Fouling of nanofiltration and reverse osmosis membranes by organic macromolecules and their mixtures

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**FOULING OF NANOFILTRATION AND REVERSE
OSMOSIS MEMBRANES BY ORGANIC
MACROMOLECULES AND THEIR MIXTURES**

WANG YINING

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WANG YINING

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School of Civil and Environmental Engineering

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Abstract

The performance of nanofiltration (NF) and reverse osmosis (RO) membranes can be significantly restricted due to fouling by organic macromolecules during water and wastewater treatment. Fouling causes a reduction of the membrane permeation flux, demands more frequent cleaning, and shortens the membrane life span. Proteins are among the main macromolecules that foul NF and RO membranes. Protein fouling (single, binary mixture and protein-polysaccharide mixture) of NF and RO membranes was systematically investigated in the current work.

In the study of single protein fouling, the effect of hydrodynamic conditions, feed solution chemistry and membrane properties on fouling by bovine serum albumin (BSA) was evaluated under crossflow conditions over a 4-day fouling period. The initial flux behavior was highly dependent on membrane properties, as membranes with a smoother, more hydrophilic and more charged (favorable electrostatic repulsion with BSA) surface experienced a slower fouling rate. Interestingly, the flux at the end of the 4-day tests (J_{96hr}) showed little dependence on membrane properties, with RO, NF and UF membrane fluxes all converging into a nearly identical value. This suggests that the long-term flux was primarily controlled by the foulant-fouled-membrane surface interaction. Membranes tested at different initial fluxes had a strong tendency to approach a surface-interaction-limited value (limiting flux), although a slightly lower J_{96hr} was observed at higher applied pressures, likely due to foulant layer compaction. BSA fouling was more severe at pH values close to its isoelectric point (IEP), at high ionic strength and in the presence of Ca^{2+} and Mg^{2+} as a result of reduced electrostatic repulsion or the promotion of specific ion interactions under these conditions. A linear correlation was observed between J_{96hr} and the square of the zeta potential of BSA (ζ^2), suggesting that ζ^2 can be potentially a good indicator for predicting the long term fouling behavior.

In the binary protein mixture fouling study, fouling by the BSA and lysozyme (LYS) mixture was compared to their individual fouling. When the solution pH was within the IEPs of the two proteins (i.e., pH 4.7 - 10.4), the mixed protein system had a severely destabilized flux compared to the respective single protein systems, which may be attributed to the electrostatic attraction between the negatively charged BSA and positively charged LYS molecules. Unlike a typical single protein system, membrane fouling by the BSA-LYS mixture was only weakly dependent on solution pH within this pH range. Increased ionic strength was found to enhance the flux stability as a result of the suppressed BSA-LYS electrostatic attraction. Once again, membrane fouling was likely controlled by foulant-fouled-membrane interaction under severe fouling conditions (elevated flux level and unfavorable solution chemistry). Compared to non-porous NF and RO membranes, the porous UF membrane was more susceptible to dramatic flux decline due to the increased risk of membrane pore plugging. This study reveals that membrane fouling by mixed macromolecules may behave very differently when compared to the typical single foulant system, especially when the inter-foulant-species interaction dominates over the intra-species-interaction in the mixed foulant system.

Study of NF fouling by oppositely charged LYS (positively charged) and alginate (negatively charged) was aimed to gain a more mechanistic understanding of foulant mass deposition. Besides the effect of pH and Ca^{2+} concentration, the feed composition (i.e., ratio of the two foulants) was also investigated. Similar to the fouling by the binary protein mixture, the overall flux performance showed extremely severe flux reduction for LYS-alginate mixture, due likely to the strong electrostatic attraction between the two oppositely charged macromolecules. However, the flux decline rate and extent were not significantly influenced by the relative concentration of the foulants (30 - 70%) in the feed and solution pH, and even the presence of calcium only marginally affected the flux decline trend. The LYS/alginate ratio in the deposited cake layer was nearly a constant for the feed waters containing 30-70% LYS, suggesting the dominance of the strong electrostatic attraction. A lower pH led to reduced LYS and increased alginate deposition, likely caused by increased LYS charge (zeta potential). Increasing the

Ca^{2+} concentration from 0 to 1 mM resulted in even less LYS and much more alginate deposition, presumably due to the preferential specific Ca^{2+} -alginate complexation, which renders less LYS-alginate interaction. Higher initial flux led to more mass deposition of each foulant and denser packing of the cake layer.

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Table of Contents

ABSTRACT I

ACKNOWLEDGEMENTSIV

TABLE OF CONTENTS VI

LIST OF PUBLICATIONS X

LIST OF TABLESXI

LIST OF FIGURES XII

LIST OF SYMBOLS XVII

LIST OF ABBREVIATIONSXIX

CHAPTER 1 INTRODUCTION 1

1.1	PROBLEM STATEMENT	1
1.2	OBJECTIVES	2
1.3	SCOPE AND OUTLINE	3

CHAPTER 2 LITERATURE REVIEW 5

2.1	PRESSURE DRIVEN MEMBRANE SEPARATION	5
2.2	MEMBRANE MATERIALS AND STRUCTURE.....	6
2.2.1	<i>Formation methods of composite membranes.....</i>	<i>7</i>
2.2.2	<i>Composite membrane materials and properties</i>	<i>7</i>
2.3	MEMBRANE FOULING	9
2.3.1	<i>Types of fouling.....</i>	<i>10</i>
2.3.2	<i>Organic foulants in water and wastewater treatment.....</i>	<i>11</i>
2.3.3	<i>Typical organic foulants and important properties</i>	<i>12</i>
2.4	INFLUENCING FACTORS FOR MEMBRANE FOULING	15
2.4.1	<i>Hydrodynamic conditions</i>	<i>17</i>
2.4.2	<i>Feed solution composition and chemistry.....</i>	<i>18</i>
2.4.2.1	Effect of feed solution chemistry	18
2.4.2.2	Effect of feed composition	20
2.4.3	<i>Membrane properties</i>	<i>21</i>

2.4.4	<i>Effect of cake layer formation</i>	22
2.4.4.1	Cake layer resistance	22
2.4.4.2	Cake enhanced concentration polarization	23
2.4.4.3	Effects of cake layer on retention of ions and foulants	24
2.4.5	<i>Other factors affecting protein fouling</i>	25
2.5	CONCEPTS OF CRITICAL FLUX AND LIMITING FLUX	27
2.6	MEMBRANE CHARACTERIZATION	29
2.6.1	<i>Streaming potential measurement</i>	30
2.6.2	<i>Contact angle</i>	31
2.6.3	<i>Microscopy</i>	31
2.6.4	<i>Chemical structure</i>	31
CHAPTER 3 METHODOLOGY		33
3.1	CHEMICALS AND MATERIALS	33
3.1.1	<i>General chemicals</i>	33
3.1.2	<i>Model foulants</i>	33
3.1.3	<i>Four membranes for filtration tests</i>	34
3.2	EXPERIMENTAL DESIGN	35
3.2.1	<i>Setup, filtration test conditions and protocol</i>	35
3.2.2	<i>Characterization methods</i>	37
3.2.2.1	Zeta potential measurement of macromolecules	37
3.2.2.2	Conductivity rejection	38
3.2.2.3	Foulant mass deposition analysis.....	38
3.2.2.4	Contact angle measurement	39
3.2.2.5	Ion concentration measurement	39
CHAPTER 4 PROTEIN FOULING OF NANOFILTRATION, REVERSE OSMOSIS AND ULTRAFILTRATION MEMBRANES: THE ROLE OF HYDRODYNAMIC CONDITIONS, SOLUTION CHEMISTRY AND MEMBRANE PROPERTIES.....		40
4.1	INTRODUCTION.....	40
4.2	MATERIALS AND METHODS.....	41
4.2.1	<i>Chemicals</i>	41
4.2.2	<i>Membranes</i>	42
4.2.3	<i>Membrane fouling experiment</i>	43
4.2.4	<i>Zeta potential measurement of BSA</i>	43
4.3	RESULTS AND DISCUSSION	44

4.3.1	<i>Effect of hydrodynamic conditions</i>	44
4.3.2	<i>Effect of membrane properties</i>	51
4.3.3	<i>Effect of solution chemistry</i>	54
4.4	CONCLUSIONS	59
CHAPTER 5 FOULING OF NANOFILTRATION, REVERSE OSMOSIS AND ULTRAFILTRATION MEMBRANES BY PROTEIN MIXTURES: THE ROLE OF INTER-FOULANT-SPECIES INTERACTION		60
5.1	INTRODUCTION.....	60
5.2	MATERIALS AND METHODS.....	61
5.2.1	<i>Chemicals and materials</i>	61
5.2.2	<i>Contact angle measurement</i>	63
5.3	RESULTS AND DISCUSSION	64
5.3.1	<i>Zeta potential of BSA and LYS</i>	64
5.3.2	<i>Mixed protein fouling versus single protein fouling</i>	64
5.3.3	<i>Effect of solution chemistry on mixed protein fouling</i>	66
5.3.4	<i>Effect of membrane properties on mixed protein fouling</i>	71
5.3.5	<i>Effect of initial flux on mixed protein fouling</i>	78
5.4	CONCLUSIONS	80
CHAPTER 6 NANOFILTRATION MEMBRANE FOULING BY OPPOSITELY CHARGED MACROMOLECULES - AN INVESTIGATION ON FLUX BEHAVIOR, FOULANT MASS DEPOSITION, AND SOLUTE REJECTION.....		82
6.1	INTRODUCTION.....	82
6.2	MATERIALS AND METHODS.....	83
6.2.1	<i>Design considerations</i>	83
6.2.2	<i>Chemicals</i>	84
6.2.3	<i>Nanofiltration membrane</i>	84
6.2.4	<i>Filtration setup and experiment</i>	85
6.2.5	<i>Foulant mass deposition analysis</i>	85
6.2.6	<i>Zeta potential measurement of macromolecules</i>	86
6.3	RESULTS AND DISCUSSION	86
6.3.1	<i>Overview of the results</i>	86
6.3.2	<i>Zeta potential of foulants</i>	87
6.3.3	<i>Effect of relative concentration of foulants</i>	87
6.3.3.1	<i>Flux behavior</i>	87

6.3.3.2	Foulant mass deposition.....	88
6.3.4	<i>Effect of solution chemistry</i>	91
6.3.5	<i>Effect of initial flux</i>	94
6.3.6	<i>Salt rejection during fouling</i>	100
6.4	CONCLUSIONS	103
CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS		104
APPENDIX		107
REFERENCES		119

List of Publications

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Yi-Ning Wang, and Chuyang Y. Tang (2011). "Fouling of nanofiltration, reverse osmosis and ultrafiltration membranes by protein mixtures: The role of inter-foulant-species interaction." Environmental Science & Technology **45**(15): 6373 – 6379.

Yi-Ning Wang, and Chuyang Y. Tang (2011). "Nanofiltration membrane fouling by oppositely charged macromolecules – An investigation on flux behavior, foulant mass deposition and solute rejection." Environmental Science & Technology (accepted).

List of Tables

Table 2-1. Classification of pressure driven membranes (Mulder 1996; Fane et al. 2011)	5
Table 2-2. Membrane synthesis methods (Petersen 1993)	7
Table 2-3. Typical protein, polysaccharide and humic acid (Ang and Elimelech 2007; van de Ven et al. 2008; Tang et al. 2010).....	13
Table 2-4: A summary of membrane fouling tests	16
Table 2-5. Membrane characterization methods.....	29
Table 2-6. Fouling characterization methods	30
Table 3-1. Properties of foulants.....	34
Table 3-2. Membrane properties.....	35
Table A. Foulant mass deposition and specific cake layer resistance.....	118

List of Figures

Figure 2-1. Typical chemistry for interfacially formed TFC RO and NF membranes. (a) fully aromatic polyamide based on trimesoyl chloride and 1,3-benzenediamine; (b) semi-aromatic polyamide based on trimesoyl chloride and piperazine (Tang 2007).	9
Figure 2-2. A simple illustration of fouling mechanisms (adapted from Schäfer, Fane et al. 2005).	9
Figure 2-3. A simple sketch of various types of foulants (She 2009)	11
Figure 2-4. Illustration of potential energy for particle-particle (or particle-surface) interaction based on the DLVO theory. (a) interaction energy as a function of separation distance; (b) effect of ionic strength on energy barrier. (Adapted from Tang et al. 2010)	15
Figure 2-5. Conceptual illustration of concentration polarization (CP) of solutes in an RO membrane system. (a) virgin membrane; (b) after cake formation (Chong 2008).	24
Figure 2-6. Various stages of flux decline in MF/UF process (adapted from Marshall et al. 1993).	25
Figure 2-7. Conceptual model for foulant-foulant interaction (adapted from Palecek and Zydney 1994b)	28
Figure 3-1. Schematic description of membrane testing setup (adapted from Tang 2007).	36
Figure 3-2. Schematic diagram of fouling test protocol	37
Figure 4-1. The effect of initial flux and applied pressure on flux performance during BSA fouling. (a) flux vs. time at pH 5.8; (b) flux vs. time at pH 7; (c) flux at 96 hrs vs. initial flux at pH 5.8 and pH 7. Other test conditions: membrane NF270, feed water containing 20 mg/L BSA and 10 mM NaCl, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$.	45
Figure 4-2. Conceptual model. (a) drag force and barrier force exerted on a foulant macromolecule when it approaches a membrane surface; (b) final flux vs. initial flux.	48
Figure 4-3. Compaction of BSA foulant layer. The membranes used (NF270) here had already been fouled for 4 days under the following conditions: 20 mg/L BSA, 10 mM NaCl, pH 5.8, and temperature at $20 \pm 1^\circ\text{C}$. In the subsequent compaction period (96 th – 138 th hour), the background electrolyte (10 mM NaCl and pH 5.8, no BSA) was used.	49

Figure 4-4. The effect of crossflow velocity on flux performance during BSA fouling. Other test conditions: membrane NF270, feed water containing 20 mg/L BSA and 10 mM NaCl at pH 5.8, and temperature at $20 \pm 1^\circ\text{C}$. The normalized flux was determined as the ratio of flux at time t over the initial flux (the flux at $t = 0$).	51
Figure 4-5. The effect of membrane properties on flux performance during BSA fouling. Other test conditions: feed water containing 20 mg/L BSA and 10 mM NaCl at pH 5.8, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. The normalized flux was determined as the ratio of flux at time t over the initial flux (the flux at $t = 0$).	53
Figure 4-6. The effect of feed water chemistry on flux performance during BSA fouling. (a) the effect of pH; (b) the effect of ionic strength; and (c) the effect of divalent cations. Unless otherwise specified, the solution pH was 7 and ionic strength (IS) was 10 mM. Other test conditions: membrane NF270, feed water containing 20 mg/L BSA, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. The normalized flux was determined as the ratio of flux at time t over the initial flux (the flux at $t = 0$).	56
Figure 4-7. The effect of foulant-foulant electrostatic interaction on BSA fouling. (a) flux at 96 hrs and zeta potential squared as a function of pH for a feed water containing 20 mg/L BSA and 10 mM NaCl; (b) flux at 96 hrs vs. zeta potential squared for various feed water chemistry. Other test conditions: membrane NF270, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$	58
Figure 5-1. Zeta potential of BSA and LYS in 10 mM NaCl as a function of pH. At least 2 replicate measurements were performed for each condition.	62
Figure 5-2. Comparison of flux behavior of mixed protein fouling with single protein fouling. (a) initial permeate flux at $75 \text{ L/m}^2\cdot\text{h}$; (b) initial permeate flux at $120 \text{ L/m}^2\cdot\text{h}$. Other test conditions: membrane NF270, total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS for the mixed protein case), pH 7, ionic strength of 10 mM (adjusted by the addition of NaCl), crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$	65
Figure 5-3. Effect of ionic strength on flux performance during mixed protein fouling. Other test conditions: membrane NF270, total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS), pH 7, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$	67
Figure 5-4. Effect of solution pH on flux performance during mixed protein fouling. (a) flux as a function of time at various solution pHs; (b) final flux at 96 hours as a function of pH for both fixed protein and single protein fouling; (c) a simple conceptual model for mixed protein fouling. Other test conditions: membrane NF270, total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS for the mixed protein case), ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and	

temperature at $20 \pm 1^\circ\text{C}$. Error bars in (b) were based on analysis of 2-3 replicates under the identical fouling conditions.	70
Figure 5-5. Effect of solution pH on flux performance during single protein fouling. The feed solution contained either 20 mg/L BSA or LYS. Other test conditions: membrane NF270, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$	71
Figure 5-6. Effect of membrane properties on flux performance during mixed protein fouling at (a) pH 7.0, (b) pH 4.7, and (c) pH 3.5. Other test conditions: total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS), ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$	74
Figure 5-7. Contact angles of virgin and 96-hr fouled membranes. Fouling conditions: total foulant concentration of 20 mg/L (10 mg/L BSA + 10 mg/L LYS), pH 7, ionic strength of 10 mM (NaCl), crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Each reported contact angle is the average of at least 5 measurements for the same membrane sample at different locations, with the error indicating one standard deviation.	75
Figure 5-8. Effect of membrane properties on flux performance during single protein fouling. The feed solution contained either 20 mg/L BSA or LYS. Other test conditions: pH 4.7, ionic strength of 10 mM (adjusted by the addition of NaCl), crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$	76
Figure 5-9. Comparison of flux behavior of mixed protein fouling with single protein fouling for the UF membrane GM. Other test conditions: total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS for the mixed protein case), initial permeate flux at $75 \text{ L/m}^2\cdot\text{h}$, pH 7, ionic strength of 10 mM (adjusted by the addition of NaCl), crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$	77
Figure 5-10. Effect of initial flux on the flux performance during mixed protein fouling. (a) pH 7, ionic strength of 10 mM; (b) pH 7, ionic strength of 100 mM. Other test conditions: membrane NF270, total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS), crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$	79
Figure 6-1. Zeta potential of Alginate and LYS in 10 mM NaCl as a function of pH. At least 2 replicate measurements were performed for each condition.	87
Figure 6-2. Flux behavior and mass accumulation to show the effect of relative concentration of LYS (or relative concentration of alginate) in feed solution on fouling. (a) flux performance; (b) foulant mass accumulation after 96-hr fouling. Other test conditions: total foulant concentration of 20 mg/L, initial flux of $75 \text{ L/m}^2\cdot\text{h}$, pH 7, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$	90

Figure 6-3. Flux behavior and mass accumulation comparison to show the effect of solution chemistry on fouling. (a) flux performance; (b) mass accumulation after 96-hr fouling. Other test conditions: initial flux of 75 L/m ² ·h, total foulant concentration of 20 mg/L (50% LYS), total ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1°C.	92
Figure 6-4. Effect of ionic composition on flux behavior during LYS fouling. Test conditions: membrane NF270, LYS of 20 mg/L, pH 7, initial flux of 120 L/m ² ·h, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1 °C.	94
Figure 6-5. Flux behavior and mass accumulation to show the effect of initial flux on fouling. (a) flux performance at Ca ²⁺ = 1 mM; (b) mass accumulation after 96-hr fouling (Ca ²⁺ = 1 mM); (c) flux performance (Ca ²⁺ = 0 mM); (d) mass accumulation after 96-hr fouling (Ca ²⁺ = 0 mM). Other test conditions: total foulant concentration of 20 mg/L (50% LYS), pH 7, calcium ion of 1 mM, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1°C.	98
Figure 6-6. %LYS accumulation on fouled membrane as a function of %LYS in initial feed solution. Other test conditions: a total foulant concentration of 20 mg/L, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1°C.	99
Figure 6-7. Foulant hydraulic resistance and specific cake layer resistance as a function of total mass deposition. Test conditions: total foulant concentration of 20 mg/L (10 mg/L LYS + 10 mg/L alginate), calcium ion of 1 mM, total ionic strength of 10 mM (by addition of NaCl), crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1°C.	100
Figure 6-8. Salt rejection as a function of time during fouling. (a) effect of relative concentration of foulant in feed; (b) effect of solution chemistry (i.e, pH and Ca ²⁺ concentration). Other test conditions: pH 7, total ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1°C.	102
Figure A. 1. Mass deposition and cake resistance after 96-hr BSA fouling. (a) BSA mass deposition and hydraulic cake resistance as a function of the square of protein zeta potential (over pH 4.7 ~ 7.8); (b) specific cake layer resistance as a function of the square of protein zeta potential (over pH 4.7~7.8). Other conditions: membrane NF270, BSA concentration of 20 mg/L, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1 °C. Error bar: 2-4 replicates were analyzed for each membrane sample.	108
Figure A. 2. Foulant mass deposition after 96-hr fouling for feed containing single protein or protein mixture. (a) effect of initial flux (pH 7); (b) effect of solution pH (initial flux of 120 L/m ² ·h). Other conditions: membrane NF270, total foulant concentration of 20 mg/L (for mixture system, BSA:LYS=1:1), ionic strength of 10	

mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1 °C. Error bar: 2-4 replicates were analyzed for each membrane sample.	110
Figure A. 3. Mass deposition and specific cake resistance of the 96-hr protein fouled membranes, showing the comparison of different feeds (BSA, LYS or BSA+LYS). Fouling conditions: membrane NF270, total protein concentration of 20 mg/L (for mixture system, BSA:LYS=1:1), pH 7, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1 °C. Error bar: 2-4 replicates were analyzed for each membrane sample.	111
Figure B. 1. Typical calibration curves for concentration of macromolecules. (a) BSA and LYS concentration analyzed with protein assay kit (QuantiPro™ BCA Assay Kit) at 562 nm; (b) alginate concentration analyzed with phenol-sulfuric acid method at 485 nm.	113
Figure C. 1. Manually measured flux vs. digital flow meter reading for a digital flow meter during a fouling run.	114
Figure D. 1. Permeability of membrane NF270 as a function of pH. Test conditions: flux of 120 L/m ² ·h, ionic strength of 10 mM (NaCl), crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1 °C. Error bars were based on analysis of 3 membrane samples.....	115
Figure D. 2. Ion and conductivity rejection of membrane NF270 over a range of pHs. Test conditions: flux of 120 L/m ² ·h, ionic strength of 10 mM, and temperature at 20 ± 1 °C. Error bars were based on analysis of 3 membrane samples	116
Figure D. 3. Zeta potential (as a function of pH) of virgin RO and NF membranes used in current study. pH was adjusted by NaOH and HCl, ionic strength of 10 mM (by addition of NaCl), and temperature at ~23 °C.	117

