^{-1}\)). The concentration (0.2g/L) of the polymer feed solution was very low in this study, and thus the solution’s osmotic pressure calculated based on Eq. (6.7), is considered negligible as compared to the applied pressure.

4. Combined concentration polarization resistance (\( R_{cp} \)) and cake resistance (\( R_c \))

When the feed contains salt ions and polymer (shown in Fig. 6.1d), both of them contribute to the total hydraulic resistance. The experiment started with compaction of the membrane using DI water for 2 h, followed by another 2 h stabilization and equilibration of membrane using background electrolyte solution. Afterwards the polysaccharides were added to the electrolyte solution, and the fouling test was conducted and investigated. The existence of salt ions and polymer may affect each other, and the coupled effect of both may lead to a significant increase in the total hydraulic resistance. The non-membrane resistances \( R_{cp} + R_c \) could be calculated based on the fact that \( R_m \) is constant and only water is considered to pass through the membrane.

In this case,

\[ J_w = \Delta P_m / (\mu_{\text{DI}} \cdot R_t) = (P - P_0 - \pi_{\text{feed}}) / [\mu_{\text{DI}} (R_m + R_{cp} + R_c)] \]  \hspace{1cm} (6.9)

\[ (R_{cp} + R_c) = (P - P_0 - \pi_{\text{feed}}) / (\mu_{\text{DI}} \cdot J_w) - R_m \]  \hspace{1cm} (6.10)

The total flux decline can be described as \( 1 - J_{w0}/J_{w0} \), where \( J_{w0} \) and \( J_{wt} \) are the fluxes at time 0 and time \( t \). As time 0 represented the starting point of the fouling test, both \( R_{cp} \) and \( R_c \) equal 0, and therefore \( J_{w0} \) is calculated using Eq. (6.11).

\[ J_{w0} = (P - P_0 - \pi_{\text{feed}}) / \mu_{\text{DI}} \cdot R_m \]  \hspace{1cm} (6.11)

At time \( t \),

\[ J_{wt} = (P - P_0 - \pi_{\text{feed}}) / [\mu_{\text{DI}} (R_m + R_{cp} + R_c)] \]  \hspace{1cm} (6.12)
where $R_{cpt}$ and $R_{ct}$ are resistances due to concentration polarization and cake formation, respectively, at time $t$.

Based on Eq. (6.11) and (6.12), the normalized flux and the total flux decline at time $t$ can be represented by:

$$\frac{J_{wt}}{J_{w0}} = \frac{R_m}{R_m + R_{cpt} + R_{ct}} \quad (6.13)$$

$$1 - \frac{J_{wt}}{J_{w0}} = \frac{(R_{cpt} + R_{ct})}{(R_m + R_{cpt} + R_{ct})} \quad (6.14)$$

Eq. (6.14) demonstrates the relationship between flux and the hydraulic resistances. The ratio of membrane resistance $R_m$ to $R_t$ represents the normalized flux whist the flux decline can be represented using the ratio of the non-membrane resistance $R_{cpt} + R_{ct}$ to $R_t$.

### 6.2 Concentration polarization in the control experiment

![Figure 6.2](image)

Fig.6.2 Osmotic pressure and concentration of the salt on the membrane surface during the baseline experiment in the absence of polymer. A hydraulic pressure of 400 psi (2757.9 kPa) was applied to generate an initial flux of 9.5 L/(m²·h). The feed solution contained 1 mM Ca²⁺ ions and its ionic strength was adjusted to be 50 mM by adding NaCl. The cross-flow velocity and the temperature of feed solution were adjusted to be 8.5 cm/s and 25 ± 1 °C.