List of Symbols

<i>Symbol</i>	<i>Description</i>
a	Proportionality constant for describing the relationship between J_s and ζ^2
A	Cross-sectional area of the channel (streaming potential measurement)
C_b	Concentration at bulk
c_{drag}	Hydraulic drag coefficient
C_p	Concentration of permeate
C_w	Concentration at membrane wall
E_s	Streaming potential
$F_{barrier}$	Barrier force resisting foulant from deposition
F_{EDL}^{f-f}	Foulant-foulant interaction arising from electrical double-layer interaction
$F_{non-EDL}^{f-f}$	Foulant-foulant interaction not arising from electrical double-layer interaction
F_{drag}	Hydrodynamic drag force
J	Membrane permeate flux
J_0	Initial flux of clean membrane at time 0
J_L	Limiting flux
J_s	Pseudo-stable flux
J_t	Membrane flux at time t
k_{ow}	Octanol-water partition coefficient
L	Length of the channel (streaming potential measurement)
m_{LYS}/m_{alg}	Deposited mass ratio (LYS: alginate)
m_f	Foulant mass deposition per unit membrane area
ΔP	Hydraulic pressure difference
R	Total hydraulic resistance
r_f	Specific cake layer resistance
R_f	Hydraulic resistance of foulant layer
R_h	Characteristic hydrodynamic radius of the foulants
R_m	Intrinsic hydraulic resistance of membrane

<i>Symbol</i>	<i>Description</i>
<i>Greek letters</i>	
$\Delta\pi$	Osmotic pressure difference
η	Dynamic viscosity
ζ	Zeta potential
ε	Liquid permittivity
ε_0	Permittivity in vacuum
θ	Contact angle
γ_{LV}	Interfacial tension of liquid-vapor interface
γ_{SL}	Interfacial tension of solid-liquid interface
γ_{SV}	Interfacial tension of solid-vapor interface

List of Abbreviations

<i>Abbreviation</i>	<i>Description</i>
AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflection fourier transform infrared spectroscopy
BSA	Bovine serum albumin
CA	Cellulose acetate
CEOP	Cake enhanced osmotic pressure
CFV	Crossflow velocity
CP	Concentration polarization
DLVO	Derjaguin, Landau, Verwey, Overbeck
DOTM	Direct observation through the membrane
EDC	Endocrine disrupting compounds
EDL	Electrical double-layer
EDX	Energy dispersive spectroscopy
EfOM	Effluent organic matter
IEP	Isoelectric point
IP	Interfacial polymerization
LYS	Lysozyme
MBR	Membrane bioreactor
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NOM	Natural organic matter
PA	Polyamide
PhAC	Pharmaceutically active compound
RBS	Rutherford back-scattering
RO	Reverse osmosis
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy

<i>Abbreviation</i>	<i>Description</i>
TFC	Thin film composite
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultrafiltration
UTDR	Ultrasonic time-domain reflectometry
UV	Ultraviolet
VDW	Van der Waals
XPS	X-ray photoelectron spectroscopy

Chapter 1 Introduction

1.1 Problem statement

Membrane separation is achieved by simultaneously allowing the transport of desired product (gaseous or liquid) across the membrane material and retaining the other species. The permeation or rejection of a certain component in the feed might be based on its size, charge, solubility and the presence or absence of other components. Clean water scarcity worldwide has stimulated strong interest in applying reverse osmosis (RO) and nanofiltration (NF) technology in wastewater reclamation and surface water treatment (Fane et al. 2011). Membrane technology has many advantages over conventional treatment technologies, as it requires smaller footprints, allows module design, and provides consistent and high quality product water (Riley 1990).

However, the efficiency of a membrane process is significantly hampered by membrane fouling (Goosen et al. 2004), which leads to more energy consumption, lower productivity, worse product quality and more frequent chemical cleaning. During RO and NF membrane filtration, membrane permeability decreases due to the accumulation of organic molecules, sparingly soluble inorganic compounds, colloidal matter and microorganisms on membrane surfaces. In many cases, organic macromolecules may play a dominant role in fouling (Barker et al. 2000; Jarusutthirak and Amy 2006; Her et al. 2007; Ang 2008; Tang et al. 2010). Proteins, polysaccharides and humic acids have been identified as the main foulants in various RO plants (Her et al. 2007; Karime et al. 2008; Xu et al. 2010).

Fouling by macromolecules could be affected by a great number of factors; in general, they can be grouped into solution chemistry (Palecek and Zydney 1994a; Hong and Elimelech 1997a; Ang and Elimelech 2007; Tang et al. 2010), hydrodynamic conditions (Braghetta et al. 1998; She et al. 2009) and membrane properties (Zhu and Elimelech 1997; Vrijenhoek et al. 2001; Goosen et al. 2004; Li et al. 2007). The results of prior studies show that fouling by macromolecules is more severe at pH values close to the isoelectric-points (IEPs) of the molecules,

high ionic strength, high divalent cation concentration (such as Ca^{2+} and Mg^{2+}), high permeate flux (or trans-membrane pressure), and low crossflow velocity.

Most of the past protein fouling studies used porous microfiltration (MF) and ultrafiltration (UF) membranes due to their wide application in pretreatment, membrane bioreactors (MBRs), some industrial separations, etc. For the limited number of existing studies on RO fouling by proteins, relatively high protein concentration and short experimental duration (~ 1 day) were used.

In addition, the majority of lab-scale fouling studies used a single foulant feed that may present an over-simplified system of real feed waters. In recent years, there has been increased emphasis on membrane fouling by mixtures of well-defined foulants (Ang and Elimelech 2007; Li et al. 2007; Zazouli et al. 2010) in attempts to elucidate the fundamental fouling mechanisms in more complicated (and realistic) systems. However, the effects of solution chemistry and hydrodynamic conditions on the mixture fouling have not yet been systematically investigated.

1.2 Objectives

The overall objective of this study was to systematically investigate long-term NF fouling by organic macromolecules on a lab-scale setup under crossflow and constant pressure conditions. Bovine serum albumin (BSA) and lysozyme (LYS) were used as model proteins, and sodium alginate was the model polysaccharide. The effect of hydrodynamic conditions (flux level and crossflow velocity), feed solution chemistry and composition (pH, ionic strength, $\text{Ca}^{2+}/\text{Mg}^{2+}$ concentration, and foulant mixture), and membrane properties on protein fouling were evaluated. The specific objectives were:

- 1) To understand the effect of solution chemistry and hydrodynamic conditions on flux performance of the NF membrane during protein fouling;

- 2) To understand how the membrane properties affect the fouling rate, and to demonstrate the importance of foulant-foulant and foulant-membrane interactions at different stages of membrane fouling;
- 3) To investigate the effect of solution chemistry (pH and ionic strength) on NF fouling by feed containing mixture of oppositely charged proteins (LYS and BSA);
- 4) To explore the effect of solution composition and chemistry on the NF fouling by an oppositely charged protein (LYS) and polysaccharide (alginate).

1.3 Scope and outline

The study focused on the effect of the solution chemistry, solution composition, hydrodynamic conditions and membrane properties on NF/RO membrane fouling by organic macromolecules.

This thesis contains seven chapters and one appendix. **Chapter 1-3** and **Chapter 7** present the introduction, literature review, experimental details and conclusions, respectively. The major results and discussions are presented in Chapters 4-6. Chapter 4 has been accepted for publication in the Journal of Membrane Science, Chapter 5 has been accepted for publication in the Environmental Science & Technology, and Chapter 6 has been submitted for potential publication. The contents of Chapters 4-6 and appendix are summarized below in brief.

Chapter 4 presents the effects of solution chemistry, hydrodynamic conditions, and membrane properties on BSA fouling. Severe flux reduction occurred at high initial flux, low crossflow velocity, pH values away from the IEP of BSA, high ionic strength, and high $\text{Ca}^{2+}/\text{Mg}^{2+}$ concentration. Protein charge played a significant role in fouling. Membrane properties influence the initial fouling rate while the foulant-foulant interaction may dominate at the later stage.

Chapter 5 demonstrates the effect of solution chemistry on the binary protein mixture fouling with an NF membrane and highlights the apparent different trends observed compared to those for single protein fouling. Flux decline has no pH dependency for protein mixture fouling when the pH is within the two IEPs of the proteins. In addition, increasing ionic strength was found to stabilize permeate flux for the protein mixture – a trend directly opposite to that for single protein fouling. Both effects reveal the important role of the inter-protein attractive interaction.

Chapter 6 discusses the NF fouling by two oppositely charged macromolecules (i.e., LYS and alginate). The effect of feed composition (the mass ratio of the two foulants), solution pH and Ca^{2+} concentration are investigated. The composition of the foulant cake layer was analyzed, and its dependence on the feed composition, solution chemistry, and initial permeate flux level was studied.

Appendix presents 1) results for mass deposition analysis, 2) the standard curves for measuring BSA, LYS and alginate concentration (using UV spectrophotometry), 3) an example of digital flow meter calibration to demonstrate the reliability of flux measurement, and 4) the zeta potential, permeability and salt/conductivity rejection properties of the virgin membranes used in the current studies.

Chapter 2

Literature review

2.1 Pressure driven membrane separation

Membrane filtration separation is achieved by a membrane displaying a different permeability to the solvent and solutes (or particles) (Sven 1979). According to their pore size and rejection properties, pressure driven membranes can be classified into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes (Table 2-1).

Table 2-1. Classification of pressure driven membranes (Mulder 1996; Fane et al. 2011).

Membrane	Pore size (apprx.) (nm)	MWCO (Da)	Operating pressure (bars)	Removes
MF microfiltration	50 – 10000	Not applicable	0.1-2	Suspensions and emulsions, bacteria/protozoa
UF ultrafiltration	1 – 100	1000-300 000	1-5	Colloids, bacteria, viruses and macromolecules
NF nanofiltration	~ 2	>100	2-10	Organic compounds with MW> 200-500 depending on pore size, and di-/multivalent ions
RO reverse osmosis	< 2	>10	10-100	Small organics and ions

MF and UF are widely used in removing suspended solids, colloids, bacteria, and viruses during water and wastewater treatment, and they may serve as a pretreatment step for RO and NF processes. Another use of MF and UF is to concentrate or separate valuable solutes such as proteins and dyes in biomedical and industrial applications. The pore size of NF membranes is typically less than 2 nm and RO membranes do not have observable pores. It is common to consider RO and some NF membranes as non-porous membranes (Schäfer et al. 2005). Both RO and NF membranes are capable of selectively rejecting ions and organic matters in feed

water. RO, capable of retaining monovalent ions, is a mainstream technology used for desalinating seawater and brackish water. On the other hand, NF is used in a wide range of drinking water, wastewater, and industrial applications (Childress and Elimelech 2000), mainly for softening (rejecting multivalent ions), and selective removal of certain molecular and ionic species.

RO and NF membrane filtration is typically operated in crossflow mode due to its important advantage in reducing fouling. During a crossflow filtration, the direction of permeate flux is perpendicular to the membrane surface, and the solutes or particles may deposit onto it along with the permeation drag. The feed water flows in a direction parallel to a membrane surface (Riley 1990), and high crossflow velocity (CFV) helps to alleviate fouling by 1) promoting mass transfer and enhancing advective transport thus reducing concentration polarization, and 2) increasing shear rate over the foulant layer. A permeate flux J (volumetric) under a net pressure difference ΔP across the membrane can be expressed as (Yuan and Zydney 2000):

$$J = \frac{\Delta P - \Delta \pi}{\eta R}, \quad (\text{Permeate flux given by Darcy's law}) \quad (2.1)$$

where ΔP and $\Delta \pi$ are the hydraulic pressure difference and the osmotic pressure difference between the feed and permeate sides of the membrane, respectively, η is the dynamic viscosity of the permeate water, and R is the total hydraulic resistance of the membrane (and the fouling layer if any).

2.2 Membrane materials and structure

The successful application of a membrane separation process depends on proper selection of membranes. A good membrane should exhibit high permeate flux and contaminant rejection, good chemical resistant and durability, and low cost. Up to now organic polymers remain the most widely used commercial membrane materials, and almost all the RO and many NF membranes used for water and wastewater treatment are fabricated by polymers in a composite form.

2.2.1 Formation methods of composite membranes

The two commonly used methods for fabricating RO and NF membranes are phase inversion and interfacial polymerization (IP). Phase inversion method refers to a single-step synthesis for casting asymmetric RO or NF membranes. Such membranes have the same chemical composition for both skin and sub layer, and they are typically cast onto a woven or non-woven fabric for mechanical strength. In contrast, a composite membrane has different compositions in skin and sub layer, typically formed by interfacial polymerization (Petersen 1993).

Table 2-2. Membrane synthesis methods (Petersen 1993).

	Typical materials	Advantages	Disadvantages
Interfacial Polymerization (IP)	Polyamide (skin) Polysulfone (substrate)	<ul style="list-style-type: none"> Each individual layer can be optimized for its particular function More choices of chemical compositions 	<ul style="list-style-type: none"> More expensive approach
Phase Inversion	Cellulose Acetate (CA) Linear aromatic polyamides	<ul style="list-style-type: none"> Low cost 	<ul style="list-style-type: none"> Materials are limited to linear and soluble polymers

Although the composite membrane has the disadvantage of being slightly more expensive, the extra cost is counterbalanced by improved performance characteristics of the resulting membrane products. Therefore, IP still dominates in the RO and NF membrane manufacturing, especially for more demanding water treatment applications (Petersen 1993).

2.2.2 Composite membrane materials and properties

Many commercial RO and NF membranes for water and wastewater treatment use are interfacially polymerized (IP) thin film composite (TFC) polyamide (PA)

membranes (Petersen and Cadotte 1990; Petersen 1993). One most commonly used recipe is the IP of aromatic amine monomers (such as 1,3-benzenediamine in aqueous solution) and aromatic acid chloride monomers (such as trimesoyl chloride in an organic solvent). Some other TFC NF membranes are semi-aromatic, formed by aliphatic amine monomers (such as piperazine) and aromatic trimesoyl chloride (Petersen 1993) (Figure 2-1).

A typical TFC PA membrane comprises a top polyamide layer as the selective barrier layer (thickness of 0.1 – 0.3 μm), a porous layer being manufactured by polysulfone (PS) (thickness of about 20 – 100 μm) and a non-woven fabric layer as a support (Petersen 1993; Tang 2007). Among them, the top layer is the most critical one that affects the physicochemical properties of membranes, such as permeability, rejection, surface charge, and roughness/morphology. The effect of the properties on membrane fouling is discussed in section 2.4.3.

(a)

Figure 2-1. Typical chemistry for interfacially formed TFC RO and NF membranes. (a) Fully aromatic polyamide based on trimesoyl chloride and 1,3-benzenediamine; (b) Semi-aromatic polyamide based on trimesoyl chloride and piperazine (Tang 2007).

2.3 Membrane fouling

Membrane fouling and subsequent permeate flux decline is common for pressure-driven membrane processes. Membrane fouling is defined as “the process resulting in loss of performance of a membrane due to deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores” (Koros et al. 1996). Main mechanisms include adsorption of feed components, clogging of pores, chemical interaction between solutes and membrane material, gel formation, and bacterial growth (Goosen et al. 2004). In general, membrane fouling can be classified as pore closure, pore plugging and cake formation (Figure 2-2). Closure or plugging of pores is usually not a problem for non-porous NF and RO membranes.

Figure 2-2. A simple illustration of fouling mechanisms (adapted from Schäfer, Fane et al. 2005).

In addition to membrane fouling, concentration polarization (CP) and membrane compaction under pressure (Ohya 1978; Cohen and Probstein 1986), can also result in flux reduction. CP is the development of a concentration gradient of the retained components near the membrane surface (Gekas 1988). The increased solute concentration at the membrane surface due to CP can lead to reduced membrane flux as a result of higher osmotic pressure as well as reduced solute rejection. Different from fouling, CP disappears once the applied pressure is removed.

2.3.1 Types of fouling

RO and NF membrane fouling is strongly dependent on feedwater characteristics. According to different types of foulants, membrane fouling can be classified into four basic categories as below (Goosen et al. 2004) (Figure 2-3):

1) Scaling by sparingly soluble inorganic compounds

Membrane scaling occurs when the solubility of sparingly soluble inorganic compounds is exceeded. It often happens to RO and NF membranes as salt rejection may lead to severe concentration polarization adjacent to membrane surfaces. Scaling can be controlled by adding antiscalant and lowering flux which in turn reduces concentration polarization (Bartels et al. 2005b).

2) Fouling by colloids and suspended solids

Inorganic colloids and particulate matter in feed water, if not effectively removed during pretreatment, can lead to severe membrane flux drop due to the formation of a cake layer (Cohen and Probstein 1986).

3) Organic fouling by organic matter

High molecular weight organic matter (organic macromolecules) widely exist in natural water and wastewater (secondary effluent), namely natural organic matter (NOM) and effluent organic matter (EfOM), respectively. They can cause severe fouling of NF and RO membranes. Examples of organic fouling include fouling by humic acid (Hong and Elimelech 1997a; Jones and O'Melia 2000; Seidel and Elimelech 2002; Tang et al. 2007c), proteins (Ang and

Elimelech 2007; Li et al. 2007; Mo et al. 2008), polysaccharides (Mänttari et al. 2000; Li et al. 2007), and fatty acids (Ang and Elimelech 2008). Low molecular weight organic matter like surfactants may also cause significant flux reduction (Akay and Wakeman 1993; Tang et al. 2006; Boussu et al. 2007).

4) Biofouling by microorganisms

The formation of a biofilm on a membrane can cause severe flux decline (Goosen et al. 2004; Bartels et al. 2005b). Biofilms may be difficult to remove even with the help of chemical cleaning or disinfection. Furthermore, some disinfectants such as chlorine may alter membrane chemistry and properties (Kwon et al. 2006).

Figure 2-3. A simple sketch of various types of foulants (She 2009).

2.3.2 Organic foulants in water and wastewater treatment

Tang (2007) summarized the data for important parameters of secondary effluents from a number of wastewater reclamation plants. The total organic carbon (TOC) content in raw secondary effluent is around 5 - 20 mg/L; TOC is usually below 5 mg/L after conventional pretreatment such as coagulation and activated carbon adsorption, and it is slightly lower after MF and UF pretreatment. Some earlier classification of organic matter in wastewater effluent reported that carbohydrates, proteins, and humic substances accounted for about 12%, 22%, and 40–50%, respectively, of the soluble organics in secondary wastewater effluents (Rebhun and Manka 1971). Proteins, polysaccharides and aminosugars in secondary effluent were found to play an important role in fouling NF and UF membranes (Jarusutthirak et al. 2002). Several studies (Doumèche et al. 2007; Her et al. 2007; Tran et al. 2007; Karime et al. 2008; Xu et al. 2010) have identified proteins,

polysaccharides and humic substances as important foulants in RO desalination and NF/RO water treatment/reclamation plants.

2.3.3 Typical organic foulants and important properties

The properties of macromolecular foulants (proteins, polysaccharides and humic acids) have been well summarized by Tang and coworkers (Tang et al. 2010).

Proteins are generally globular macromolecules. They have well defined molecular weight and IEP. At a pH below their IEP, proteins carry a net positive charge and above their IEP they carry a net negative charge. Such amphoteric charge behavior is due to the presence of both carboxylic ($-\text{COO}^-$) and amine ($-\text{NH}_3^+$) groups. Bovine serum albumin (BSA), a widely used model protein foulant, has an IEP of pH 4.7 and it is negatively charged above pH 4.7. Polysaccharides have wide range of molecular weight and variable charge properties (some are charged and some are neutral). Alginate is a very commonly used model polysaccharide for membrane fouling studies. It is negatively charged over a wide range of pH due to the carboxylic groups. Humic acid has a highly polydispersed size range, and is highly negatively charged over a broad pH range due to deprotonation of both carboxylic and phenolic functional groups. Its carboxylic acidity is generally higher than that of BSA and alginate. The properties of BSA (a model protein), alginate (a model polysaccharide) and humic acid are listed in Table 2-3.

Table 2-3. Typical protein, polysaccharide and humic acid (Ang and Elimelech 2007; van de Ven et al. 2008; Tang et al. 2010).