The osmotic pressure ($\pi_{cp}$) and concentration of the salt ($C_{cp}$) on the membrane surface when the feed solution solely contained 50mM salt (NaCl+CaCl₂) were
calculated based on Eq. (6.5) and (6.7) and their trends over time were shown in Fig. 6.2. \( \pi_{cp} \) and \( C_{cp} \) increased under the hydraulic pressure over time, indicating the promotion of concentration polarization. Within the first 8 h, concentration polarization reflected by \( \pi_{cp} \) and \( C_{cp} \) increased slowly and fluctuated. This phenomenon was also observed in previous study [157]. Then \( \pi_{cp} \) and \( C_{cp} \) increased sharply from 8 to 12 h, and tended to be more stable afterwards. After 18 h, \( C_{cp} \) reached about 85 mM, with an increase of about 70% in concentration compared to the initial feed concentration, and correspondingly an increase of 174.1 kPa in \( \pi_{cp} \) (from 247.9 kPa when the experiment commenced to 422.0 kPa after 18 h), which is insignificant as compared to the applied hydraulic pressure (2757.9 kPa). This indicates that salt at a low concentration in feed solution could slightly reduce the effectiveness of applied hydraulic pressure and cause concentration polarization resistance to permeate flux. On one hand, continuous transport of the salt solutes from the bulk feed solution towards the membrane surface under the convective flux generated by the applied hydraulic pressure and rejection of the salt solutes by the membrane might cause accumulation of salt onto the membrane surface, increasing the osmotic pressure and concentration polarization resistance near the membrane surface. This was supported by the salt rejection decreasing from 99.53% to 99.05%. On the other hand, the accumulation of salt solutes on the membrane surface was hindered by the shear force generated by the cross-flow velocity [8], as the cross flow continuously swept some salt solutes away from the membrane surface. Therefore, the accumulated salt caused an increase in osmotic pressure and concentration polarization near the membrane surface, yet the increase was slight.
6.3 Comparison of coupled effect of concentration polarization and cake formation on the increase in hydraulic resistance to the permeate flux and sum of their individual effects

Fig. 6.3 Comparison between the hydraulic resistances due to coupled effect and sum of the individual effects of concentration polarization and cake formation: Plot A, resistance caused by alginate fouling in the absence of salt; Plot B, resistance caused by salts in the absence of alginate; Plot C, resistance caused by fouling in the presence of both salt and alginate; and Plot A+B, sum of Plot A and Plot B. A hydraulic pressure of 400 psi (2757.9 kPa) was applied to generate an initial flux of 9.5 L/(m²·h). The feed solution contained either salt (1 mM Ca²⁺ ions and its ionic strength was adjusted to be 50 mM by adding NaCl) or alginate (0.2 g/L), or both. The cross-flow velocity and the temperature of polysaccharide solution were adjusted to be 8.5 cm/s and 25 ± 1 °C.

The hydraulic resistances due to coupled effect of concentration polarization ($R_{cp}$) and cake formation ($R_c$) and the sum of their individual effects were compared (Fig.6.3). In the absence of salt (See Plot A), alginate caused an increase of about $19\times10^{13}$ m⁻¹ in $R_c$ (Alginate) after 18 h fouling test; while the feed solution containing the salt in the absence of alginate (see Plot B) caused an increase in resistance due to $R_{cp}$ (NaCl+CaCl₂) by about $6\times10^{13}$ m⁻¹ after 18 h. The sum of the two caused an increase in hydraulic resistance by $25\times10^{13}$ m⁻¹ (shown as Plot A+B). When the feed solution contained both salt and alginate
(Plot C), an increase of about $39 \times 10^{13} \text{ m}^{-1}$ in hydraulic resistance $(R_{cp}+R_c(\text{NaCl}+\text{CaCl}_2+\text{alginate}))$ after 18 h fouling test was observed, which was much higher than $25 \times 10^{13} \text{ m}^{-1}$ as shown in Plot A+B. The results demonstrate that coupled effect of concentration polarization and cake formation on the increase in hydraulic resistance to the permeate flux is much greater than the sum of their individual effects. This could be explained by the interaction between the salt and alginate when both of them existed in the feed solution. First of all, calcium ions in the solution could interact with the carboxylic functional groups on the alginate molecules and the negatively charged membrane, which promoted accumulation of alginate [5, 8, 65, 66, 75]. In addition, calcium ions could serve as a linkage between adjacent alginate molecules, resulting in coagulation and complexation of alginate and hence formation of a macromolecule gel network [5, 8, 66, 75], which was compressed under the hydraulic pressure and became compact. Thus, the hydraulic resistance due to cake formation $(R_c(\text{NaCl}+\text{CaCl}_2+\text{alginate}))$ was significantly increased in the presence of salt. In return, the compact alginate gel layer prevented the back diffusion of salt from the membrane surface to the bulk feed solution [3, 29, 51-53], leading to a great increase in salt accumulation on the membrane surface, which greatly increased the concentration and osmotic pressure of the salt solution near the membrane surface. As a result, the hydraulic pressure due to concentration polarization $(R_{cp}(\text{NaCl}+\text{CaCl}_2+\text{alginate}))$ was greatly increased. Therefore, when both salt and alginate were present in the feed solution, the resistances due to concentration polarization and cake formation were increased significantly. Thus, the value of the hydraulic resistance in the presence of both salt and alginate $(R_{cp}+R_c(\text{NaCl}+\text{CaCl}_2+\text{alginate}))$ became higher than the sum of the individuals $(R_{cp} (\text{NaCl}+\text{CaCl}_2)+ R_c(\text{Alginate}))$. 
6.4 Contribution of membrane and non-membrane resistances to permeate flux during polysaccharide fouling tests