Properties	BSA (protein)	Alginate (polysaccharide)	Humic acid
Size and morphology (nm)	Ellipsoidal, 9.5 x 5 x 5 nm	Extended random coil, 10-100 nm	Vary
Molecular weight	66-67kDa	12-80kDa	A few to a few hundred kDa
Main functional groups	-COOH -NH ₂	-COOH aromatic-OH	-COOH aromatic-OH
Carboxylic acidity (meq/g)	1-1.5	3-3.5	5-10
Isoelectric point (IEP)	pH 4.7	< pH 2	Very low
Hydrophobicity	Hydrophobic	Hydrophilic	Hydrophobic

Since macromolecules are colloids in nature, they also share the properties of common colloids. In general, interactions between colloids involve essentially two types of forces [DLVO (Derjaguin, Landau, Verwey, Overbeek) theory]: electrical double-layer (EDL) interaction and van der Waals (VDW) interaction (Derjaguin and Landau 1941; Verwey and Overbeek 1948; Bhattacharjee and Elimelech 1997; Tang et al. 2010). These interactions depend on the distance between the two surfaces and surface properties. VDW interaction predominates at small and large interparticle distances, whereas EDL repulsion may dominate at intermediate distances (Smith and Simons 2005). The summation of the two components can therefore result in an energy barrier which prevents particles from aggregation (Figure 2-4(a)). Any action of decreasing the energy barrier, such as the presence of electrolytes in solution, reduces this barrier and leads to reduced colloidal stability (Figure 2-4(b)). Based on the classical colloidal stability theories, the rate of colloidal aggregation depends on both the particle collision frequency and the attachment coefficient (the ratio of successful attachment over the total number of collision events) (Filella 2007). Tang et al. (Tang et al. 2007c; She et al. 2009; Tang et al. 2010) suggested that this concept could also be applied to model membrane fouling (Section 2.4.1). The intrinsic properties of particles/colloids and solution

chemistries are important to colloidal stability. A stable solution or suspension usually causes less membrane fouling.

Another attractive force, hydrophobic interaction, may also affect the stability of colloids. Hydrophobic interaction originates from the disruption of highly dynamic hydrogen bonds between molecules of liquid water and the non-polar solute (increase in entropy /freedom or randomness) that accompanies the release of water into the bulk solvent on interaction of two surfaces (Salgin et al. 2005). It can be qualitatively understood as an interaction that causes hydrophobic moieties to aggregate or cluster (Meyer et al. 2006). For example, hydrophobic particles and solutes in feed water prefer to attach to a hydrophobic membrane surface to reduce their exposed surfaces, accompanied by the reduction of surrounded water molecules. Hydrophobic interaction can dominate over van der Waals (VDW) attraction, especially for non-polar molecules with a high octanol-water partition coefficient (k_{ow}) (Meyer et al. 2006).

(a)

Figure 2-4. Illustration of potential energy for particle-particle (or particle-surface) interaction based on the DLVO theory. (a) interaction energy as a function of separation distance; (b) effect of ionic strength on energy barrier. (Adapted from Tang et al. 2010)

2.4 Influencing factors for membrane fouling

The factors affecting membrane fouling can be summarized into three major groups: 1) hydrodynamic conditions, 2) feed solution chemistry/composition, and 3) membrane properties (Tang et al. 2010). The important prior studies on these factors are briefly summarized in Table 2-4. Additional factors such as recovery and temperature can also affect fouling.

Table 2-4: A summary of membrane fouling tests.

	References	Parameters of interest	Membranes and foulants	Comments
Membrane properties	Cohen and Probststein 1986	axial flow Reynolds No.(-)	RO; ferric hydroxide	weakly dependent on CFV at laminar regime
	Jönsson and Jönsson 1995	membrane hydrophobicity and pore size	8 UF; octanoic acid, sodium octanoate	low MW foulants, high MWCO membranes
	Zhu and Elimelech 1997	membrane roughness(+)	TFC & CA RO; silica colloids, Al ₂ O ₃	chemical heterogeneity
	Childress and Elimelech 2000	membrane surface charge(-) initial fouling rate, ion rejection	NF; humic acid, surfactants	surface modification (absorption study)
	Vrijenhoek et al. 2001	roughness (+), zeta potential (?), contact angle(?)	NF & RO; silica colloids	fouling correlated well with roughness
	Hoek et al. 2003	roughness(+)	polymeric RO & NF; colloids	modeling, interaction energy method
	Li et al. 2007	roughness(+), morphology, coating, mixture fouling	RO; BSA, Na-alginate	
	Tang et al. 2007d	XPS, ATR-FTIR, TEM, streaming potential	coated and uncoated RO membranes	differentiate coated and uncoated membranes
	Xu et al. 2010	roughness(+) and hydrophobicity(+) of membranes	NF and RO; secondary effluent	
Solution chemistry and hydrodynamic conditions	Cohen and Probststein 1986	feed concentration (+)	RO; Ferric hydroxide	threshold flux observed
	Palecek and Zydney 1994a, 1994b	IS (+), pH, protein surface charge density(-), quasi-steady flux	MF & UF; 5 diff proteins including BSA and lysozyme	high initial flux, high IS, high foulant concentration
	Hong and Elimelech 1997a	IS (+), Ca ²⁺ /Mg ²⁺ (+), pH (-)	NF; humic acid	low CFV, low initial permeate flux
	Zhu and Elimelech 1995, 1997	colloidal concentration, IS, divalent ions, permeation drag, surfactant	RO; silica colloids, aluminum oxide	reversible colloidal fouling
	Hong et al. 1997	colloids size & concn, colloidal stability, pressure(+), CFV(-), cake accumulation & porosity	0.02 µm zirconia tubular ceramic membrane; silica colloids	modeling, CFV has no effect on flux (laminar flow)
	Eagles and Wakeman 2002	foulant concentration (+)	MF; Starch, casein	high foulant concn, high CFV
	Lee et al. 2006	pH, IS(+), Ca ²⁺ /Mg ²⁺ (+), CFV(-), initial permeate flux(+)	RO; Alginate (hydrophilic)	Ca ²⁺ caused more fouling than Mg ²⁺
	Ang and Elimelech 2007	IS(+), Ca ²⁺ /Mg ²⁺ (+), pH, combined foulants (+)	RO; BSA, alginate	high foulant concentration
	Tang et al. 2007c	pH (-), IS (+), Ca ²⁺ (+), concentration(+), initial flux(+)	RO & NF; Humic acid	concn does not affect pseudo-stable flux
	Tang and Leckie 2007	foulant-foulant electrostatic interaction(-)	TFC RO & NF; humic acid	limiting flux
	Mo et al. 2008	pH, IS(+), Ca ²⁺ and Mg ²⁺ (+), temperature	RO; BSA	relatively high foulant concentration
	Lin et al. 2008	pH (6~7.5), IS(-), protein concn (+), concn ratio	UF(100 kDa); mixed BSA & hemoglobin	dead-end, oppositely charged proteins
	Rohani and Zydney 2009	surface charge distribution of proteins	UF; 2 proteins of similar size and net charge	minimal effect from charge distribution
	Contreras et al. 2009	combined fouling (organics & silica), adsorption of organics on silica, zeta potential of foulants	NF; silica colloids, humic acid, Na-alginate, dextran and BSA	synergistic effect in combined fouling, BSA adsorption on silica
	Zazouli et al. 2010	pH, IS(+, single foulant), foulant concentration (+, single)	NF; mixed humic acid & alginate	averaging effect on flux in combined fouling

Note: (+) more fouling at higher values; (-) less fouling at higher values.

2.4.1 Hydrodynamic conditions

Past studies have demonstrated that increasing initial flux and reducing crossflow velocity (CFV) cause greater flux decline rate during NF and RO fouling by organic macromolecules (Hong and Elimelech 1997a; Braghetta et al. 1998; Ang and Elimelech 2007; Tang et al. 2007c). Similar results were also observed for MF and UF (Kim et al. 1992; She et al. 2009). A recent review (Tang et al. 2010) on colloidal fouling of NF and RO membranes summarized that high flux usually induced severe fouling due to: 1) larger permeate volume, 2) greater concentration polarization, and 3) greater hydrodynamic drag towards membrane surface. The electron microscopic observations by Buffle and Leppard (1995) revealed that the number and size of retained particles increases with permeate flow rate. Tang et al. (Tang and Leckie 2007) observed a pseudo-stable flux for elevated initial fluxes towards the end of a 10-day fouling test with NF and RO membranes fouled by humic acid. Increasing initial flux beyond the limiting value does not increase the pseudo-stable flux. Tang and coworkers (Tang et al. 2007c; She et al. 2009) further suggested that the rate of colloidal fouling is determined by frequency of collision and attachment coefficient. The collision frequency could be determined from foulant concentration and permeate flux, and attachment coefficient is related to energy barrier (influenced by solution chemistry, membrane properties, etc.) and flux (hydrodynamic drag resulted from the flux).

Many studies (Hong and Elimelech 1997a; Chong et al. 2007) demonstrated that the more severe fouling caused by a lower crossflow velocity, was likely due to the increased concentration polarization and reduced mass transfer. However, Hong's study on kinetics of permeate flux decline in crossflow membrane filtration of colloidal suspensions showed that CFV had limited effect on permeate flux at transient stages of filtration (before reaching steady-state flux) (Hong et al. 1997). Moderate effect of CFV on flux performance has also been observed during humic acid fouling (Tang et al. 2007c).

2.4.2 Feed solution composition and chemistry

2.4.2.1 Effect of feed solution chemistry

Researchers have generally agreed that foulant concentration, solution pH, ionic strength, and divalent cation concentration affect membrane fouling (Palecek et al. 1993; Hong and Elimelech 1997a; Ang and Elimelech 2007; Tang 2007; Mo et al. 2008).

Foulants may carry different charges under different pH conditions due to protonation or deprotonation of functional groups. For instance, the carboxylic groups in humic acid, polysaccharide and protein molecules cause these substances to be negatively charged at high pH as deprotonation takes place (Ang and Elimelech 2007; Tang 2007). Palecek and Zydney (1994b) observed quasi-steady microfiltrate fluxes during protein fouling and concluded that the flux increased at pH values away from the IEP, with the data well-correlated with the protein surface charge density. It has also been observed that RO membrane fouling by BSA was enhanced at the IEP (pH 4.7) of BSA where its overall charge was zero (Ang and Elimelech 2007). The effect of charge distribution of proteins was investigated during UF by Rohani and Zydney (2009), and a minimal contribution from surface charge distribution was affirmed. The charge effects of macromolecules has also been observed for humic acid (Hong and Elimelech 1997a; Tang et al. 2007c) and alginate (Lee et al. 2006).

Prior studies show that protein fouling of RO membranes is more significant at higher divalent cation concentration and higher ionic strength (IS) (Ang and Elimelech 2007; Salgin 2007; Mo et al. 2008). Divalent ions such as Ca^{2+} and Mg^{2+} tend to complex with protein molecules and thus reduce their total charges for negatively charged proteins (Ang and Elimelech 2007). High ionic strength results in electrical double layer (EDL) compression and thus the depression of electrostatic repulsion between foulants (and between foulants and membrane surfaces) (Ang and Elimelech 2007; Mo et al. 2008). Besides proteins, other macromolecules such as humic acid and alginate are also affected in a similar way. It has been documented that Ca^{2+} can intensively complex with alginate to form a

gel-like structure, which causes dramatic fouling. In contrast, the presence of Mg^{2+} has little effect on alginate fouling of RO membranes (Lee et al. 2006).

Furthermore, pH and ionic strength also influence the solubility of proteins. The solubility is minimal at its IEP, and first increases (salting-in) and then decreases (salting-out) with increasing ionic strength for well-folded proteins (Shih et al. 1992; Song 2009). Chan and Chen (2001) investigated the effect of electrolyte concentration on BSA aggregation and deposition in constant-flux MF, and they found a concentration of 0.02 M NaCl was sufficient to dampen any electrostatic interaction and a higher concentration of 0.1 M NaCl may result in higher solubility (salting-in) and cause a lower TMP increase (less fouling). The concentration of BSA for their study was 0.1 wt.% (1000 mg/L), which is much higher than typical protein concentrations of RO and NF feed waters.

It has been experimentally observed that the fouling rates increase at higher foulant concentrations (Zhu and Elimelech 1995; Zhu and Elimelech 1997; Eagles and Wakeman 2002; She et al. 2009). Cohen and Probstein (1986) investigated colloidal fouling of RO membrane with ferric hydroxide colloids and both their experiments and theoretical model suggested that the rate of fouling increases linearly with foulant concentration for a stable solution. In addition, the authors also suggested that the threshold flux does not depend on foulant concentration. Such threshold flux independence of foulant concentration was later verified by Tang and coworkers using humic acid and BSA as modal foulants (Tang et al. 2007c; She et al. 2009; Tang et al. 2009c).

The effect of size of organic macromolecules has been less addressed in past studies, as direct comparison requires particles with different size but with the same surface properties. An MF study (Kwon et al. 2000) on polystyrene latex particles of seven sizes from 100 to 10,000 nm showed a minimum in the critical flux (more details in Section 2.5) for a particle size of about 200 nm (most prone to fouling). It has been generally agreed that the critical flux for big particles (>100 nm) increases with particle size due to enhanced shear-induced diffusion (Bacchin et al. 1995; Tang et

al. 2010). On the other hand, an increased critical flux for smaller particles (<100 nm) may suggest the importance of a brownian diffusion mechanism (Bacchin et al. 2006). Cohen and Probstein suggested that the stable flux should be independent of particle size for systems dominated by electrical double layer interaction (Cohen and Probstein 1986). This charge dominated (over size) effect was also observed during MF of various protein solutions, where the quasi-steady fluxes for the different proteins appeared to be strongly correlated to the square of the surface charge density, despite the large differences in molecular weight and physicochemical characteristics of those proteins (Palecek and Zydney 1994b).

2.4.2.2 Effect of feed composition

The majority of existing fouling studies used feeds containing a single type of foulant. Studies on membrane fouling by feeds containing a foulant mixture may provide more insights for understanding the membrane filtration of real water. Researchers have made efforts to study the fouling by binary and tertiary foulant mixtures. In the literature, quite a few MF and UF were conducted with protein mixtures because of the industrial application of separating one protein from the others. The charge of proteins has been revealed to be important for separation (Van Eijndhoven et al. 1995): controlling pH at or close to the IEP of one protein would allow more passage of this protein while rejecting the other, i.e., more effective separation. Within the handful of studies performed with RO and NF membranes, some different interactions and effects were observed and suggested: 1) a synergistic effect that explains the more severe flux decline by the mixed foulants rather than that by any single foulant (Ang and Elimelech 2007); 2) adsorption of macromolecules on inorganic particles that alters the surface properties of the latter (Lee et al. 2005; Contreras et al. 2009); and 3) an averaging effect that the rate and the extent of flux reduction for the mixture falls in between that of the two single foulants (Lee and Elimelech 2006; Zazouli et al. 2010). Some phenomena observed in MF and UF may also occur during RO and NF processes: 1) a pre-filtering effect, i.e., one foulant acts as a pre-filter for another to reduce fouling in MF/UF (Arora and Davis 1994; Palacio et al. 2003; Hughes et al. 2007); and 2) an effect arising

from oppositely charged macromolecules that was shown by UF of a feed containing binary proteins of different IEP (Iritani et al. 1997; Lin et al. 2008).

2.4.3 Membrane properties

Membrane properties such as surface charge, roughness, hydrophobicity, and pore size can significantly affect membrane fouling.

It has been well recognized that membrane roughness has profound influence on the fouling rate. RO and NF membranes with rough surfaces are more prone to fouling during colloidal filtration (Zhu and Elimelech 1997; Vrijenhoek et al. 2001; Hoek et al. 2003). This has been attributed to the reduced local shear rate (Zhu and Elimelech 1997) and possibly the high local flux (Tang et al. 2007c) over the valley regions. Tang et al. suggested that macromolecules were able to penetrate into the valleys of the ridge-and-valley structures (Tang et al. 2007d). Nevertheless, they reported that the pseudo stable flux under severe membrane fouling conditions was independent of membrane properties (Tang et al. 2006).

Membrane surface charge may influence fouling rate and rejection especially for charged particles and solutes (Lipp et al. 1994; Childress and Elimelech 2000). The surface charge itself can be affected by solution chemistry such as ionic strength, pH and other charged ions, etc. (Childress and Elimelech 2000). An increase in salt concentration (ionic strength) can suppress electrical double layer and lower the zeta potential (Afonso et al. 2001). The membrane surface generally becomes more negatively charged at high pH due to the deprotonation of certain functional groups (e.g., -COOH) (Tang et al. 2007d). The adsorption of anionic species can also render a surface more negatively charged (Deshmukh and Childress 2001). TFC PA membranes are negatively charged under typical water and wastewater treatment applications, and it has been believed that negatively charged membranes can reduce the fouling rate by negatively charged foulants (Goosen et al. 2004). On the other hand, Bartels and coworkers reported that the “low fouling composite” LFC membranes with nearly neutral surfaces tend to be less fouled during wastewater reclamation (Bartels et al. 2005a). According to Tang et al. (2007d), such low

fouling membranes have a polyvinyl alcohol coating layer that makes the surfaces less rough, neutrally charged, and more hydrophilic.

Membrane hydrophobicity also plays an important role in fouling as hydrophobic foulants have high potential to interact with hydrophobic membranes and cause fast foulant deposition (Jönsson and Jönsson 1995; Bartels et al. 2005a; Yang et al. 2010). Mänttari et al. found that hydrophobic interactions may dominate over electrostatic repulsion, which caused more severe fouling of the more hydrophobic membranes (Mänttari et al. 2000). This is also consistent with the observation that PA membranes are easier to be fouled than cellulose acetate (CA) membranes due likely to their greater hydrophobicity (Jönsson and Jönsson 1995), although other factors make the comparison complicated, such as the different surface roughness and charge properties of PA and CA membranes (Elimelech et al. 1997; Vrijenhoek et al. 2001).

2.4.4 Effect of cake layer formation

2.4.4.1 Cake layer resistance

The main fouling mechanism in NF and RO is cake layer formation. RO and NF membranes typically have excellent rejection of organic macromolecules (Schäfer et al. 2005). The retained foulant may deposit on the membrane surface, which results in additional hydraulic resistance to the permeate water flow. The decline in water flux due to the fouling layer can be described by Darcy's law (Belfort et al. 1994; Li et al. 2008):

$$J = \frac{\Delta P - \Delta \pi}{\eta(R_m + R_f)} \quad (2.2)$$

where ΔP and $\Delta \pi$ are the hydraulic pressure difference and the osmotic pressure difference between the feed and permeate sides of the membrane, respectively, R_m and R_f denotes membrane resistance and foulant layer resistance, respectively, and η is the dynamic viscosity of the permeate water.

It has been found that the porosity of the cake layer changes as the layer builds up. Marshall and coworkers (Marshall et al. 1993) observed from scanning electron microscopy (SEM) images (UF membrane) that the protein layers initially deposited on the membrane were much more densely packed than those during the subsequent deposition. Tang et al. (Tang et al. 2007b) studied the specific cake layer resistance (r_f , the ratio of the cake layer resistance R_f to the mass accumulation m_f) of the humic acid fouled RO/NF membranes using transmission electron microscopy (TEM) and foulant mass assay, and they observed increased foulant layer density at higher initial flux, lower pH, and higher calcium concentration.

In a cake layer model, the flux of a clean membrane (J_0) is,

$$J_0 = \frac{\Delta P}{\eta R_m} \quad (2.3)$$

From Equation 2.2 and 2.3, the cake layer resistance, R_f can be determined by,

$$R_f = \frac{\Delta P}{\eta} \left(\frac{1}{J_t} - \frac{1}{J_0} \right) \quad (2.4)$$

where J_t is the flux at time t.

The specific cake layer resistance r_f can be calculated by,

$$r_f = \frac{R_f}{m_f} = \frac{\Delta P}{\eta m_f} \left(\frac{1}{J_t} - \frac{1}{J_0} \right) \quad (2.5)$$

where m_f is the foulant mass deposition per unit membrane area.

2.4.4.2 Cake enhanced concentration polarization

Concentration polarization (CP) of dissolved ions results in increased osmotic pressure and thus reduces membrane flux. CP can be further enhanced by cake deposition, a phenomenon known as cake enhanced osmotic pressure (CEOP, Figure 2-5) (Hoek and Elimelech 2003; Chong et al. 2008). The cake layer with

tortuous flow paths hinders the back diffusion of solutes. In addition, the tangential shear that helps to minimize CP is not available within the cake layer. These effects led to reduced mass transfer and greatly enhanced the concentration of solutes at the membrane wall (Hoek and Elimelech 2003). The CEOP effect could reduce the permeate flux and increase the solute passage (see section 2.4.4.3) (Hoek and Elimelech 2003; Kim et al. 2009).

Figure 2-5. Conceptual illustration of concentration polarization (CP) of solutes in an RO membrane system (a) virgin membrane, and (b) after cake formation (Chong 2008).

2.4.4.3 Effects of cake layer on retention of ions and foulants

In many MF/UF processes, the retention of macromolecules increases as the foulant adsorption and deposition takes place (Gergen et al. 1989; Marshall et al. 1993).

RO/NF membrane filtration can achieve nearly complete retention of almost all the organic macromolecules and thus the focus is usually on rejection of ions or other small solutes (e.g., trace contaminants) upon fouling by macromolecules. Tang et al. (2007c) and Comerton et al. (2009) observed increased salt rejection during humic acid fouling, and they suggested both size exclusion and Donnan exclusion could influence rejection. A similar salt rejection trend has been observed during moderate fouling by alginate (Jin et al. 2009; Kim et al. 2009), although a severe CEOP effect can result in solute passage (Chong et al. 2007). In addition, Comerton

et al. found that the effective MWCO of an NF membrane (NF270) was shifted to a lower value after its fouling by organic matter. They also hypothesized that compound interaction and association with organic matter in the water matrix itself may be a major contributor to the increases in rejection of endocrine disrupting compounds (EDCs) and pharmaceutically active compounds (PhACs) in addition to the reduced-effective MWCO effect. On the other hand, more porous cake layers formed by silica colloids or other relatively big particles tend to reduce salt rejection due to cake enhanced concentration polarization (Lee et al. 2004; Kim et al. 2009).

2.4.5 Other factors affecting protein fouling

Protein fouling has been extensively studied for MF and UF membranes. The flux decline phenomenon has been summarized into three phases chronologically (Figure 2-6) (Marshall et al. 1993). The rapid initial flux drop (within the first ~ 1 min) is due primarily to concentration polarization. The flux continues to decline rapidly due to protein deposition (likely with initial monolayer adsorption and then a complete surface layer formation). Finally, a quasi-steady-state stage is reached where the flux declines slowly, probably due to further deposition of particles or consolidation of the fouling layer.

Figure 2-6. Various stages of flux decline in MF/UF process (adapted from Marshall et al. 1993).

The role of intermolecular disulfide linkages and temperature may be also important for protein fouling. Le and Howell (Le and Howell 1983) concluded that the initial fouling occurs by physical adsorption of a protein monolayer, with further deposit consolidation occurring via hydrophobic interactions (Field et al. 1994) and intermolecular disulfide linkages. Kelly and Zydney (Kelly and Zydney 1994) found that BSA aggregation can occur via the free-thiol oxidation and intermolecular thiol-disulfide interchange reactions, and thus can accelerate MF flux decline. Protein properties, solution viscosity and solute diffusivity can also be affected by temperature. Increasing temperature generally increases the membrane permeability due to the dual effect of lowering the permeate viscosity, which enhances flow rate (Marshall et al. 1993). In contrast, Meireles and coworkers found that protein denaturation and aggregation can be more severe at higher temperature, which resulted in a faster permeate flux decline (Meireles et al. 1991).

In MF and UF fouling, besides membrane pore size and pore size distribution, protein size to membrane pore size ratio could also be a crucial variable since it directly affects pore plugging of porous membranes (Fane et al. 1983b; Marshall et al. 1993). The protein to pore size ratio can be altered during filtration due to varying either the size of protein molecule or the membrane pore size (Fane et al. 1983b), and this ratio may be directly related to protein retention as well as flux performance (She et al. 2009).

Compared to the large number of studies on MF and UF fouling by proteins, there have only been a handful number of publications on protein fouling of RO and NF membranes (Ang and Elimelech 2007; Mo et al. 2008). These studies have mainly focused on the effect of solution chemistry and hydrodynamic conditions (see details in Sections 2.4.1 and 2.4.2). It is worthwhile to note that, while pore plugging is important in porous membrane fouling, protein fouling with non-porous RO and NF membranes is likely to be dominated by cake layer deposition. Another important difference is that the protein concentration in typical RO and NF feed waters is generally lower compared to that for MF and UF applications (e.g., several g/L in dairy industry) (Tang et al. 2010). The prior studies on RO and NF protein

fouling have also mainly focused on fouling by single protein feeds and limited to relatively short time duration. Further research is needed to understand the flux behavior at longer duration and in the presence of multiple foulant species.

2.5 Concepts of critical flux and limiting flux

The critical flux concept states that “on start-up there exists a flux below which a decline of flux with time does not occur; above it fouling is observed” (Field et al. 1995). It has been widely and successfully used in MF and UF for control of fouling, although its value may be affected by the measuring method (e.g., optical microscopic method vs. permeability measurement) and operating conditions (Bacchin et al. 2005; Tang et al. 2010). It is more difficult to apply this concept in RO and NF fouling because of the much higher resistance of membranes (long time and large amount of foulant deposition required) (Cohen and Probstein 1986; Tang et al. 2010).

A related concept, the limiting flux concept has also been discussed in the literature (Tang et al. 2010). Limiting flux represents the maximum stationary permeation flux which can be reached when increasing transmembrane pressure (TMP) with a given solution or suspension for a given set of hydrodynamic conditions (Bacchin 2004). This concept was originated from MF and UF operations and earlier gel-formation models that considered the foulant concentration as one of the most important factors (Porter 1972; Aimar and Field 1992; Tang et al. 2010). Tang et al. (2010) suggested that the gel-formation limiting flux model may work better for concentrated solutions or solutes with low solubility, while for a stable and dilute solution, the limiting flux is more likely governed by the foulant-membrane surface interaction.

Tang and coworkers related both critical flux and limiting flux concepts to two different forms of foulant-membrane interactions, namely the foulant-clean-membrane interaction and foulant-fouled-membrane interaction (Tang and Leckie 2007). In this framework, the critical flux can be considered as the triggering flux

for the initial deposition of foulant and its value is governed by the foulant-clean-membrane interaction $F_{barrier}^{f-m}$ (Tang and Leckie 2007). By comparison, the limiting flux is reached when the hydrodynamic drag force balances the foulant-fouled-membrane interaction $F_{barrier}^{f-f}$ (Tang and Leckie 2007). In addition, the deposition of colloids is principally determined by the barrier force ($F_{barrier}^{f-m}$ or $F_{barrier}^{f-f}$) and the hydrodynamic drag force F_{drag} that is proportional to the flux J according to Stokes' Law:

$$F_{drag} = 6\pi\eta R_h J \quad (2.6)$$

where η is the flow viscosity and R_h is the characteristic hydrodynamic radius of the foulants. As J increases, the drag force F_{drag} may overcome the barrier force $F_{barrier}^{f-m}$, which promotes foulant deposition. If J is very high, the membrane surface will be fully covered by the foulant layer (Figure 2-7), such that the foulant-clean-membrane interaction is switched to the foulant-fouled membrane interaction. According to this surface interaction limited flux model, the limiting flux is given by:

$$J_L = \frac{F_{barrier}}{6\pi\eta R_h} \quad (2.7)$$

Figure 2-7. Conceptual model for foulant-foulant interaction (adapted from Palecek and Zydney 1994b)

2.6 Membrane characterization

Membrane characterization is important in fouling studies, in order to:

- 1) to determine the membrane physiochemical properties and their effect on fouling;
- 2) to determine the foulant deposition properties (e.g., foulant layer mass, density, charge, etc.) and their relationship with fouling conditions (solution chemistry, hydrodynamic conditions, etc.);
- 3) to understand the different stages of membrane fouling; and
- 4) to determine the dominant forces (such as hydrophobic interactions and electrostatic interactions) during membrane fouling.

Some of the common characterization methods are listed in Table 2-5 for membrane properties and Table 2-6 for foulant properties. The streaming potential and contact angle characterization are briefly discussed in Sections 2.6.1 and 2.6.2, respectively. Microscopic characterization and membrane chemistry characterization are briefly mentioned in Sections 2.6.3 and 2.6.4, respectively.

Table 2-5. Membrane characterization methods.

Instrument	Purpose
Rejection of uncharged solutes	Pore size (MWCO)
Streaming potential	Zeta potential
Contact angle	Hydrophobicity
AFM	Roughness, surface morphology
TEM	Membrane cross-section
XPS	Surface elemental composition and chemical state
ATR-FTIR	Functional group
Confocal Microscope	Structure of fouling layer

Table 2-6. Fouling characterization methods.

	<i>During fouling (real time)</i>	<i>After fouling</i>
<i>Direct methods</i>	<ul style="list-style-type: none"> • Flux performance • Transmembrane pressure (TMP) • Ultrasonic time-domain reflectometry (UTDR) ^a • Electrical impedance spectroscopy (EIS) ^b • Direct observation through the membrane (DOTM) ^c 	<ul style="list-style-type: none"> • Foulant mass deposit
<i>Indirect methods</i>	<ul style="list-style-type: none"> • Rejection/retention 	<ul style="list-style-type: none"> • All the methods listed in Table 2-5

a. refer to (Mairal et al. 1999)

b. refer to (Gaedt et al. 2002)

c. refer to (Li et al. 1998)

2.6.1 Streaming potential measurement

Since membrane surface charge density cannot be directly measured, it is estimated by assuming that the electrokinetic charge density (zeta potential, ζ) at the shear plane is close to the effective charge density of the membrane (Hagmeyer and Gimbel 1998). Streaming potential is one of the measurements for zeta potential, during which the volume flow through the slit increases slowly so that the measured pressure drop increases as well. The streaming potential E_s , created by the flow of the test solution in the slit (flow chamber) between two membrane sheets, increases linearly with the pressure drop ΔP across the slit. The slope of the line can be determined and the zeta potential is calculated using the Helmholtz-Smoluchowski equation (Equation (2.8)) (Elimelech et al. 1994):

$$\zeta = \frac{E_s}{\Delta P} \frac{\eta}{\epsilon \epsilon_0} \frac{L}{A} \frac{1}{R} \quad (2.8)$$

where η is the liquid viscosity, ϵ is the liquid permittivity, ϵ_0 is the permittivity in vacuum, R is the electrical resistance across the medium, and L and A are the length and cross-sectional area of the channel, respectively.

2.6.2 Contact angle

Hydrophobicity of a membrane is usually expressed in terms of the contact angle (θ), which is a widespread technique to assess the hydrophobicity of solid materials. Contact angle describes the edge of the two-phase boundary (e.g., liquid and solid for membranes) where it ends at a third phase (air), given by the Young's equation (Equation (2.9)) (Adam 1957).

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.9)$$

where γ_{SV} , γ_{LV} , and γ_{SL} are the interfacial tensions of the solid-vapor, the liquid-vapor, and the solid-liquid interfaces. In membrane science the contact angle is a measure of wettability of the membrane. The two commonly used methods are the captive bubble and the sessile drop techniques.

2.6.3 Microscopy

Various microscopic techniques may be used to study the morphology of membranes. Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are commonly used to exam the surfaces and cross-sections of membranes (Chan and Chen 2004; Tang et al. 2007b). Atomic force microscopy (AFM) is used to determine membrane surface roughness. Its advantages over SEM/TEM are that no electron damage occurs, and sample preparation is simple (Chan and Chen 2004).

2.6.4 Chemical structure

Attenuated total reflection fourier transform infrared (ATR-FTIR) spectroscopy is used to determine the functional groups of membranes as well as foulants (Freger et al. 2002; Howe et al. 2002). X-ray photoelectron spectroscopy (XPS) can be used for identification of the membrane surface elements, but the limitation is that only the top few nanometers of the surface can be analyzed. Other methods may include

energy dispersive spectroscopy (EDX) and Rutherford back-scattering (RBS) (Bartels 1989; Mi et al. 2006).

Chapter 3

Methodology

3.1 Chemicals and materials

3.1.1 General chemicals

Unless otherwise specified, all chemicals and reagents were analytical grade with purity over 99%. Ultrapure water with a resistivity of 18.2M Ω .cm (ELGA water purification system or Millipore Integral 10 Water Purification System) was used to prepare all working solutions. Sodium chloride, calcium chloride, magnesium chloride, sodium hydroxide, and hydrochloric acid were used to adjust the ionic composition of working solutions (pH, ionic strength, and calcium and magnesium concentration). Sodium dodecyl sulfate (SDS) (Jones and O'Melia 2000) and sodium hydroxide solutions were used for extracting proteins and carbohydrates from fouled membranes, respectively.

3.1.2 Model foulants

Bovine serum albumin (BSA, Sigma-Aldrich A7906) and lysozyme (LYS, Fluka 62971) were used as model protein foulants, and sodium alginate (Sigma A2158) was the model polysaccharide foulant. They were all received in power form with purity over 98%, and stored at 4 °C in the dark. At neutral pH range, BSA and alginate are negatively charged, and LYS is positively charged. Among the three macromolecules, LYS has the smallest size with a molecular weight of ~8 kDa. Other properties are listed in Table 3-1. The working solution of each foulant was freshly prepared prior to each fouling test.

Table 3-1. Properties of foulants.

Foulants	Molecular weight (kDa)	Size (nm) ^a	Isoelectric point (IEP) ^c	Zeta potential at pH 7 (mV) ^c
BSA	67 ^a	14×4×4	pH 4.7	-15
LYS	14.3 ^a	4.5×3×3	pH 10.4	10
Alginate	12 - 80 ^b	-	Low pH, < pH 2	-25~ -30

a. from (Palecek and Zydney 1994a)

b. from (Ang and Elimelech 2007)

c. from current study

3.1.3 Four membranes for filtration tests

Four commercial membranes were used in this study: an RO membrane XLE, two NF membranes NF90 and NF270, and a UF membrane GM. XLE, NF90 and NF270 were obtained from Dow FilmTec[®], and GM was provided by GE Osmonics[®]. All the membranes were received as dry flat sheet coupons. The properties of these membranes are summarized in Table 3-2. Membranes XLE and NF90 are fully aromatic polyamide membranes formed by *m*-phenylene-diamine and tri-mesoyl chloride (Tang et al. 2007d; Tang et al. 2009b; Tang et al. 2009a). According to Tang et al. (Tang et al. 2007a; Tang et al. 2007d; Tang et al. 2009a), these membranes have relatively rough membrane surfaces (root-mean-square roughness R_{RMS} on the order of 100 nm) as a result of their peak-and-valley structures. In contrast, the semi-aromatic piperazine based membrane NF270 has a much smoother membrane surface ($R_{RMS} \sim 9$ nm) (Tang et al. 2007a; Tang et al. 2009b; Tang et al. 2009a). Compared to XLE and NF90, the semi-aromatic NF270 has significantly higher water permeability and lower salt rejection (Table 3-2). It also has a more hydrophilic and more negatively charged membrane surface. Membrane GM is a polyamide based UF membrane with a molecular weight cutoff (MWCO) of ~ 8 kDa (Jarusutthirak et al. 2002; Shim et al. 2002). It has a smooth and relatively hydrophilic membrane surface (contact angle $\sim 39.3^\circ$).

Table 3-2. Membrane properties.

membrane	chemistry	water permeability (L/m ² ·h·psi) ^c	NaCl rejection (%) ^c	MWCO (kDa)	contact angle (°) ^c	zeta potential at pH 7 (mV)	roughness (RMS) (nm)
XLE (RO) ^a	TFC, fully aromatic polyamide	0.396	96.5	< 0.2	71.0 ± 1.0	-26 ^c	129.5 ± 23.4 ^e
NF90 (NF) ^a	TFC, fully aromatic polyamide	0.398	84.9	0.2	65.6 ± 1.9	-10 ^c	142.8 ± 9.6 ^e
NF270 (NF) ^a	TFC, poly (piperazine -amide)	0.870	35.0	0.2-0.3	29.1 ± 1.1	-35 ^c	9.0 ± 4.2 ^e
GM (UF) ^b	TFC, polyamide	1.088	20.2	8 ^d	39.3 ± 1.3	-17 ^d	10.7 ^f

a. supplied by Dow FilmTec

b. supplied by GE Osmonics

c. from current study (Figure D.3, Appendix)

d. from Ref. (Jarusutthirak and Amy 2006)

e. from Ref. (Tang et al. 2009a)

f. from Ref. (Shim et al. 2002)

3.2 Experimental design

3.2.1 Setup, filtration test conditions and protocol

Membrane fouling experiments were performed using a laboratory scale crossflow filtration setup under constant pressure conditions (Figure 3-1). Six identical crossflow cells (CF042 Membrane Cell, Sterlitech) (Sterlitech CF042 manual) were operated in parallel while the crossflow velocity and pressure of each cell could be controlled separately. The active membrane area for each cell was 42 cm². The feed solution was pumped from a 50-L polypropylene feed tank with a variable-speed diaphragm pump (Model D-03, HydraCell, Minneapolis, MN). The temperature of the feed solution was maintained at 20 ± 1°C with a refrigerated water circulating bath (BL-710, YIH DER). The pressure inside each membrane cell was maintained at the target pressure using a backpressure regulator (pressure relief valve, Swagelok, USA), and its value was monitored using a digital pressure transmitter (WIKA, 0-40 bar, Germany). The crossflow velocity was adjusted with a needle valve. Permeate flux was measured using digital flowmeter (Bronkhorst, Netherlands) as well as via a gravimetric method at predetermined time intervals to

ensure the accuracy of the digital flux measurements. Both digital pressure and flux readings were recorded with a computer data logging system.

Figure 3-1. Schematic description of membrane testing setup (adapted from Tang 2007).

The fouling test procedures shown in Figure 3-2 were adapted from Tang et al. (Tang et al. 2007c). Clean membrane coupons were used for each fouling experiment. The membrane coupons were soaked in ultrapure water overnight before being loaded into the test cells. The coupons were compacted and equilibrated for 2 days with the electrolyte solution under pressure. The background electrolyte had identical pH and ionic compositions to the targeted feed water for fouling test, except for the absence of foulant. This equilibration stage was to ensure any subsequent flux reduction after foulant addition was solely due to membrane fouling but not the mechanical compaction of the membranes. At the end of the 2-day equilibration stage, pre-dissolved foulant working solution was added to feed tank to achieve the desired foulant concentration of 20 mg/L. The initial permeate flux (water flux at time 0) immediately before the addition of foulant was taken as the membrane flux. The fouling experiments were continued for another 4 days.

Pressure and crossflow velocity were maintained constant throughout the fouling experiments. The effects of initial flux, solution pH, and ionic composition were evaluated by varying one variable at each run while maintaining the rest at constant conditions. Unless specified otherwise, the following reference conditions were applied:

- a total foulant concentration of 20 mg/L;
- a total ionic strength of 10 mM (adjusted by addition of NaCl, CaCl₂ and / or MgCl₂);
- crossflow velocity was 9.5 cm/s with diamond patterned spacer used in the feed water channel; and
- feed tank temperature at $20 \pm 1^\circ\text{C}$.

Figure 3-2. Schematic diagram of fouling test protocol.

3.2.2 Characterization methods

3.2.2.1 Zeta potential measurement of macromolecules

The zeta potential of macromolecules was measured using the Laser Doppler Velocimetry (LDV) technique (Malvern ZetaSizer Nano ZS) (Jachimska et al. 2008). Sample solutions were freshly prepared. The ionic composition was adjusted

by addition of NaCl to achieve a desired ionic strength. Then the pH of the identical solution was adjusted with HCl or NaOH to obtain sample solutions at a series of pH values. These sample solutions were injected into a zeta potential cell carefully to avoid any bubble formation that may interfere with the measurement.

3.2.2.2 Conductivity rejection

Salt rejection was determined based on conductivity measurement by a conductivity meter (Ultrameter II, Myron L Company, Carlsbad, CA). The conductivity of the permeate was measured at predetermined time intervals to obtain the variation of salt rejection during membrane fouling. Salt rejection (based on conductivity rejection) could be determined by Equation (3.1),

$$\text{Rejection \%} = 100 - \text{transmission \%} \quad (3.1)$$

where the transmission equates to the conductivity of permeate divided by the conductivity of the feed solution.

3.2.2.3 Foulant mass deposition analysis

Fouled membrane coupons were gently rinsed with Milli-Q water to remove the labile foulants. One or two samples of area of $1.267 - 2.534 \text{ cm}^2$ were cut from the coupons and soaked in extracting solution for one day. Sodium dodecyl sulfate (SDS, 5%) (Jones and O'Melia 2000) was used for dissolution of the proteins (LYS and BSA) and NaOH (0.1%) (Guo et al. 2009) was used for the alginate. At the end of 1-day of soaking, the solutions were sonicated mildly (below 30°C) for 20 minutes. The protein extractant was analyzed using a protein assay kit (Sigma, QuantiPro™ bicinchoninic acid (BCA) Assay Kit, 0.5-30 $\mu\text{g/ml}$) with UV of 562 nm (Brown et al. 1989), and that of the alginate was analyzed using the phenol-sulfuric acid method with UV of 485 nm (Dubois et al. 1956) (UV spectrophotometer, UV-1700 Shimadzu). Following the first extraction step, a second extraction step was preformed for some fouled samples. In the current study, extracted foulant mass in the second extraction was negligible.

3.2.2.4 Contact angle measurement

Both virgin and fouled membranes were rinsed with Milli-Q water and then thoroughly air dried before being transferred to a freeze dryer (CHRIST Alpha 1-4). After drying for 24 hours, the membranes were characterized by a video-based Optical Contact Angle measuring instrument (OCA, LMS Technologies PTE LTD) using the sessile drop method at room temperature of $\sim 23\text{ }^{\circ}\text{C}$ (Tang et al.; Kwon et al. 2006). Briefly, a droplet of 5 μl of Milli-Q water was delivered onto a dry membrane sample surface, and a static image of the droplet in equilibration with the membrane surface was taken with a CCD camera. Image capture, analysis and contact angle computation were performed by using the 32-bit proprietary Windows NT based software (SCA). A circular profile of the droplet was assumed, and both right and left angles were read and recorded. For at least five locations contact angle measurements were performed for each membrane sample.

3.2.2.5 Ion concentration measurement

An inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer Optima 2000) and an ion chromatography system (Dionex, ICS-1000) were used to measure the concentration of Na^{+} and Cl^{-} in the permeate, respectively. Prior to ion concentration analysis, dilution of permeate samples with Milli-Q water was done so as to ensure that the concentration of each ion was within the range of the standard curve.

Chapter 4

Protein fouling of nanofiltration, reverse osmosis and ultrafiltration membranes: the role of hydrodynamic conditions, solution chemistry and membrane properties

4.1 Introduction

Reverse osmosis (RO) and nanofiltration (NF) have stimulated wide interest in water and wastewater treatment in the recent decades due to the growing demand for high quality water, improved membrane separation properties, and reduced treatment cost. However, membrane fouling remains as a major challenge. One of the important membrane foulants is proteins, which are known to cause significant loss of membrane permeability (Jarusutthirak and Amy 2006; Gao et al. 2010). Many investigations on protein fouling have been performed for microfiltration (MF) and ultrafiltration (UF) membranes. Existing studies on these porous membranes have demonstrated that protein fouling is affected by hydrodynamic conditions (permeate flux and crossflow velocity) (Wu et al. 1999; She et al. 2009), feed water characteristics (solution pH, ionic compositions, and foulant concentration) (Fane et al. 1983a; Palecek and Zydney 1994b; Chan and Chen 2001; She et al. 2009), and membrane properties (hydrophobicity, roughness, and charge density, etc.) (Park et al. 2005; Lee et al. 2010). In general, severe protein fouling is observed at the isoelectric point (IEP) of a protein where the electrostatic repulsive force among protein molecules is at the minimum (Palecek and Zydney 1994b; She et al. 2009). In addition, increased applied pressure (and permeate flux) and reduced crossflow velocity can result in faster flux reduction (Wu et al. 1999).