Fig. 6.4 Ratios of membrane resistance ($R_m$) and non-membrane resistances ($R_{cp}+R_c$) to total hydraulic resistance over time. A hydraulic pressure of 400 psi (2757.9 kPa) was applied to generate an initial flux of 9.5 L/(m$^2$·h). The feed solution contained 1 mM Ca$^{2+}$ ions and 0.2 g/L polysaccharide (alginate or xanthan) and its ionic strength was adjusted to be 50 mM by adding NaCl, or both. The cross-flow velocity and the temperature of polysaccharide solution were adjusted to be 8.5 cm/s and 25 ± 1 ºC.

The ratios of membrane ($R_m$) and non-membrane resistances ($R_{cp}+R_c$) to total hydraulic resistance during the fouling tests using alginate and xanthan as polysaccharides were presented in Fig. 6.4. According to Eq (6.13), the proportion of membrane resistance ($R_m$) represents the normalized flux; and based on Eq (6.14), the ratio of the hydraulic resistances due to concentration polarization and cake formation (non-membrane resistances) to total hydraulic resistance represents the flux decline rate, in terms of the fact that the flux decline is only caused by concentration polarization and cake formation. The ratios of membrane resistances $R_m/R_t$ during alginate fouling and xanthan fouling decreased over time; correspondingly, non-membrane resistances ($R_{cp}+R_c$)/$R_t$ increased by 30% and 22% after 18 h for alginate and xanthan fouling, respectively (Fig. 6.4). During the fouling tests, ($R_{cp}+R_c$)/$R_t$ was much
lower than $R_m/R_t$, revealing that membrane resistance dominated the hydraulic resistances and is the major limiting factor governing permeate flux.

$$(R_{cp} + R_c)/R_t$$ during alginate fouling test is higher than that in xanthan fouling test, likely due to different chemical molecule structures between alginate and xanthan as well as their resultant fouling layer structures. On one hand, both alginate and xanthan caused an increase in non-membrane resistances. This could be attributed to formation of macromolecule fouling layers resulted from the interaction between the carboxylic function groups on their molecules and the calcium ions in the feed solution. The fouling layers increased the cake resistance and better hindered the back diffusion of salt from the membrane surface to the bulk feed solution that enhanced concentration polarization near the membrane surface. On the other hand, the non-membrane resistances in the alginate fouling test increased more significantly than that in the xanthan fouling test. This could be ascribed to the compact gel layers formed during the alginate fouling in the presence of calcium ions. Although xanthan was similar with alginate in interaction with calcium ions, and formation of macromolecule fouling layers, xanthan layers were not as compact as alginate gel layers and therefore exhibited lower cake resistance and less significant resultant cake-enhanced concentration polarization.

### 6.5 Effect of applied pressure on hydraulic resistance

Effect of applied hydraulic pressure on non-membrane resistances $R_{cp} + R_c$ during the fouling tests by alginate and xanthan was evaluated. The elevated applied hydraulic pressure could result in higher initial flux, with an initial flux of 12.6 L/(m$^2$·h) under 500 psi hydraulic pressure. However, the elevated hydraulic pressure also promoted the increase in non-membrane resistances $R_{cp} + R_c$ in both alginate and xanthan fouling tests (Fig.6.5). The values after 18 h fouling tests were 30% and 21% under 400 psi hydraulic pressure for alginate fouling and xanthan fouling, respectively; and under 500 psi hydraulic pressure, the non-membrane resistances after 18 h fouling test increased to 48% and 35% for alginate fouling and xanthan fouling, respectively. Higher applied pressure
generates higher initial flux, leading to faster accumulation of foulants including both salts and polysaccharides onto the membrane surface. The accumulated polysaccharides formed more compact fouling layer under higher hydraulic pressure and caused an increase in resistance due to cake formation as well as the resultant cake-enhanced concentration polarization. This is in good agreement with the finding in previous study that cake-enhanced osmotic pressure (CEOP) was significantly promoted by the flux [76].

**Fig. 6.5 Effect of applied hydraulic pressure on non-membrane hydraulic resistances.** Two hydraulic pressures 400 psi (2757.9 kPa) and 500 psi (3447.4 kPa) were applied to generate an initial flux of 9.5 L/(m²·h) and 12.6 L/(m²·h), respectively. The feed solution contained 1 mM Ca²⁺ ions and 0.2 g/L polysaccharide (alginate or xanthan) and its ionic strength was adjusted to be 50 mM by adding NaCl, or both. The cross-flow velocity and the temperature of polysaccharide solution were adjusted to be 8.5 cm/s and 25 ± 1 ℃.

### 6.6 Effect of calcium ions on hydraulic resistance

Non-membrane hydraulic resistances during the fouling tests by alginate and xanthan in the absence and presence of calcium ions increased over time (Fig.6.6). Addition of calcium ions led to a significant increase in R<sub>cp</sub>+R<sub>c</sub> in both alginate and xanthan fouling tests. In the absence of calcium ions, the non-membrane resistances after 18 h fouling test was 22% and 20% for alginate
and xanthan fouling, respectively; while these values correspondingly increased to 48% and 35%, respectively, in the presence of calcium ions. Effect of calcium ions on membrane fouling has been widely studied [7, 56, 98]. Calcium ions could interact with negatively charged functional groups on the polysaccharide molecules and the membrane, and neutralize them and cause more accumulation of polysaccharide onto membrane surface. Moreover, calcium ions could serve as the linkage between adjacent polysaccharide molecules leading to complexation and formation of calcium-polysaccharide macromolecule networks [5, 8, 65, 66, 75]. In particular, calcium ions interacted with alginate and formed calcium-alginate gels [5, 8, 66, 75]. Under the applied pressure, the calcium-alginate gels became compact and dense, and thus increased cake resistance and cake-enhanced concentration polarization. Therefore, the non-membrane resistances were greatly increased.

Fig. 6.6 Effect of calcium ions on non-membrane hydraulic resistances. A hydraulic pressure of 500 psi (3447.4 kPa) was applied to generate an initial flux of 12.6 L/(m²·h). The feed solution contained 0.2 g/L polysaccharide (alginate or xanthan) and its ionic strength was adjusted to be 50 mM by adding NaCl, or both. The cross-flow velocity and the temperature of polysaccharide solution were adjusted to be 8.5 cm/s and 25 ± 1 °C. When studying the effect of calcium ions, 1 mM Ca²⁺ ions were added to the feed solution after the stabilization of membrane.
6.7 Indication

Some important indications were drawn from the experimental work. First of all, the fact that membrane resistance is the major factor governing permeate flux indicates permeate flux could be greatly improved by reducing membrane resistance through membrane fabrication and modification. Secondly, the experimental results have shown that either individual polysaccharide or salt itself did not cause significant resistance to permeate flux. The value of the hydraulic resistance in the presence of both salt and alginate was higher than the sum of their individuals. And the absence of calcium ions caused an increase in the hydraulic resistance. These observations implicate that separation of ions, especially calcium ions, from polysaccharides prior to RO process could reduce membrane fouling and improve permeate flux. Thirdly, reduction in the compactness of fouling layers could be another effective method to reduce the non-membrane resistances during polysaccharide fouling. Finally but not least, while elevated hydraulic pressure generated higher initial flux, it also led to increase in non-membrane resistances during polysaccharide fouling. This indicates the importance of applying optimal hydraulic pressure for the RO separation process.