In spite of the vast literature on MF and UF protein fouling, there have been only a few systematic studies on the fouling of RO membranes by proteins (Ang and Elimelech 2007; Kim and Hoek 2007; Li et al. 2007; Mo et al. 2008), and even less attention has been paid to protein fouling of NF membranes. It is worthwhile to note

that the fouling behavior of RO and NF membranes are likely to be very different from that of MF and UF membranes – pore blocking has been reported as an important fouling mechanism for porous MF and UF membranes but is unlikely to be important for non-porous RO and NF membranes (Ang and Elimelech 2007; Wang and Tarabara 2008). In addition, most existing protein fouling studies for RO membranes were performed for relatively short durations (on the order of 1 day or less). It has been observed that the rate of protein fouling was highly dependent on membrane properties such as surface roughness and hydrophobicity (Li et al. 2007). On the other hand, prior fouling studies on humic acid revealed that the long term flux behavior was independent of membrane properties (Tang and Leckie 2007; Tang et al. 2009c). Presumably, the initial stage of membrane fouling is controlled by the interaction of hydrodynamic forces and foulant-clean-membrane interaction, while the foulant-deposited-foulant interaction becomes dominant once the membrane properties are masked by those of the foulant cake layer after the formation of the foulant layer (Tang et al. 2007a; Tang and Leckie 2007). Thus, it is important to contrast fouling behavior at the initial stage with the longer term flux behavior. It is further interesting to compare the fouling of NF and RO membranes with that of UF membranes to better understand the role of membrane properties during protein fouling.

The objective of the current study was to investigate the effect of hydrodynamic conditions, solution chemistry, and membrane properties on protein fouling of NF, RO, and UF membranes. Crossflow fouling experiments were performed under constant pressure using bovine serum albumin (BSA) as a model foulant. This study may provide important insights of the role of hydrodynamic force, foulant-clean-membrane, and foulant-deposited-foulant interactions during protein fouling.

4.2 Materials and methods

4.2.1 Chemicals

Unless otherwise specified, all reagents and chemicals were of analytical grade with purity over 99%. Ultrapure water with a resistivity of 18.2 M Ω .cm was supplied by

an ELGA water purification system (UK). The ionic compositions of the feed solution were adjusted by using reagent grade sodium chloride, calcium chloride, and magnesium chloride, and the solution pH was adjusted by hydrochloric acid and sodium hydroxide. Bovine serum albumin (BSA) was used as a model protein foulant. BSA was received in powder form (98% purity, A7906, Sigma-Aldrich) and was stored at 4 °C in the dark. It has a molecular weight of ~ 67 kDa (Palecek and Zydney 1994b; Ang and Elimelech 2007). BSA molecules are ellipsoidal (14nm × 4nm × 4nm), and have an IEP at pH 4.7 (Palecek and Zydney 1994b). BSA working solutions were freshly prepared prior to each fouling experiment.

4.2.2 Membranes

Four commercial membranes were used in this study: an RO membrane XLE, two NF membranes NF90 and NF270, and a UF membrane GM. XLE, NF90, and NF270 were obtained from Dow FilmTec[®], while GM was provided by GE Osmonics[®]. All the membranes were received as dry flat sheet coupons. The properties of these membranes are summarized in Table 3-2. Membranes XLE and NF90 are fully aromatic polyamide membranes formed by *m*-phenylene-diamine and tri-mesoyl chloride (Tang et al. 2007d; Tang et al. 2009b; Tang et al. 2009a). According to Tang et al. (Tang et al. 2007a; Tang et al. 2007d; Tang et al. 2009a), these membranes have relatively rough membrane surfaces (root-mean-square roughness R_{RMS} on the order of 100 nm) as a result of their peak-and-valley structures. In contrast, the semi-aromatic piperazine based membrane NF270 has a much smoother membrane surface ($R_{RMS} \sim 9$ nm) (Tang et al. 2007a; Tang et al. 2009b; Tang et al. 2009a). Compared to XLE and NF90, the semi-aromatic NF270 has significantly higher water permeability and lower salt rejection (Table 3-2). It also has a more hydrophilic and more negatively charged membrane surface. Membrane GM is a polyamide based UF membrane with a molecular weight cutoff (MWCO) of ~8 kDa (Shim et al. 2002). It has a smooth and relatively hydrophilic membrane surface (contact angle ~ 39.3°).

4.2.3 Membrane fouling experiment

Membrane fouling experiments were performed using a laboratory scale crossflow filtration setup under constant pressure conditions (Figure 3-1). The details and description of the setup can be found in Section 3.2.1.

The fouling test procedures were adapted from Tang et al. (Tang et al. 2007c). The membrane compaction and equilibration stage followed exactly the procedure detailed in Section 3.2.1. At the end of the 2-day equilibration stage, BSA stock solution was added into the feed water tank to achieve the desired foulant concentration of 20 mg/L. The initial permeate flux (water flux at time 0) was taken as the membrane flux immediately before the addition of the foulant. The fouling experiments were continued for another 4 days. Pressure and crossflow velocity were maintained constant throughout the fouling experiments. The effect of initial flux, crossflow velocity, pH, ionic strength, and concentration of divalent cations (Ca^{2+} and Mg^{2+}) were evaluated by varying one variable at a time while maintaining the rest at constant conditions. Where a feed solution contains Ca^{2+} and Mg^{2+} , the total ionic strength was adjusted to 10 mM by the addition of NaCl.

4.2.4 Zeta potential measurement of BSA

Zeta potential of BSA was measured using the Laser Doppler Velocimetry (LDV) technique (Malvern ZetaSizer Nano ZS) (Jachimska et al. 2008). BSA solutions were freshly prepared. The solution ionic composition was adjusted by the addition of NaCl, CaCl_2 , and/or MgCl_2 to achieve the desired ionic strength and divalent ion concentrations. The pH was adjusted by addition of HCl or NaOH to obtain a series of pH values for one solution. The sample was injected into the zeta potential cell carefully to avoid the formation of bubbles that may interfere with the measurement.

4.3 Results and discussion

4.3.1 Effect of hydrodynamic conditions

The effect of initial flux was evaluated for NF270 over an applied pressure range of 25 to 180 psi (170 to 1240 kPa). As expected, the initial flux increased linearly with the applied pressure (refer to Figure 4-1(a) and (b)). Figure 4-1(a) presents the flux performance for a feed solution containing 20 mg/L BSA at pH 5.8. Severe flux decline was observed for high initial flux conditions (corresponding to applied pressures of 180 psi and 120 psi). The flux reduction was more moderate at lower applied pressures (75 psi and 50 psi). At a low initial flux of ~ 25 L/m²·h (at 25 psi), very stable flux was achieved over the 4-day fouling period. A similar trend was observed for the feed solution at pH 7 (Figure 4-1(b)). These results agree well with prior studies (Wu et al. 1999; Ang and Elimelech 2007; Li et al. 2007; Tang et al. 2007c; She et al. 2009) that showed higher initial flux tends to promote severe membrane fouling as a result of increased permeate drag force in addition to the enhanced concentration polarization.

Figure 4-1. The effect of initial flux and applied pressure on flux performance during BSA fouling. (a) flux vs. time at pH 5.8; (b) flux vs. time at pH 7; (c) flux at 96 hrs vs. initial flux at pH 5.8 and pH 7. Other test conditions: membrane NF270, feed water containing 20 mg/L BSA and 10 mM NaCl, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bars were based on the analysis of 2-3 replicates.

Furthermore, for membrane coupons whose initial fluxes were higher than certain threshold flux, there seems to be a strong tendency for the permeate fluxes to converge to a nearly identical value for each given solution chemistry (Figure 4-1(a) and (b)). Consider the membrane coupons with initial fluxes greater than 50 L/m²·h in Figure 4-1(a); in spite of the large difference in their initial flux values (ranging from 55 – 160 L/m²·h), their final fluxes at 96 hr (J_{96hr}) were in a narrow range of 32 – 37 L/m²·h. This flux convergence phenomenon has not been systematically investigated for protein fouling of RO and NF membranes, presumably due to the relatively long testing duration required for the fluxes to converge. On the other hand, Tang and coworkers (Tang and Leckie 2007; Tang et al. 2009c) observed a similar flux behavior for RO and NF fouling by humic acid over a fouling duration of 4-10 days. Such flux convergence is likely due to the more severe foulant deposition at higher initial flux/applied pressure conditions (Tang et al. 2007a). It seems that the long-term flux was limited by the membrane intrinsic properties (i.e., membrane-limited) at low applied pressure, but it was controlled by the foulant cake layer (i.e., foulant-limited) at high applied pressure. Conceptually, membrane fouling by small colloids (<<100 nm) is dominated by the interplay of 1) the positive permeate drag force (F_{drag}) towards the membrane surface, which is proportional to the permeate flux J , and 2) the barrier force ($F_{barrier}$) resulting from colloid-membrane surface interaction (see Figure 4-2(a), and Refs. (Palecek and Zydney 1994b; Tang and Leckie 2007; Tang et al. 2009c; Tang et al. 2010)), while other effects such as lateral migration and shear induced diffusion may also play a secondary role (Bacchin et al. 1995; Bacchin et al. 2006). The net driving force ($F_{drag} - F_{barrier}$) for foulant deposition is much greater at high flux levels, which results in rapid flux decline. The flux decline becomes more moderate at reduced membrane flux. According to this conceptual model (Figure 4-2(a)), foulant deposition is negligible and relatively stable flux (J_s) can be achieved when the net driving force becomes zero:

$$F_{barrier} = F_{drag} = c_{drag} J_s \quad (4.1)$$

where c_{drag} is the hydraulic drag coefficient (Tang et al. 2009c). Thus, a membrane with high initial flux has a strong tendency to approach asymptotically to a surface interaction limited pseudo-stable flux J_s :

$$J_s = \frac{F_{barrier}}{c_{drag}} \quad (4.2)$$

The above model assumes small foulant size ($\ll 100$ nm) such that other types of forces (e.g., shear induced inertial force and lateral migration (Bacchin et al. 1995; Bacchin et al. 2006)) are less important. This model offers a good explanation for the flux convergence phenomenon observed in Figure 4-1(a), where the pseudo-stable flux was likely ~ 35 L/m²·h at solution pH 5.8. This pseudo-stable flux was also dependent on colloid-membrane surface interaction, with higher J_s observed at pH 7 (Figure 4-1(b)) as a result of enhanced electrostatic repulsion (see Section 4.3.3). In addition, Equation (4.2) also explains the stable flux behavior when the initial flux was less than J_s – foulant deposition was negligible when the net driving force was less than zero.

The final flux at the end of fouling test J_{96hr} is plotted as a function of the initial flux J_0 in Figure 4-1(c). Previous studies on humic acid fouling demonstrated that a plot of this type was characterized by a 45° line at low initial flux (no fouling condition) followed by a horizontal line representing the surface interaction limited pseudo-stable flux (see Figure 4-2(b), and Refs. (Tang and Leckie 2007; Tang et al. 2009c)). To a first approximation, BSA fouling followed a similar type of behavior: 1) no or little flux reduction was observed at low initial flux levels ($J_0 < 40$ L/m²·h), and 2) increasing J_0 did not result in any enhancement of the final flux once J_0 was beyond some threshold limiting value. A closer examination of Figure 4-1(c), however, revealed a secondary trend for BSA fouling – J_{96hr} decreased slightly at higher J_0 (greater applied pressure). If the flux decline were solely governed by the interplay of drag force and surface interaction, one would expect all membranes with high initial fluxes to reach the same pseudo-stable flux given by Equation (4.2). While such behavior was observed for humic acid (see the horizontal line in Figure 4-2(b)),

the line for BSA at high initial flux had a slightly negative slope, suggesting that there might be an additional mechanism(s) involved in BSA fouling.

Figure 4-2. Conceptual model. (a) drag force and barrier force exerted on a foulant macromolecule when it approaches a membrane surface; (b) final flux vs. initial flux.

It is hypothesized that the additional flux reduction at higher initial flux (higher applied pressure) was due to the compaction of the BSA foulant layer. BSA compaction has been reported for microfiltration and ultrafiltration, where the hydraulic resistance of BSA foulant layer increased at higher applied pressure (Marshall et al. 1993; Iritani et al. 2002). To verify such foulant compaction behavior, BSA fouled membrane coupons were filtered with foulant-free electrolyte

solution after the 4-day fouling test. Despite the foulant-free environment, the membrane flux continued to decrease, and the further flux decline beyond the 4-day fouling test was slightly more at higher applied pressure (Figure 4-3). These observations support the BSA compaction hypothesis. Figure 4-1(c) further reveals that the BSA foulant layer was likely more compressible at pH 7 compared to pH 5.8, consistent with the observation by Iritani et al. (Iritani et al. 2002) that BSA foulant layers formed at reduced electrostatic repulsion conditions were more compact and less compressible. Thus, the current study suggests that, while the long term flux behavior during BSA fouling was dominated by the balance of permeate drag force and foulant-membrane surface interaction, the foulant layer compaction nevertheless played a secondary role. In contrast, foulant layer compaction does not seem to play a significant role during humic acid fouling (see Figure 4-2(b) and (Tang and Leckie 2007; Tang et al. 2009c)). Further investigation on foulant compressibility is needed, especially in the context of RO and NF fouling.

Figure 4-3. Compaction of BSA foulant layer. The membranes used (NF270) here had already been fouled for 4 days under the following conditions: 20 mg/L BSA, 10 mM NaCl, pH 5.8, and temperature at $20 \pm 1^\circ\text{C}$. In the subsequent compaction period (96th – 138th hour), the background electrolyte (10 mM NaCl and pH 5.8, no BSA) was used.

To evaluate the effect of crossflow velocity, NF270 was tested at the same initial flux of $120 \text{ L/m}^2\cdot\text{h}$ with three different crossflow velocities (4.8, 9.5 and 19.0 cm/s). The required applied pressure was slightly lower at higher crossflow velocity (125 psi at 19.0 cm/s , compared to 129 psi at 4.8 cm/s), which was likely due to the reduced concentration polarization effects. Figure 4-4 shows that increased crossflow velocity only had a marginal effect on BSA fouling, with J_{96hr} slightly improved at higher crossflow velocity. Similar behavior was observed for RO and NF membranes fouled by humic acid (Tang et al. 2007c). The effect of crossflow was much more pronounced for larger particles (Li et al. 2003) by comparison. This apparent discrepancy on the effect of crossflow may be reconciled by considering the shear induced inertial force and lateral migration experienced by the foulant particles. It has been well documented in the membrane fouling literature (Cohen and Probstein 1986; Bacchin et al. 1995; Bacchin et al. 2006; Tang et al. 2010) that a foulant particle experiences a shear induced inertial force and lateral migration in addition to the permeate drag and surface interaction forces. These additional forces increase at higher crossflow velocities and tend to mitigate membrane fouling. However, the shear induced inertial force and lateral migration have a strong size-dependency and are only important for relatively large particles (size $\sim$ or $> 100 \text{ nm}$) (Bacchin et al. 1995; Bacchin et al. 2006). Thus, the limited effectiveness of increasing crossflow for BSA and humic acid was likely due to the small particle sizes for these macromolecules ($\ll 100 \text{ nm}$) such that the shear induced inertial force and lateral migration are less important (Bacchin et al. 2006). This justifies the conceptual model in Figure 3(a) that the pseudo-stable flux during BSA fouling was determined by the foulant-membrane surface interaction to a first approximation. When larger foulant particles are present, the limiting flux model presented in the current study may be extended to incorporate the additional colloidal forces (Bacchin et al. 1995; Bacchin et al. 2006). Further investigation on the size dependency of membrane fouling and its relationship to the limiting flux concept is warranted (Tang et al. 2010).

Figure 4-4. The effect of crossflow velocity on flux performance during BSA fouling. Other test conditions: membrane NF270, feed water containing 20 mg/L BSA and 10 mM NaCl at pH 5.8, and temperature at $20 \pm 1^\circ\text{C}$. The normalized flux was determined as the ratio of flux at time t over the initial flux (the flux at $t = 0$). Error bars were based on the analysis of duplicate measurements.

4.3.2 Effect of membrane properties

The effect of membrane properties on BSA fouling was evaluated using four commercial membranes: an RO membrane XLE, two NF membranes NF90 and NF270, as well as a UF membrane GM. Despite the large differences in their membrane properties (Table 3-2), it was observed that all these membranes reached a nearly identical final flux ($\sim 35 \text{ L/m}^2\cdot\text{h}$, see Figure 4-5). The membrane properties seemed to play little role towards the end of the 4-day fouling test, and even the porous UF membrane GM had the same long-term flux behavior as the non-porous RO and NF membranes. The current study suggests that the long-term flux behavior tends to be controlled by the foulant-fouled-membrane interaction (F_{barrier}^{f-f}), not the foulant-clean-membrane interaction (F_{barrier}^{f-m}) (Tang and Leckie 2007; Tang et al. 2009c). Once a cake layer forms on a membrane surface, the surface properties of the clean membrane are completely masked by the foulant layer (Tang et al. 2007a)

such that the additional foulants approaching the membrane surface only experience foulant-deposited-foulant interaction. Thus, Equation (4.3) may be re-written as:

$$J_s = \frac{F_{barrier}^{f-f}}{C_{drag}} \quad (4.3)$$

While the long term flux was independent of membrane types and properties, the short term flux during BSA fouling was clearly membrane-dependent (Figure 4-5). Among the non-porous membranes (XLE, NF90 and NF270), NF270 had the slowest flux decline during the first day of fouling. The superior anti-fouling behavior of NF270 may be attributed to its smooth and highly hydrophilic membrane surface (Table 3-2) (Park et al. 2005). In addition, NF270 also has a highly negatively charged surface, which may help to repel away negatively charged BSA molecules at pHs above the IEP. Compared to XLE, NF90 experienced much faster flux decline, presumably due to its rougher and less negatively charged membrane surface. Consistent with existing literature, the current study suggests that smooth and hydrophilic membranes with favorable electrostatic interaction are preferred for improved fouling performance (Vrijenhoek et al. 2001; Park et al. 2005). Interestingly, the porous UF membrane GM experienced a dramatic flux decline within the first 6 hrs of fouling test, despite its smooth and relatively hydrophilic membrane surface. This was likely due to the highly non-homogenous flux distribution over a UF membrane – the local (micro-scale) membrane flux over a membrane pore is expected to be much higher than the macro-scale flux averaged over the entire membrane area. The high local flux tends to promote severe UF fouling (i.e., pore plugging) (She et al. 2009). One may further hypothesize that the flux becomes more evenly distributed when membrane fouling proceeds, as a consequence of the preferential foulant deposition over high flux regions. Eventually, the flux becomes more homogeneous when a thick foulant cake layer is formed. This cake layer also completely masks the properties of the UF membrane including its pore structure, which explains the membrane-independent long-term flux observed in the current study.

Figure 4-5. The effect of membrane properties on flux performance during BSA fouling. Other test conditions: feed water containing 20 mg/L BSA and 10 mM NaCl at pH 5.8, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. The normalized flux was determined as the ratio of flux at time t over the initial flux (the flux at $t = 0$). Error bars were based on the analysis of duplicate measurements.

Another interesting observation in Figure 4-5 is that membranes NF270 and XLE had a relatively stable flux in the initial fouling stage (i.e., a meta-stable condition within the 6th – 24th hours). According to our earlier discussion, both membranes had favorable foulant-clean-membrane interactions that tend to retard severe fouling. Thus, this meta-stable flux behavior was likely due to the slow conditioning of the clean membranes by the deposition of foulant molecules (Lee et al. 2010). Once the favorable foulant-clean-membrane interaction was transitioned to a less favorable foulant-fouled-membrane interaction, flux decline started to accelerate (after the 1st day fouling, Figure 4-5). Similar transitions can also be observed in Figure 4-1(a) and Figure 4-1(b), with the duration for the membrane conditioning phase significantly longer for lower initial flux and more favorable solution conditions (e.g., pH 7 over pH 5.8 due to enhanced electrostatic repulsion, see Section 4.3.3).

A prolonged meta-stable period with very slow or no flux decline is of high practical interest, and further research on this important aspect is warranted.

4.3.3 Effect of solution chemistry

Figure 4-6(a) shows the effect of solution pH on BSA fouling of NF270. Consistent with existing literature, we observed least stable flux behavior at the IEP (pH 4.7) of BSA. At pH > 4.7, the flux became more stable at higher solution pH. An extended meta-stable period (see Section 4.3.2) was observed for pH 7 and pH 7.8. Relatively stable flux was also observed at pH 3.8. This flux behavior can be understood via the foulant-foulant electrostatic interaction. As the pH deviates away from the IEP, the BSA molecules experience stronger intermolecular electrostatic repulsion, which helps to reduce membrane fouling (Ang and Elimelech 2007; Mo et al. 2008; She et al. 2009).