6.8 Summary

The membrane fouling was elucidated using the hydraulic analysis data. The membrane resistance was the dominant hydraulic resistance to permeate flux, accounting for over 50% within 18 h fouling tests. The value of the hydraulic resistance in the presence of both salt and alginate was much higher than the sum of that of individuals with either salt or polysaccharide in the feed solution. This could be due to the interaction of salt and polysaccharide, that salt formed linkage between adjacent polysaccharide molecules and built up a macromolecular fouling layer, and the fouling layer in return prevented back diffusion of salt from the membrane surface to the bulk feed solution. The non-membrane resistances were enhanced under higher applied pressure and in
the presence of calcium ions. The experimental results have important implication for reducing membrane fouling and improving membrane performance.
CHAPTER 7

Chapter 7. Conclusions and recommendations for future research

7.1 Conclusions

This study compared membrane fouling by commercial and isolated polysaccharides in forward osmosis (FO) and reverse osmosis (RO), and polysaccharide fouling control by using alleviating agents.

For better comparison between the fouling in FO and RO, all the conditions including feed solution chemistry (i.e. polysaccharide concentration, ionic strength and calcium ions) and operating conditions (i.e. initial flux, cross-flow velocity and temperature) were set identical (Chapter 3). In particular, constantly saturated draw solution was used in FO to maintain a constant osmotic pressure enabling direct comparison of fouling. Three types of model polysaccharides, named alginate, xanthan and pullulan, as well as four types of polysaccharides isolated from bacteria, FSW 6, RSW 8, RSW 12 and RSW 14 were used for membrane fouling tests (Chapter 4).

It was found that membrane fouling by both commercial and isolated polysaccharides was more severe in RO than FO, demonstrating that applied pressure had a greater influence on membrane fouling compared to equivalent osmotic pressure. Interestingly, the isolated polysaccharides caused membrane fouling in RO while they improved water flux in FO. The dominating mechanism of polysaccharide fouling in FO was found to be different from that in RO. In RO, molecular structure of polysaccharide played an important role in membrane fouling, indicating foulant – foulant interaction governing polysaccharide fouling in RO; while fouling behavior of polysaccharide in FO is majorly affected by solution viscosity, indicating foulant – membrane interaction governing membrane fouling in FO.
Two kinds of alleviating agents, sodium nitroprusside (SNP) and potassium ferricyanide (KFCN), were tested for alleviation of polysaccharide fouling in FO and RO (Chapter 5). SNP was found to be a better alleviating agent compared to KFCN based on its alleviating efficiency during alginate and xanthan fouling. Alleviation of polysaccharide fouling could be explained by rather the increased electrostatic repulsion between polysaccharides and alleviating agents than reduced solution viscosity. In RO, calcium ions were found to enhance the membrane fouling and reduced the alleviation efficiency; and alleviation of polysaccharide fouling was found to be more effective at higher applied pressure. Alleviation effect of SNP was more significant in FO than that in RO. Over-dosage of alleviating agents could reduce alleviation efficiency or even enhance membrane fouling.

A model of resistance in series was developed to demonstrate the contribution of hydraulic resistance (membrane resistance, resistance due to concentration polarization and resistance due to cake formation) to permeate flux decline in RO (Chapter 6). The membrane resistance was found to be the dominant resistance among the three resistances. The hydraulic resistances was slightly increased by individual of either polysaccharide or salt, but greatly increased by their synergistic effect, especially in the presence of calcium ions.

7.2 Recommendations for future research

Alginate is not a good model polysaccharide, as its fouling behavior was different from that of both the commercial and isolated polysaccharides in both RO and FO membrane fouling. It is recommend that further research should be conducted on exploration of better polysaccharides to affirm a model to represent the natural polymers for polysaccharide fouling.

Alleviation of polysaccharide fouling can be achieved by dosing a proper concentration of SNP. However, it is necessary to test the permeate quality to affirm the residue of SNP to ensure that SNP is used safely. It is also
recommended that more economic alleviating agents should be tested in future research.

The model of resistance in series in RO well demonstrated the membrane fouling by different foulants. Future research on a model of resistance in FO that includes ICP as a hydraulic resistance is recommended to better compare membrane fouling in FO and RO.
References


133. Nagaraja, N., Skillman, L., and Ho, G., Isolation and identification of key bacterial species and extraction of their exopolysaccharides from a full scale desalination plant in Western Australia. 2013.