The effect of ionic composition on BSA fouling is shown in Figure 4-6(b) and Figure 4-6(c). Increasing ionic strength from 1 to 100 mM seems to promote BSA fouling (Figure 4-6(b)). The more severe flux decline at higher ionic strength can be explained by the reduced electrostatic repulsion as a result of electrical double layer compression (i.e., enhanced charge screening due to greater counterion concentration) (Ang and Elimelech 2007; She et al. 2009). Figure 4-6(c) shows the effect of Ca^{2+} and Mg^{2+} on BSA fouling, where the total ionic strength was kept constant (10 mM) by the addition of NaCl. Clearly, the presence of Ca^{2+} and Mg^{2+} in the feed water promoted severe membrane fouling. Divalent cations such as Ca^{2+} and Mg^{2+} are known to form a complex with carboxylic ($-\text{COO}^-$) moieties of natural organic matter and proteins, which neutralizes the negative charges carried by these macromolecules or binds them together via divalent ion bridging (Ang and Elimelech 2007; Tang et al. 2009c). Membrane surface charge density can be similarly reduced due to this charge neutralization effect. As a result of the weakened electrostatic repulsive force as well as the presence of specific ion interactions, the barrier force is significantly reduced to allow rapid deposition of BSA molecules and thus increase the rate of flux loss.

Figure 4-6. The effect of feed water chemistry on flux performance during BSA fouling. (a) the effect of pH; (b) the effect of ionic strength; and (c) the effect of divalent cations. Unless otherwise specified, the solution pH was 7 and ionic strength (IS) was 10 mM. Other test conditions: membrane NF270, feed water containing 20 mg/L BSA, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. The normalized flux was determined as the ratio of flux at time t over the initial flux (the flux at $t = 0$). Error bars were based on the analysis of duplicate measurements.

The role of electrostatic interaction in BSA fouling is further confirmed by Figure 4-7(a), which shows a strong correlation between J_{96hr} and the square of the zeta potential (ζ^2) of BSA under various solution pHs. Once again, this correlation can be explained by the conceptual model in the current study. In Figure 4-2 and Equation (4.4), the foulant-deposited-foulant interactions can arise from electrical double layer interaction (EDL interaction, F_{EDL}^{f-f}) as well as interactions of a non-EDL nature ($F_{non-EDL}^{f-f}$, such as van der Waals interaction and acid-base interaction), where F_{EDL}^{f-f} is proportional to ζ^2 (Hogg et al. 1966). Thus, J_s is linearly dependent on ζ^2 :

$$J_s = a \zeta^2 + \frac{F_{non-EDL}^{f-f}}{c_{drag}} \quad (4.4)$$

where a is a proportionality constant with a unit of $\text{L}/\text{m}^2 \cdot \text{h} \cdot \text{mV}^2$.

Equation (4.4) is useful to understand the effect of ionic composition in addition to the effect of pH. The final flux J_{96hr} is plotted against ζ^2 for a wide range of feed water chemistries (pH 4.7 – 7.8, ionic strength of 1 – 100 mM, 0-3 mM Ca^{2+} , and 0-1 mM Mg^{2+}) in Figure 4-7(b). The data point corresponding to pH 3.8 is excluded from the plot, as significant conformational changes occur at such a low pH (Palecek and Zydney 1994b). Figure 4-7(b) shows a clear linear correlation between J_{96hr} and ζ^2 , once again confirming the important role of foulant-foulant electrostatic interaction on the long term flux behavior of macromolecules. This also agrees well with earlier investigations (Palecek and Zydney 1994b; Tang et al. 2009c) that reported linear correlations between J_s and the square of foulant charge density (q^2). The advantage of using zeta potential lies in its simplicity and versatility compared to charge density measurements via potentiometric titration, especially when the effect of ionic composition needs to be evaluated (Tang et al. 2007c; Tang et al. 2009c). The current study suggests that ζ^2 can be potentially used as a good indicator to predict the long term fouling behavior of macromolecules, although further research is still needed to verify its applicability for other types of foulants.

(a)

(b)

Figure 4-7. The effect of foulant-foulant electrostatic interaction on BSA fouling. (a) flux at 96 hrs and zeta potential squared as a function of pH for a feed water containing 20 mg/L BSA and 10 mM NaCl; (b) flux at 96 hrs vs. zeta potential squared for various feed water chemistry. Other test conditions: membrane NF270, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bars were based on the analysis of duplicate measurements.

4.4 Conclusions

The effects of hydrodynamic conditions, membrane properties, and feed solution chemistry on BSA fouling were systematically evaluated in the current study. The results suggest that the long term flux decline was primarily determined by the interplay of permeate drag force and the resisting barrier force, although higher applied pressure tends to slightly reduce the long term flux likely due to the compaction of the foulant layer. While the initial flux behavior was highly dependent on membrane properties (and thus foulant-clean-membrane interaction), the long term flux behavior was independent of membrane properties and was largely controlled by foulant-deposited-foulant interaction. The current study also demonstrated the important role of electrostatic interaction during BSA fouling, with ζ^2 of the foulant being potentially a good indicator for predicting the long term fouling behavior.

Chapter 5

Fouling of nanofiltration, reverse osmosis and ultrafiltration membranes by protein mixtures: The role of inter-foulant-species interaction

5.1 Introduction

In Chapter 4, reverse osmosis (RO) and nanofiltration (NF) fouling by a single protein feed containing BSA has been systematically studied, which suggests that protein fouling is highly dependent on solution chemistry. Likewise, existing literature (Palecek and Zydney 1994b; Ang and Elimelech 2007; Mo et al. 2008; She et al. 2009) reported that membrane flux is generally least stable when the solution pH is close to the isoelectric point (IEP) of a protein due to the lack of electrostatic repulsion between the molecules. Studies of RO and NF fouling by BSA revealed that fouling was more severe at higher ionic strength, which is attributed to the electric double layer compression effect and the associated suppression of intermolecular electrostatic repulsive force between BSA molecules (Ang and Elimelech 2007; Mo et al. 2008; Wang and Tang 2011). In addition to unfavorable solution conditions, protein fouling can also be promoted by elevated membrane permeate flux (Wu et al. 1999; Ang and Elimelech 2007; She et al. 2009; Wang and Tang 2011). A similar effect of permeate flux has also been observed for other macromolecules (Hong and Elimelech 1997b; Lee and Elimelech 2006; Tang and Leckie 2007).

However, many of these fouling studies involved only a single type of protein in the feed water (such as bovine serum albumin (BSA)) (Tang et al. 2010). In practice, typical feed water for RO and NF contains a mixture of foulants rather than a single well-defined foulant. Thus, investigations on fouling by mixed foulant species can be highly valuable. Compared to a single-foulant feed, a binary-foulant system is much more complicated (Palacio et al. 2003; Hughes et al. 2007; Tang et al. 2010).

Controlled laboratory studies on fouling by the mixture of BSA and alginate revealed accelerated membrane permeability loss compared to that induced by BSA or alginate alone (Ang and Elimelech 2007). In contrast, filtration of a feed consisting of humic acid and polysaccharide (Mänttari et al. 2000) showed that the presence of humic acid might help to mitigate polysaccharide fouling. Complicated fouling behavior was also reported for organic-inorganic foulant mixtures (Lee et al. 2005; Contreras et al. 2009). Presumably, the inter-foulant-species interaction may play a critical role in a mixed foulant system in addition to the intra-foulant-species interaction and foulant-membrane interaction (Tang et al. 2010). To date, systematic investigations on the role of foulant-foulant interaction on membrane fouling by mixed foulants are still scarce. In addition, the dependence of fouling on solution chemistry, membrane properties, and hydrodynamic conditions is poorly understood for such systems.

The objective of the current study was to investigate the effect of solution chemistry, membrane properties, and hydrodynamic conditions on binary protein fouling of RO, NF, and UF membranes. BSA, lysozyme (LYS) and their binary mixture were used as the model foulants. The current study may provide important insights on the role of foulant-foulant interactions and hydrodynamic forces in mixed foulant systems.

5.2 Materials and methods

5.2.1 Chemicals and materials

Unless specified otherwise, all reagents and chemicals were of analytical grade with purity over 99%. Ultrapure water (resistivity of 18.2 MΩ.cm) was used to prepare working solutions. The pH and ionic compositions of the feed solution were adjusted by the addition of sodium chloride, hydrochloric acid, and sodium hydroxide.

Bovine serum albumin (BSA, Sigma-Aldrich A7906) and lysozyme (LYS, Fluka 62971) were used as model protein foulants to represent two proteins of very

different IEPs. Based on the zeta potential measurements performed in the current study (Malvern ZetaSizer Nano ZS, following the method reported in Ref. (Wang and Tang 2011)), the IEP for BSA is $\sim$ pH 4.7 and that for LYS is $\sim$ pH 10.4 (Figure 5-1). Both proteins were received in powder form with $\geq 98\%$ purity and were stored at 4°C in the dark. The molecular weights of BSA and LYS are 67 kDa and 14.3 kDa, respectively (Palecek and Zydney 1994b; Palacio et al. 2003; Ang and Elimelech 2007). Protein working solutions were freshly prepared prior to each fouling experiment.

Figure 5-1. Zeta potential of BSA and LYS in 10 mM NaCl as a function of pH. At least 2 replicate measurements were performed for each condition. Error bars were based on the analysis of duplicate measurements.

The membranes investigated in the current study include three Dow FilmTec[®] membranes (an RO membrane XLE and two NF membranes NF90 and NF270), and one GE Osmonics[®] UF membrane (membrane GM). Their properties have been reported in our previous studies (Tang et al. 2007d; Tang et al. 2009b; Tang et al. 2009a; Wang and Tang 2011), and are summarized in Table 3-2.

Membrane fouling experiments were performed using a laboratory scale crossflow filtration setup under constant pressure conditions (Figure 3-1). The details and description of the setup can be found elsewhere ((Wang and Tang 2011) and Section 3.2.1). For each fouling run, a new membrane coupon was soaked in ultrapure water overnight before being loaded into the test cell. The coupon was first compacted for 2 days under pressure to ensure that any subsequent flux decline after the addition of foulant was not influenced by the mechanical compaction of the membrane (see section 3.2.1). The desired amount of foulant was added to the feed solution at the end of the 2-day compaction stage to initiate membrane fouling, and the test was continued for another 4 days. During the entire 6-day test, the same applied pressure, crossflow velocity and background electrolyte solution chemistry (pH and ionic composition) were used. Unless specified otherwise, the following reference conditions were applied:

- a total foulant concentration of 20 mg/L (10 mg/L BSA + 10 mg/L LYS for the BSA-LYS mixture)
- pH 7 and total ionic strength of 10 mM (adjusted by addition of NaCl)
- crossflow velocity at 9.5 cm/s with diamond patterned spacer used in the feed water channel
- feed tank temperature at $20 \pm 1^\circ\text{C}$

5.2.2 Contact angle measurement

Both virgin and fouled membranes were rinsed with Milli-Q water and then air dried before being transferred to a freeze dryer (CHRIST Alpha 1-4). After drying for 24 hours in the freeze dryer, the membranes were characterized with a contact angle analyzer (OCA, LMS Technologies PTE LTD) using the sessile drop method at room temperature of $\sim 23^\circ\text{C}$ (refers to Section 3.2.2.4). Each reported contact angle is the average of at least five measurements for the same membrane sample at different locations.

5.3 Results and discussion

5.3.1 Zeta potential of BSA and LYS

The zeta potential results of BSA and LYS as a function of pH are presented in Figure 5-1. The IEPs of BSA and LYS were $\sim$ pH 4.7 and pH 10.4, respectively, consistent with the values reported in the literature (Palecek and Zydney 1994b). Around neutral pH, BSA was negatively charged while LYS was positively charged.

5.3.2 Mixed protein fouling versus single protein fouling

Figure 5-2 shows the flux behavior of an NF membrane (NF270) in the presence of binary mixture of BSA and LYS (10 mg/L BSA and 10 mg/L LYS). For comparison purposes, the flux during fouling by a single protein (20 mg/L BSA or LYS) is also shown in the same figure. Two different initial fluxes (75 and 120 L/m²·h) were evaluated. In both cases, the flux decline caused by the BSA-LYS mixture was much more extensive compared to that due to either BSA or LYS alone, in despite of the same total protein concentration used for all the experimental runs. The more severe fouling of the mixed protein system may be attributed to the electrostatic attraction between the oppositely charged BSA and LYS molecules, which tends to destabilize the mixture and promote protein attachment onto the membrane.

Figure 5-2. Comparison of flux behavior of mixed protein fouling with single protein fouling. (a) initial permeate flux at 75 L/m²·h; (b) initial permeate flux at 120 L/m²·h. Other test conditions: membrane NF270, total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS for the mixed protein case), pH 7, ionic strength of 10 mM (adjusted by the addition of NaCl), crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1°C. Error bars were based on the analysis of duplicate measurements.

5.3.3 Effect of solution chemistry on mixed protein fouling

While the effect of solution chemistry on single protein fouling of RO/NF membranes has been well documented in the literature (Ang and Elimelech 2007; Mo et al. 2008; Wang and Tang 2011), information on mixed protein systems is still lacking. Figure 5-3 shows the effect of ionic strength on BSA-LYS mixture fouling at a solution pH of 7.0. More severe fouling was observed at reduced ionic strength. At lower ionic strength (1 and 10 mM), rapid flux decline was observed within the first 12 hours of the fouling tests ($\sim 70\%$ flux loss at 1 mM and 50% at 10 mM). In comparison, the rate of flux loss at 100 mM was much slower. The pseudo-stable flux at the end of the fouling test (J_{96hr}) was $\sim 42 \text{ L/m}^2\cdot\text{h}$ at 100 mM, nearly double that of the corresponding values at 1 and 10 mM. It is interesting to note that the trend observed for the mixed protein system in the current study was directly opposite to those reported in the literature for single protein systems. Many previous studies reported that RO and NF membrane fouling by BSA was more severe at higher ionic strength as a result of weakened electrostatic repulsion between BSA molecules (i.e., the electrical double layer (EDL) compression effect (Ang and Elimelech 2007; Mo et al. 2008; Wang and Tang 2011)). This apparent contradiction may be reconciled by considering the major difference between a single protein system and a mixed protein system – the presence of additional inter-foulant-species interaction (i.e., the BSA-LYS interaction) for the latter. In the current study, BSA and LYS were oppositely charged at pHs within their respective IEPs ($4.7 < \text{pH} < 10.4$, Figure 5-1), such that the BSA-LYS electrostatic interaction was attractive under these conditions. Consequently, increasing ionic strength suppresses the electrostatic attraction between adjacent BSA and LYS molecules due to the EDL compression and thus retards membrane fouling by the protein mixture. The results in Figure 5-3 further suggests that the BSA-LYS inter-species electrostatic attraction may play a dominant role over the BSA-BSA or LYS-LYS intra-species electrostatic repulsion at pH 7.0, which is consistent with the more severe fouling for the mixed protein system (Figure 5-2).

The effect of pH on mixture fouling is shown in Figure 5-4(a) over a pH range of 3.5-8.2. The permeate flux at pH 3.5 was reduced by $\sim 1/3$ over the 4 day fouling

test. In contrast, the flux losses at pH 4.7, 7.0, and 8.2 were much more prominent ($\sim 2/3$ flux reduction in the first 24 hours and $> 80\%$ over 4 days). At pH 3.5 (pH below IEP_{BSA} and IEP_{LYS}), both BSA and LYS were positively charged (Figure 5-1) and thus the more stable flux at this solution pH may be explained by the BSA-LYS interspecies electrostatic repulsive force. By comparison, such electrostatic repulsion did not occur at pH 4.7, 7.0, and 8.2 ($\text{IEP}_{\text{BSA}} \leq \text{pH} \leq \text{IEP}_{\text{LYS}}$).

Figure 5-3. Effect of ionic strength on flux performance during mixed protein fouling. Other test conditions: membrane NF270, total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS), pH 7, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bars were based on the analysis of duplicate measurements.

It is also interesting to observe that the final fluxes (J_{96hr}) were nearly identical at pH 4.7, 7.0, and 8.2 (Figure 5-4(a)), which suggests that the BSA-LYS mixture fouling had very weak pH-dependence within this pH range. This is in direct contrast to the strong pH-dependence when there was either BSA or LYS alone in the feed solution (Figure 5-5). Figure 5-4(b) plots J_{96hr} as a function of pH. When there was only a single protein (either BSA or LYS) in the feed water, improved J_{96hr} was observed at pHs away from the protein's IEP. For instance, the J_{96hr} value increased from its minimum value $\sim 25 \text{ L/m}^2\cdot\text{h}$ at pH 4.7 (i.e., IEP of BSA) to nearly $60 \text{ L/m}^2\cdot\text{h}$ at pH 7.8, which may be attributed to the enhanced BSA-BSA

electrostatic repulsion (Palecek and Zydney 1994b; Ang and Elimelech 2007; Mo et al. 2008). Similar flux enhancement was observed at a lower pH ($J_{96hr} \sim 85 \text{ L/m}^2\cdot\text{h}$ at pH 3.8). The BSA-LYS mixture had comparable J_{96hr} values to those for BSA alone at a pH around or below 4.7, where the BSA-LYS electrostatic interaction was either repulsive (pH 3.5) or negligible (pH 4.7). However, when the solution pH was within the IEPs of the two proteins, the pseudo-stable fluxes for the binary mixture were significantly lower compared to those for BSA alone. Within the two IEPs (pH 4.7-10.4), the final flux did not seem to benefit from the enhanced BSA-BSA electrostatic repulsion, likely due to the presence of the BSA-LYS attractive interaction. As discussed earlier (Figure 5-2 and related discussion on the effect of ionic strength), the flux behavior for the mixed proteins in this pH range was likely dominated by the BSA-LYS interaction. Presumably, the mixed foulants may deposit in a fashion that the negatively charged BSA molecules may be surrounded by the oppositely charged LYS molecules (and vice versa) to energetically achieve a more stable arrangement (Hogg et al. 1966), which renders the BSA-BSA (or LYS-LYS) interaction less important.

The above discussion may be captured by the simple conceptual model presented in Figure 5-4(c). For a mixture containing proteins A and B (where $\text{IEP}_A < \text{IEP}_B$), the flux behavior may be dominated by the attractive A-B interaction if the solution pH is within the two IEPs. In this region, a rise in ionic strength tends to increase the pseudo-stable flux as a result of the weakened A-B electrostatic attraction. In contrast, at pH below IEP_A or above IEP_B , the fouling behavior is likely governed by the respective A-A or B-B interaction, such that the mixed protein fouling behaves in a similar manner as the corresponding single protein case. This conceptual model interprets the effect of solution chemistry via both inter-species and intra-species foulant-foulant electrostatic interactions. Despite the fact that other non-electrostatic interactions may also play a role in a binary protein mixture, the conceptual model was able to provide an insightful and consistent explanation of the flux dependence on pH and ionic strength during mixed protein fouling. This is because that the electrostatic interactions for charged molecules and particles are much more strongly affected by solution pH and ionic strength compared to non-

electrostatic interactions (Tang et al. 2010). Future research is warranted to further address the role of both electrostatic and non-electrostatic interactions in mixed foulant systems.

(c)

Figure 5-4. Effect of solution pH on flux performance during mixed protein fouling. (a) flux as a function of time at various solution pHs; (b) final flux at 96 hours as a function of pH for both fixed protein and single protein fouling; (c) a simple conceptual model for mixed protein fouling. Other test conditions: membrane NF270, total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS for the mixed protein case), ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bars in (a) and (b) were based on the analysis of 2-3 replicates under the identical fouling conditions.

Figure 5-5. Effect of solution pH on flux performance during single protein fouling. The feed solution contained either 20 mg/L BSA or LYS. Other test conditions: membrane NF270, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$.

5.3.4 Effect of membrane properties on mixed protein fouling

Figure 5-6 shows the flux behavior of the four membranes (NF270, XLE, NF90 and GM) fouled by the binary protein mixture at various solution pHs. To ensure that the experimental results are directly comparable, the membranes were subjected to the same initial permeate flux of $75 \text{ L/m}^2\cdot\text{h}$. Under all cases, the three nonporous membranes (NF270, XLE and NF90) had higher pseudo-stable fluxes compared to the porous UF membrane GM. At pH 7.0 and 4.7 where severe membrane fouling had occurred (Figure 5-6(a) and Figure 5-6(b)), nearly identical fluxes were obtained for NF270, XLE and NF90 at long filtration times, notwithstanding the clean membranes had very different membrane properties (Table 3-2). This suggests that the long-term fouling tends to be controlled by the foulant-fouled-membrane interaction, which is a strong function of the solution chemistry. Under severe fouling conditions, the membrane surface can be completely masked by the foulant cake layer (Tang et al. 2007a), which renders the pseudo-stable flux

independent of the properties of RO and NF membranes (Tang and Leckie 2007; Tang et al. 2009c; Wang and Tang 2011). One example is that the contact angle results showed similar hydrophobicity of the fouled membranes, although they were very different for clean membranes (Figure 5-7). However, a strong membrane dependency was observed at pH 3.5 (Figure 5-6(c)), with J_{96hr} increased in the following order: NF90 < XLE < NF270. Membrane fouling at pH 3.5 was relatively mild such that the foulant-clean-membrane interaction may still play an important role. A closer examination of the initial flux behavior for the three membranes at pH 7.0 and 4.7 showed that the membrane flux within the first several hours followed the same order (NF90 < XLE < NF270). As well, this order was also consistently observed for single protein fouling (either BSA or LYS, see Figure 5-8). The current study revealed that the behavior of initial fouling and the long term flux under mild fouling conditions were dominated by foulant-clean-membrane interaction, while the long term flux behavior under severe fouling conditions was controlled by foulant-fouled-membrane interaction. The better anti-fouling performance of NF270 was likely attributed to its more hydrophilic and smoother membrane surface compared to XLE and NF90 (Table 3-2). On the other hand, the membrane surface charge was probably less influential in the current study, based on following two observations: 1) that the same order was achieved regardless of the charge of the foulant molecules (whether it is negatively charged BSA alone, or positively charged LYS, or their binary mixture, see Figure 5-6 and Figure 5-8), and 2) that this order was not affected by the solution pH (Figure 5-6) despite the fact that the membrane surface charge can be strongly affected by pH (Tang et al. 2007d).

Figure 5-6. Effect of membrane properties on flux performance during mixed protein fouling at (a) pH 7.0, (b) pH 4.7, and (c) pH 3.5. Other test conditions: total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS), ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$.

Figure 5-7. Contact angles of virgin and 96-hr fouled membranes. Fouling conditions: total foulant concentration of 20 mg/L (10 mg/L BSA + 10 mg/L LYS), pH 7, ionic strength of 10 mM (NaCl), crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1 °C. Each reported contact angle is the average of at least 5 measurements for the same membrane sample at different locations, with the error indicating one standard deviation.

Figure 5-8. Effect of membrane properties on flux performance during single protein fouling. The feed solution contained either 20 mg/L BSA or LYS. Other test conditions: pH 4.7, ionic strength of 10 mM (adjusted by the addition of NaCl), crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bars were based on the analysis of duplicate measurements.

Figure 5-9. Comparison of flux behavior of mixed protein fouling with single protein fouling for the UF membrane GM. Other test conditions: total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS for the mixed protein case), initial permeate flux at 75 L/m²·h, pH 7, ionic strength of 10 mM (adjusted by the addition of NaCl), crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1°C.

As shown in Figure 5-6, the UF membrane GM suffered drastic flux loss under a wide pH range (~ 80% flux reduction within the first hour of fouling at pH 7.0 and 4.7, and ~ 50% at pH 3.5). In the current study, the porous GM membrane has an MWCO of ~ 8 kDa, which is comparable to the molecular weight of LYS (14.3 kDa) (The molecular weight of BSA is significantly larger (67 kDa)). Thus, it might be hypothesized that the severe initial flux decline experienced by GM was due to membrane pore plugging by the small LYS molecules. In Figure 5-9, the flux behavior of membrane GM due to BSA-LYS mixture fouling was compared to the respective single protein cases. The fouling curve for LYS alone was nearly identical to that for the mixture fouling. This observation is consistent with the hypothesis that the dramatic flux decline of GM in the presence of the mixture was mainly caused by pore plugging by the small LYS molecules. When the feed water contained only BSA, the membrane GM experienced less severe flux decline and

the final stable flux was almost identical to those of the non-porous membranes (NF270, XLE and NF90, see Figure 5-8), suggesting that cake layer formation was likely playing a more significant role for fouling by the larger BSA molecules.

5.3.5 Effect of initial flux on mixed protein fouling

The effect of initial permeate flux on the mixture fouling is presented in this section. Figure 5-10(a) shows the flux behavior of NF270 under two different initial flux values (120 and 75 L/m²·h), where the feed solution contained 10 mg/L BSA and 10 mg/L LYS in 10 mM NaCl at pH 7. Severe membrane fouling occurred in both cases, and the test with higher initial flux suffered greater flux decline; it is interesting to note the similar long term flux behavior - both reached an identical J_{96hr} value of ~ 22 L/m²·h. As also shown in Figure 5-6(a), the same pseudo-stable flux value was attained for the other non-porous membranes XLE and NF90. Figure 5-10(b) shows the membrane flux behavior under an initial flux of 15-120 L/m²·h at an ionic strength of 100 mM. As discussed in Section 5.3.3, membrane fouling by oppositely charged proteins experienced a decrease in flux decline at the higher ionic strength due to the depression of BSA-LYS electrostatic attraction. For the test with an initial flux of 120 L/m²·h at 100 mM ionic strength, its J_{96hr} was ~ 44 L/m²·h. The same J_{96hr} value was also attained when the initial flux was 50 L/m²·h. However, only mild flux decline was observed when the initial flux level was lower than or close to 44 L/m²·h. These results revealed that the permeate flux of a non-porous membrane was largely membrane-limited under low initial flux conditions (minimal membrane fouling and flux controlled by membrane resistance), and foulant-limited under elevated initial flux conditions. In the latter case, severe flux reduction may occur, and there was a strong tendency to approach an identical limiting value (i.e., the limiting flux (Tang and Leckie 2007; Tang et al. 2009c; Tang et al. 2010)) that was independent of membrane surface properties and initial flux conditions. Furthermore, consistent with our discussion in Sections 5.3.3 and 5.3.4, the long term flux behavior was likely limited by the foulant-fouled-membrane interaction (thus solution chemistry) at elevated initial flux conditions (initial flux > limiting flux).

Figure 5-10. Effect of initial flux on the flux performance during mixed protein fouling. (a) pH 7, ionic strength of 10 mM; (b) pH 7, ionic strength of 100 mM. Other test conditions: membrane NF270, total foulant concentration 20 mg/L (10 mg/L BSA + 10 mg/L LYS), crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bars in (a) were based on the analysis of duplicate measurements.

5.4 Conclusions

The current study has important implications for membrane fouling by protein mixtures (or mixture of other types of macromolecules):

- 1) For a binary system containing macromolecules A and B (where $IEP_A < IEP_B$), the inter-foulant-species interaction (A-B interaction) may play a critical role in addition to the intra-foulant-species interactions (A-A and B-B interactions). When the pH is within the two IEPs of A and B, membrane permeate flux can be significantly destabilized by the A-B electrostatic attraction. In order to achieve optimal flux stability (or enhanced cleaning efficiency), the solution pH needs to be either below IEP_A or above IEP_B .
- 2) The effect of solution chemistry in a mixed foulant system can be potentially different from (or even directly opposite to) a single foulant system. For example, while the majority of existing studies reported reduced flux stability at higher ionic strength in the presence of a single type of charged macromolecules, the current study clearly demonstrated the opposite trend when the inter-species electrostatic attraction dominates the system. Further investigations are necessary to achieve improved mechanistic understanding of the foulant behavior in such multi-foulant systems.
- 3) The long term flux behavior can be either membrane-controlled or foulant-controlled. In the foulant controlled region (e.g., this can be promoted by a higher initial flux or unfavorable solution conditions), the membrane surface properties had little influence of the long term flux behavior, and this is usually accompanied with severe flux decline. From a practical point of view, this region needs to be avoided by either stabilizing the feed solution or reducing the permeate flux.
- 4) Compared to non-porous NF and RO membranes, porous membranes are more likely to experience dramatic flux decline due to the risk of pore plugging. One

potential way to enhance the anti-fouling performance of a UF membrane is to control the surface pore size and pore size distribution via surface modification.

Chapter 6

Nanofiltration membrane fouling by oppositely charged macromolecules - An investigation on flux behavior, foulant mass deposition, and solute rejection

6.1 Introduction

RO and NF fouling by colloids and macromolecules has received considerable attention in the past few decades. Prior fouling studies with various feeds have revealed many important factors that affect fouling; they can be summarized as solution chemistry, hydrodynamic conditions and membrane properties. A recent review of the mechanisms and factors controlling fouling of both RO and NF membranes (Tang et al. 2010) pointed out the importance of mass transfer near the membrane surface and colloid-membrane (colloid-colloid) interactions that are directly linked to the feed solution chemistry. Past studies on porous ultrafiltration (UF) and microfiltration (MF) of single macromolecular feeds showed that electrostatic interactions between molecules play an important role. This was inferred from the effect of solution pH and ionic strength on fouling (Palecek et al. 1993; Palecek and Zydney 1994b; Yuan and Zydney 2000; She et al. 2009). This interaction has also been observed in non-porous RO and NF fouling studies; similar trends were usually observed for both porous and non-porous membranes: fouling was more severe at pH values close to the isoelectric point (IEP) of the macromolecules and at higher ionic strength due to reduced electrostatic interaction (Ang and Elimelech 2007; Tang and Leckie 2007; Tang et al. 2009c). Calcium complexation with macromolecules was also observed to increase the fouling rate markedly (Lee and Elimelech 2006; Li et al. 2007).

The feed water for NF or RO often contains more than one potential foulant. In fact, more complex studies with more than one model foulant were proposed a long time ago (Belfort et al. 1994). A few studies of mixed foulant feeds have shown different

dominant effects and fouling mechanisms: 1) a pre-filtering effect, i.e., one foulant acts as a pre-filter for another to reduce fouling in MF/UF (Arora and Davis 1994; Palacio et al. 2003); 2) a synergistic effect that explains the more severe flux decline by the mixed foulants rather than that by any single foulant (Ang and Elimelech 2007; Susanto et al. 2008); 3) an averaging effect where the rate and the extent of flux reduction for the mixture falls in between that of the two single foulants (Lee and Elimelech 2006; Zazouli et al. 2010); 4) an adsorption effect where macromolecules coated inorganic particles that alters the surface properties of the latter (Lee et al. 2005; Contreras et al. 2009); and 5) an effect arising from oppositely charged macromolecules that was shown by UF of feed containing binary proteins of different IEP (Iritani et al. 1997; Lin et al. 2008).

However, almost all NF/RO fouling studies used like-charged foulants for the test conditions. The handful of studies on UF fouling by oppositely charged macromolecules is not representative for non-porous RO and NF membranes due to their different fouling mechanisms. There has been no systematic study of the effect of solution chemistry on RO/NF fouling by mixed foulants. Moreover, an understanding of cake formation and ion rejection due to fouling by mixed macromolecules is lacking. Therefore, this study had three main objectives: 1) to systematically investigate solution chemistry effects on NF membrane fouling by a feed solution containing oppositely charged macromolecules; 2) to correlate mass deposition with flux decline at various conditions; and 3) to compare the change in salt rejection and correlation with cake deposition for different solution chemistries.

6.2 Materials and methods

6.2.1 Design considerations

The experiment was properly designed to include the considerations of membrane, chemicals, setup and fouling tests. The membrane chosen for the study was a commercial NF membrane from Dow FilmTec[®], in order to be consistent with our previous studies (see Chapters 4 and 5). Foulants needed to be oppositely charged, and were able to be quantified individually from the mixture. During fouling

experiments the conditions such as crossflow velocity, pressure, solution chemistry (pH, ionic strength, etc) and temperature should be well controlled.

6.2.2 Chemicals

Unless specified otherwise, all reagents and chemicals were of analytical grade with purity over 99%. Ultrapure water with a resistivity of 18.2 M Ω .cm (Millipore Integral 10 Water Purification System) was used to prepare all working solutions. The pH and ionic compositions of the feed solution were adjusted by the addition of sodium chloride, calcium chloride, hydrochloric acid, and sodium hydroxide.

Sodium alginate (Sigma A2158) and lysozyme (LYS, Fluka 62971) were used to represent polysaccharide and protein foulants of opposite charges under testing conditions. Alginate is negatively charged at neutral pH (pH 5-7) due to its high content of carboxylic groups, and LYS is positively charged below pH 10.4. The molecular weights of alginate and LYS are ~12-80 and 14.3 kDa, respectively (Palecek and Zydney 1994b; Palacio et al. 2003; Ang and Elimelech 2007). Both were received in powder form with purity above 98% and were stored at 4°C in the dark. Working solutions were freshly prepared prior to each fouling experiment.

6.2.3 Nanofiltration membrane

A commercial nanofiltration membrane NF270 (Dow FilmTec[®]) was used in the current study. Its properties have been reported in our previous studies ((Tang et al. 2007d; Tang et al. 2009b; Tang et al. 2009a; Wang and Tang 2011) and Table 3-2). This semi-aromatic piperazine based thin film composite membrane has an extremely smooth surface with a root mean square roughness R_{RMS} of ~ 9 nm (Tang et al. 2007a; Tang et al. 2007d; Tang et al. 2009b; Tang et al. 2009a). Its surface is negatively charged at neutral pH range with a zeta potential of ~ 35 mV at pH 7 (in 10 mM NaCl). The surface is highly hydrophilic with a contact angle below 30°. The permeability and the NaCl rejection of the membrane are ~0.87 L/m²·h·psi and 50-60 %, respectively (tested at 90 psi (620 kPa) with a 10 mM NaCl feed water).

6.2.4 Filtration setup and experiment

Membrane fouling experiments were performed using a laboratory scale crossflow filtration setup under constant pressure conditions (Figure 3-1). The details and description of the setup can be found elsewhere ((Wang and Tang 2011) and in Section 3.2.1).

The fouling test procedures were adapted from Tang et al. (Tang et al. 2007c). The membrane compaction and equilibration stage followed exactly the procedure detailed in Section 3.2.1. At the end of the 2-day equilibration stage, pre-dissolved foulant solutions were added to achieve the desired total foulant concentration of 20 mg/L. The initial permeate flux (at time 0) was taken as the membrane flux immediately before the addition of foulants. The fouling experiments continued for another 4 days. Pressure and crossflow velocity were maintained constant throughout the fouling experiments. The effect of relative foulant concentration, pH, calcium concentration and initial flux were evaluated by varying one variable at a time while maintaining the rest at constant conditions. Unless specified otherwise, the following reference conditions were applied:

- a total foulant concentration of 20 mg/L (LYS + alginate for the mixed system);
- a total ionic strength of 10 mM (adjusted by addition of NaCl and CaCl₂);
- crossflow velocity was 9.5 cm/s with diamond patterned spacer used in the feed water channel; and
- feed tank temperature was controlled at $20 \pm 1^\circ\text{C}$.

The conductivity of the permeate was measured with a conductivity meter (Ultrameter II, Myron L company) at predetermined time intervals to record the conductivity rejection at different fouling stages.

6.2.5 Foulant mass deposition analysis

Fouled membrane coupons were gently rinsed with Milli-Q water to remove the labile foulants. One or two samples of area of $1.267 - 2.534 \text{ cm}^2$ were cut from the

fouled coupons and soaked in extraction solution. Sodium dodecyl sulfate (SDS, 5%) (Jones and O'Melia 2000) and NaOH (0.1%) (Guo et al. 2009) were used for LYS and alginate extraction, respectively. Mild sonication (below 30 °C, 20 minutes) was employed after one day of soaking. The extractant of LYS was analyzed using a protein assay kit (Sigma, QuantiPro™ BCA Assay Kit, 0.5-30 µg/ml) at UV of 562 nm (Brown et al. 1989), and that of alginate was examined using the phenol-sulfuric acid method at UV of 485 nm (Dubois et al. 1956) (UV spectrophotometer, UV-1700 Shimadzu). Sample standard curves are provided in the Appendix (Figure B.1).

6.2.6 Zeta potential measurement of macromolecules

The zeta potential of the macromolecules was measured using the Laser Doppler Velocimetry (LDV) technique (Malvern ZetaSizer Nano ZS) (Jachimska et al. 2008). Solutions of LYS or alginate were freshly prepared. The ionic composition was adjusted by the addition of NaCl to achieve the desired ionic strength, and pH adjustment was done by adding HCl or NaOH. The sample solution was then injected into the zeta potential cell carefully to avoid any formation of bubbles that might interfere with the measurement.

6.3 Results and discussion

6.3.1 Overview of the results

Both flux behavior and mass deposition were analyzed and correlated for investigating the effect of relative concentration of macromolecules, solution pH, calcium concentration and initial flux on fouling. Salt rejection was also tracked during the 96-hr fouling to gain some understanding of the effect of cake formation on dissolved ion rejection.

6.3.2 Zeta potential of foulants

Zeta potential results of LYS and alginate are plotted in Figure 6-1. The measurements were done with 10 mM NaCl as background electrolyte. The zeta potential of LYS was ~ 7 mV at pH 7, and it increased with reducing pH. Alginate was highly negatively charged over a wide pH range. The zeta potential value became more negative as pH increased, but this increase in charge did not continue when $\text{pH} > 5$, likely due to the complete deprotonation of carboxylic groups at $\sim \text{pH} 5$ (and further increase in pH had no significant effect on deprotonation).

Figure 6-1. Zeta potential of alginate and LYS in 10 mM NaCl as a function of pH. Error bars: at least 2 replicate measurements were performed for each condition.

6.3.3 Effect of relative concentration of foulants

6.3.3.1 Flux behavior

The total foulant concentration of the feed was 20 mg/L for all the fouling tests. The feed composition was studied by varying the relative concentration of the foulant, and 0, 5, 30, 50, 70 and 100 wt.% of LYS concentration (% of LYS refers to the amount of LYS over the total amount of foulants in feed) were chosen for the

current study. Figure 6-2(a) shows the flux performances of the membrane NF270 at these feed compositions operated with an initial flux of $75 \text{ L/m}^2\cdot\text{h}$. Least fouling was observed for single foulant conditions (i.e., 0 and 100% LYS content). When a single foulant was present in feed solution, the flux reduction at 96 hours was about 20% and 30% for LYS and alginate fouling, respectively. However, when only replacing a small amount of alginate with LYS (5%), the loss of flux changed from 30% to 50%, probably due to the more foulant cake deposition as a result of electrostatic attraction between the oppositely charged LYS and alginate molecules. The most severe fouling occurred at the relative concentrations of 30, 50 and 70% where about an 80% membrane flux drop after 96-hr of filtration was observed. The rate of initial flux decline could be seen clearly from the inset in Figure 6-2(a), which is a magnified graph and shows that the feed with 70% LYS led to the most rapid decrease in flux, followed by the feeds containing 50% and 30% LYS. The explanation for the effect of foulant relative concentration is discussed in detail based on the mass deposition analysis in Section 6.3.3.2.

6.3.3.2 Foulant mass deposition

Correspondingly, mass deposition was analyzed and determined for the 96-hour fouled membranes, shown in Figure 6-2(b). Feed solutions consisting of a sole foulant led to the least foulant deposition. In contrast, replacing 5% of alginate with LYS in the feed containing only alginate increased the mass deposition to about 3 times of the original amount; this observation proved the previous hypothesis that more foulant deposition caused severe flux decline by changing a single foulant system to a mixture system. Remarkable foulant deposition was observed for the feeds containing 30, 50 and 70% LYS, which corresponded very well with the flux reduction results. Interestingly, the deposited mass ratio of LYS to alginate in the foulant layer was nearly constant ($m_{\text{LYS}}/m_{\text{alg}} \sim 4$) for feeds with 30-70% LYS content. There seemed to be a strong tendency that the relative quantity of LYS on the fouled membranes approached a quite constant value ($\sim 80\%$ of the total deposited mass) when sufficient concentrations of LYS and alginate were available in the feed solution. Conceptually, there exists a thermodynamically most stable arrangement (corresponding to a minimum free energy state (Greiner et al. 1995))

of foulant cake deposition. To achieve such a minimum energy arrangement, it is reasonable to assume that the oppositely charged LYS and alginate may deposit in a certain configuration to minimize the electrostatic interaction energy (e.g., a mosaic arrangement that each molecule is surrounded by adjacent oppositely charged molecules). Therefore, the mass ratio $m_{\text{LYS}}/m_{\text{alg}}$ is presumably determined by the relative charge densities of the two foulants, their geometry, and the presence of other additional interactions (e.g., hydrophobic interaction or specific interactions). This thermodynamic tendency (i.e., constant $m_{\text{LYS}}/m_{\text{alg}}$) will be preserved regardless of the foulant mass ratio in the feed water as long as both LYS and alginate are present in sufficient quantity (LYS 30-70% in this study). This constant $m_{\text{LYS}}/m_{\text{alg}}$ ratio is also somewhat analogous to the precipitation of inorganic minerals such as CaSO_4 (gypsum) where the calcium to sulfate ratio in the precipitation is fixed (in this particular case, at 1:1) irrespective of their ratio in the bulk solution (Stumm and Morgan 1996).

The fouling behavior at lower LYS content in the feed is also interesting. Even when there was only 5% LYS in the feed water, the relative LYS content in the foulant layer was as high as 53%. The corresponding $m_{\text{LYS}}/m_{\text{alg}}$ ratio was ~ 1 . While it was still significantly lower than the “thermodynamic constant ratio” of ~ 4 , this ratio was an order of magnitude higher than the concentration ratio of LYS to alginate in the feed (~ 0.053). This observation may suggest that there is a thermodynamic tendency to approach the constant ratio even for 5% LYS in feed, although this ratio was also limited by the slow deposition of LYS due to its low feed concentration (i.e., a kinetic consideration). The same kinetic consideration could also explain why the feeds with 30, 50, and 70% LYS content fouled the membrane more severely. It could predict that the fastest initial flux drop shall occur for the feed containing $\sim 80\%$ LYS and $\sim 20\%$ alginate (where the total mass remains 20 mg/L), as this composition matches the “desired” proportion for cake formation on the membrane surface. Similarly, the feed containing 70% LYS initiated faster flux decline compared to 50% and 30% LYS content, likely due to the foulants composed of 70% LYS and 30% alginate having the most proximal composition to the desired proportion of cake formation.

Figure 6-2. Flux behavior and mass accumulation to show the effect of relative concentration of LYS (or relative concentration of alginate) in feed solution on fouling. (a) flux performance; (b) foulant mass accumulation after 96-hr

fouling. Other test conditions: total foulant concentration of 20 mg/L, initial flux of 75 L/m²·h, pH 7, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1°C. Error bars in (b) were based on the analysis of 2-3 replicates.

6.3.4 Effect of solution chemistry

The effect of pH and calcium concentration on flux behavior is shown in Figure 6-3(a). An almost identical trend was observed for the flux decline at both pH 5 and pH 7 without the presence of Ca²⁺, presumably resulting from the similar strong electrostatic attraction between the oppositely charged macromolecules. Unlike the important role of solution pH in single protein fouling (Chapter 4), it became less crucial during mixture fouling at least for certain conditions, i.e., the flux decline was weakly dependent on the pH when it was between the IEPs of the two foulants. This phenomenon has also been observed in binary protein mixture fouling (see Chapter 5).

Notwithstanding the identical flux behavior at different solution pHs, the results of foulant mass deposition showed some remarkable differences (Figure 6-3(b)). There was more alginate and less LYS deposition at pH 5 compared to pH 7 at the end of fouling tests, and the relative mass of LYS on the fouled membrane reduced to 66% at pH 5 compared to ~ 80% at pH 7. This may result from the more positively charged LYS molecules at pH 5 (Figure 6-1), where the required amount of LYS to balance the negatively charged alginate is reduced. This is consistent with our hypothesis that the m_{LYS}/m_{alg} ratio is dependent on the relative charge density of the foulants – an increased LYS to alginate charge ratio leads to reduced m_{LYS}/m_{alg} .

Figure 6-3. Flux behavior and mass accumulation comparison to show the effect of solution chemistry on fouling. (a) flux performance; (b) mass accumulation after 96-hr fouling. Other test conditions: initial flux of 75 L/m²·h, total foulant concentration of 20 mg/L (50% LYS), total ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1°C. Error bars were based on the analysis of 2-3 replicates.

The effect of calcium concentration was studied by comparing the feeds containing 1 and 0 mM Ca^{2+} with a total ionic strength of 10 mM (adjusted by the addition of NaCl) at pH 7. In Figure 6-3(a), 86% and 80% flux reductions were observed at the end of fouling in the presence of 1 mM Ca^{2+} and the absence of Ca^{2+} , respectively. Increased Ca^{2+} concentration only led to slightly more flux reduction. It has been well recognized that calcium and alginate can form a cross-linked gel layer as a result of calcium complexation with alginate carboxylic groups (Lee and Elimelech 2006). When alginate is the sole foulant in the feed, increasing the calcium concentration tends to drastically reduce the membrane permeate flux (Lee and Elimelech 2006; Ang 2008). In contrast, this marked effect by Ca^{2+} was not obviously shown in the fouling by the LYS-alginate mixture. The reduced effect of Ca^{2+} on flux reduction was probably due to the presence of LYS in feed solution, which can cause a strong LYS-alginate attraction and form a dense cake layer even if Ca^{2+} was not present. Alternatively, the positively charged LYS may compete with Ca^{2+} for the negatively charged sites ($-\text{COO}^-$ groups) in the alginate, leading to a reduced degree of Ca^{2+} -alginate complexation. Introduction Ca^{2+} into the feed solution only marginally accelerated flux decline at the beginning (within 10 hours) of foulant addition. During such a fouling process, a compound effect of LYS-alginate and Ca^{2+} -alginate complexation may take place (since Ca^{2+} had a minimal effect on the fouling by LYS alone, see Figure 6-4).

Mass deposition results (Figure 6-3(b)) show a significant increase (more than doubled) in the amount of alginate accumulated on the fouled membrane due to the addition of Ca^{2+} , despite the insignificant variation in flux performance. The increased alginate deposition may be attributed to the Ca^{2+} -alginate complexation. On the other hand, LYS deposition was reduced, and the relative mass of LYS on membrane was reduced to $\sim 52\%$. This further suggested the existence of the compound effect of LYS-alginate and Ca^{2+} -alginate complexation, where both LYS and Ca^{2+} compete for negatively charged $-\text{COO}^-$ sites in the alginate. The specific Ca^{2+} -alginate interaction and subsequent reduction in the charge density of alginate may also explain the drastically reduced $m_{\text{LYS}}/m_{\text{alg}}$ ratio (~ 4 when there was no

calcium and ~ 1 in the presence of 1 mM Ca^{2+}). Once again, the reduced LYS to alginate mass ratio corresponds to an increased ratio of charge density.

Figure 6-4. Effect of ionic composition on flux behavior during LYS fouling. Test conditions: membrane NF270, LYS of 20 mg/L, pH 7, initial flux of 120 $\text{L/m}^2\cdot\text{h}$, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$.

6.3.5 Effect of initial flux

The effect of initial flux was evaluated for filtration tests with an initial fluxes over a range of 15-120 $\text{L/m}^2\cdot\text{h}$ under conditions of pH 7 and 1 mM calcium concentration, based on the flux performance and foulant deposition results (Figure 6-5(a) and (b)). Much more severe flux reduction was observed at a higher initial flux (Figure 6-5(a)), which was consistent with the results from our previous fouling studies with single protein and binary protein mixtures (Chapter 4 and 5) as well as from many other existing publications (Wu et al. 1999; Tang et al. 2007c; She et al. 2009). The fluxes started to converge to an identical limiting value although they began with different initial values; this was consistent with our observation in protein fouling and humic acid fouling (Tang et al. 2007c). The

surface-interaction controlled limiting flux model that the mutual action of hydrodynamic drag and foulant-deposited-foulant (foulant-membrane) interaction on the foulant molecules determines the fouling and the extent of fouling is appropriate to explain the limiting flux phenomenon (see Section 4.3.1 and (Tang and Leckie 2007)). As the fouling occurred rapidly for the feed containing a LYS-alginate mixture, limiting flux was reached only after a few hours upon foulant addition. Under such severe fouling conditions, it would be easy and clear to observe the limiting flux within a short fouling time (no transition stage that appeared in BSA fouling, chapter 4). A similar effect of initial flux was also observed for the feed without Ca^{2+} content (Figure 6-5(d)).

Foulant mass deposition results (Figure 6-5(b) and (d)) show the expected trend that more LYS and alginate deposited on membranes fouled for 96 hours under higher initial flux (or applied pressure). It is worthwhile to note that the deposited mass of the two foulants varied proportionately such that their mass ratio remained nearly constant ($m_{\text{LYS}}/m_{\text{alg}} = \sim 1$ for the feed containing 1 mM Ca^{2+} and ~ 4 for the feed without Ca^{2+}). This suggests that increasing initial flux or applied pressure may have a negligible effect on the relative mass of the deposited foulants and that the $m_{\text{LYS}}/m_{\text{alg}}$ ratio may be primarily determined by the foulant-foulant interactions but not the hydrodynamic forces. The various effects (solution chemistry, composition and initial flux) on the relative mass of the deposited foulants are gathered in Figure 6-6, where clear trends and relationships can be identified. These can be summarized into three aspects: 1) the relative concentration of foulants in the feed solution had a weak influence on the relative mass of deposited foulants (see the dashed curve in Figure 6-6) as long as both foulants were present in the feed in sufficient concentrations (such that the $m_{\text{LYS}}/m_{\text{alg}}$ ratio was not kinetically limited); 2) the initial flux had a negligible effect on the relative mass of deposited foulants; and 3) the solution chemistry such as pH and Ca^{2+} concentration affected the $m_{\text{LYS}}/m_{\text{alg}}$ ratio as a result of the changes in foulant-foulant interactions (e.g., the LYS-alginate electrostatic attraction and the calcium-alginate specific interaction).

As most hydraulic cake resistance was built up during the initial period where the flux dropped significantly (Figure 6-5(a) and (c)), the large difference in the deposited cake mass under different initial fluxes may develop within the initial fouling period (or transition stage before pseudo-stable flux stage). Operating at a higher applied pressure had no noticeable benefit on the longer term membrane flux (say, at 96 hr), probably due to the densely formed cake layer under the primary electrostatic attractive forces between macromolecules. Figure 6-7 shows that hydraulic resistance of the foulant R_f increased with the deposited mass m_f , and the specific cake layer resistance R_f / m_f (i.e., the slope of the R_f vs. m_f curve) also increased with m_f . In other words, higher initial flux resulted in more mass deposition, greater flux reduction and a more densely packed cake layer, which agrees well with Tang's observation during humic acid fouling with RO and NF membranes (Tang et al. 2007b).

(b)

(c)

Figure 6-5. Flux behavior and mass accumulation to show the effect of initial flux on fouling. (a) flux performance at $\text{Ca}^{2+} = 1$ mM; (b) mass accumulation after 96-hr fouling ($\text{Ca}^{2+} = 1$ mM); (c) flux performance ($\text{Ca}^{2+} = 0$ mM); (d) mass accumulation after 96-hr fouling ($\text{Ca}^{2+} = 0$ mM). Other test conditions: total foulant concentration of 20 mg/L (50% LYS), pH 7, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bars were based on the analysis of 2-3 replicate measurements.

Figure 6-6. % LYS accumulation on fouled membrane as a function of % LYS in initial feed solution. Other test conditions: a total foulant concentration of 20 mg/L, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bars were based on the analysis of 2-3 replicates. The dashed curve corresponds to the LYS deposition (%) at pH 7 and $\text{Ca}^{2+} = 0$ mM.

Figure 6-7. Foulant hydraulic resistance and specific cake layer resistance as a function of total mass deposition. Test conditions: total foulant concentration of 20 mg/L (10 mg/L LYS + 10 mg/L alginate), calcium ion of 1 mM, total ionic strength of 10 mM (by addition of NaCl), crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bars were based on the analysis of 2-3 replicates.

6.3.6 Salt rejection during fouling

Salt rejection performances of both virgin and fouled membranes were determined based on conductivity measurements. Figure 6-8 shows the normalized salt rejection performances (normalized against the corresponding virgin membrane rejection) as a function of fouling time for different solution compositions. The effect of relative foulant concentration is compared in Figure 6-8(a). It is interesting to observe an initial increase in salt rejection upon fouling for all cases. Tang et al. (Tang et al. 2007c) attributed this beneficial effect to the preferential deposition of foulants over membrane defects where the localized flux was at a maximum. In this way, even a small amount of foulant deposition may cause significant improvement in salt rejection by sealing of defects (Tang et al. 2007c). However, the rejection

started to decrease at later stages of fouling probably due to a combination of several factors: 1) the decreased membrane flux which resulted in a reduced dilution factor to the permeate concentration; 2) the cake-enhanced concentration polarization of solutes in an extensive foulant cake layer (Hoek and Elimelech 2003); and 3) the significant change of membrane surface charge properties upon fouling, which may turn a very negatively charged surface into a quite neutrally charged surface (by the deposition of the oppositely charged LYS and alginate molecules). Consistent with the above explanations, the decrease in salt rejection in the later stage of fouling seemed to be more obvious for more severe fouling conditions that are accompanied by greater permeate flux reduction and more foulant mass deposition.

Figure 6-8(b) presents the effect of solution chemistry on salt rejection during fouling. An initial salt rejection enhancement was clearly observable when there was no Ca^{2+} in the feed solution (at both pH 5 and pH 7). In contrast, such initial enhancement was not observed for the feed containing 1 mM Ca^{2+} , even though 1) the flux decline in the presence of calcium was only slightly more severe than that without calcium, and 2) the foulant cake layer was likely to be more compacted in the presence of calcium (see Table A in Appendix). A possible explanation may be that the foulant charge neutralization associated with the calcium-alginate complex formation may result in a cake layer with a reduced ability for solute retention. Prior studies have demonstrated that rejection of charged solutes can be enhanced by Donnan exclusion (Schaep et al. 1999). Thus, the reduced rejection due to the presence of 1 mM Ca^{2+} might be attributed to the weakening of Donnan exclusion effect in addition to the enhanced solute polarization inside the foulant cake layer.

Figure 6-8. Salt rejection as a function of time during fouling. (a) effect of relative concentration of foulant in feed; (b) effect of solution chemistry (i.e., pH and Ca^{2+} concentration). Other test conditions: pH 7, total ionic strength of 10 mM, initial flux of $75 \text{ L/m}^2\cdot\text{hr}$, crossflow velocity of 9.5 cm/s , and temperature at $20 \pm 1^\circ\text{C}$. Error bars in (b) were based on the analysis of duplicate measurements.

6.4 Conclusions

Nanofiltration membrane fouling by oppositely charged macromolecules (positively charged LYS and negatively charged alginate) was systematically studied through flux behavior, foulant mass deposition and salt rejection. The effects of relative foulant concentration in the feed solution, solution chemistry (pH and Ca^{2+} concentration) and initial flux were evaluated. The results revealed that:

- 1) Flux decline was only weakly influenced by the solution composition (relative concentration of the foulants) when both foulants were present in the feed solution at sufficient concentration. Solution pH and calcium concentration showed a minimal and a moderate effect on flux performance, respectively. These effects can be explained by the strong electrostatic attraction existing between the two oppositely charged foulants. Higher initial flux tended to cause more flux decline and more mass deposition, probably due to greater permeate drag in addition to increased concentration polarization.
- 2) The two oppositely charged macromolecules had a strong tendency to maintain a constant mass ratio in the deposited foulant cake layer. This ratio was only weakly dependent on their relative concentration in the feed solution and was independent of the initial flux. On the other hand, solution chemistry such as pH and calcium concentration had a marked effect on this mass ratio, likely due to the resulting changes in the foulant-foulant interaction (e.g., LYS-alginate electrostatic attraction and the calcium-alginate specific interaction).
- 3) The mixed alginate-LYS fouling could result in an initial enhancement in salt rejection, which was probably caused by sealing of defects. However, such initial rejection enhancement was not observed when there was 1 mM Calcium present in the feed water, which may be attributed to the formation of a less charged foulant layer as a result of calcium-alginate specific interaction.

Chapter 7

Conclusions and recommendations

Nanofiltration (NF) and reverse osmosis (RO) fouling by feeds containing a single protein (BSA), a binary protein mixture (BSA and LYS) and a protein-polysaccharide mixture (LYS and alginate) were systematically investigated. The effects of feed solution chemistry, hydrodynamic conditions and membrane properties on fouling were evaluated. The major findings and conclusions are summarized as:

- 1) A more severe flux reduction associated with a higher initial flux for all three feeds (i.e., BSA, LYS + BSA and LYS + alginate). The limiting flux phenomena were observed under most of the cases provided that the fouling duration was sufficiently long. The simple model involving the interplay of foulant-membrane interaction and hydrodynamic drag was used to explain this limiting flux phenomenon.
- 2) Foulant mass deposition and packing density was strongly correlated to flux reduction. Increased initial flux led to more foulant mass deposition and higher specific cake layer resistance, which resulted in more severe flux reduction.
- 3) BSA fouling was highly dependent on solution chemistry (such as solution pH, ionic strength and divalent cation concentration). Flux reduction was more severe at pH values close to the IEP of BSA, higher ionic strength and higher divalent cation concentration. These effects may result from the electrostatic repulsion between the BSA molecules, as well as the specific calcium-protein interaction. The pseudo-stable flux (J_{96hr}) correlated well with the square of protein zeta potential, suggesting that the foulant-fouled-membrane interaction plays a dominant role.

- 4) The solution chemistry (pH and ionic strength) showed apparently different effects on the oppositely charged macromolecular mixture fouling compared to that of single protein fouling. The flux decline during mixture fouling was less sensitive to pH variation when the pH was between the IEPs of the two macromolecules (demonstrated for both BSA-LYS fouling and LYS-alginate fouling). Increasing ionic strength led to slower flux decline during macromolecular mixture fouling (contrary to the trend in single protein fouling). These effects may result from the strong attractive interaction between the oppositely charged macromolecules, where increased ionic strength could reduce electrostatic attraction between the two macromolecules.
- 5) Solution composition had a weak influence on the flux performance when the two oppositely charged foulants (LYS and alginate) were present at sufficient concentrations in the feed solution. Once again, the dominance of the electrostatic attraction between the LYS and alginate was demonstrated.
- 6) During fouling by a feed consisting of two oppositely charged macromolecules, the mass ratio of the two deposited foulants was independent of initial flux and foulant composition in the feed solution and there was a strong tendency for the foulants to reach a constant mass deposition ratio when both foulants had a sufficient concentration in the feed solution. However, this ratio was significantly affected by solution chemistry (i.e., pH and Ca^{2+} concentration, etc.), likely due to the corresponding change in foulant-foulant or foulant-membrane interaction.
- 7) Membrane properties had a strong influence over the initial fouling behavior; hydrophilic and smooth membranes are preferred for achieving a slower fouling rate. On the other hand, the long-term flux under severe fouling conditions was primarily controlled by the foulant-fouled-membrane surface interaction with little dependence on membrane properties.

In order to gain further understanding of membrane fouling mechanisms, the following work is suggested:

- 1) The effect of the foulant conformation/size on RO/NF membrane fouling. The fouling studies on the effect of foulant conformation/size are available for MF/UF membranes, but this topic has not been well addressed for RO/NF membranes, probably due to the difficulties in fouling condition control and in the availability of small foulant.
- 2) The prolonged meta-stable flux phenomenon and the associated conditions and factors. The reasons for observing the meta-stable fluxes can be further investigated, which may help the understanding of sustainable flux.
- 3) The non-electrostatic interactions in RO/NF fouling by a feed containing a single foulant or a foulant mixture. The non-electrostatic interactions may play an important role for the fouling by uncharged foulants and the retention of uncharged trace organics.

Appendix

Section A

Foulant mass deposition analysis

Effect of initial flux and solution pH on NF fouling by single protein and binary protein mixtures was revealed from the mass deposition and specific cake layer resistance results.

Mass deposition was correlated well with flux decline (i.e., hydraulic resistance of foulant) for NF fouling by BSA molecules. The increase in the value of the protein zeta potential squared resulted in less BSA deposition and less hydraulic cake resistance.

(a)

Figure A. 1. Mass deposition and cake resistance after 96-hr BSA fouling. (a) BSA mass deposition and hydraulic cake resistance as a function of the square of protein zeta potential (over pH 4.7 ~ pH 7.8); (b) specific cake layer resistance as a function of the square of protein zeta potential (over pH 4.7 ~ pH 7.8). Other conditions: membrane NF270, BSA concentration of 20 mg/L, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1 °C. Error bar: 2-4 replicates were analyzed for each membrane sample.

By comparing the mass deposition results for fouling by BSA, LYS and their mixture, the mixture led to the greatest deposition after 96 hr fouling, no matter how the pH and initial flux varied. Filtration with LYS solely caused the least mass deposition under all testing conditions. These results as well agreed with flux reduction results (see Chapter 4 and 5).

As expected, the specific cake layer resistance (r_f) was the highest when the feed solution contained both proteins (Figure A.3), which could be explained by the strong electrostatic attraction between BSA and LYS molecules. The r_f of the LYS cake layer was slightly higher than that of the BSA cake layer although the LYS deposition was less. This was likely due to the sealing of membrane surface defects and/or close packing of the cake layer during the initial fouling when the permeate flux was relatively higher.

Figure A. 2. Foulant mass deposition after 96-hr fouling for feed containing single protein or protein mixture. (a) effect of initial flux (pH 7); (b) effect of solution pH (initial flux of 120 L/m²·h). Other conditions: membrane NF270, total foulant concentration of 20 mg/L (for mixture system, BSA:LYS=1:1), ionic strength of 10 mM (NaCl), crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1 °C. Error bar: 2-4 replicates were analyzed for each membrane sample.

Figure A. 3. Mass deposition and specific cake resistance of the 96-hr protein fouled membranes, showing the comparison of different feeds (BSA, LYS or BSA+LYS). Fouling conditions: membrane NF270, total protein concentration of 20 mg/L (for mixture system, BSA:LYS=1:1), pH 7, ionic strength of 10 mM, crossflow velocity of 9.5 cm/s, and temperature at $20 \pm 1^\circ\text{C}$. Error bar: 2-4 replicates were analyzed for each membrane sample.

Section B

Calibration curves for determination of BSA, LYS and alginate concentration

The protein and alginate standard curves were prepared with the respective macromolecules. For example, the solutions of a range of alginate concentrations were used to prepare the standard curve used for alginate concentration determination. The background content of standard solutions was the same as the sample solutions (i.e., 5% SDS and 0.1% NaOH were used to prepare protein standard solutions and alginate standard solutions, respectively).

(a)

Figure B. 1. Typical calibration curves for concentration of macromolecules. (a) BSA and LYS concentration analyzed using protein assay kit (QuantiPro™ BCA Assay Kit) at 562 nm; (b) alginate concentration analyzed using phenol-sulfuric acid method at 485 nm. Error bars were based on the analysis of 2-3 replicate measurements.

Section C

Reliability of flux measurement –

An example showing digital flow meter calibration

The measured flux and digital flow meter reading had a linear relationship. The flux was manually measured for each cell during every fouling test.

Figure C. 1. Manually measured flux vs. digital flow meter reading during a fouling run. Error bars were based on the analysis of duplicate measurements.

Section D

Membrane permeability, conductivity/salt rejection and zeta potential

The permeability of membrane NF270 varies with solution pH. The highest membrane permeability was obtained at pH 4.7, presumably due to the enlargement of the membrane “pore” opening (Childress and Elimelech 2000).

Figure D. 1. Permeability of membrane NF270 as a function of pH. Test conditions: flux of 120 L/m²·h, ionic strength of 10 mM (NaCl), crossflow velocity of 9.5 cm/s, and temperature at 20 ± 1 °C. Error bars: analysis of 3 membrane samples.

Conductivity rejection and ion rejection results show that the lowest rejection of membrane NF270 occurred at pH 4.7, which correlated with the highest permeability at this condition. Conductivity rejection is a good indicator for salt rejection except for the condition at very low pH, where more hydrogen ions passed through the membrane instead of sodium ions.

Figure D. 2. Ion and conductivity rejection of membrane NF270 over a range of pHs. Test conditions: flux of 120 L/m²·h, ionic strength of 10 mM, and temperature at 20 ± 1 °C. Error bars: analysis of 3 membrane samples.

Zeta potential of virgin membranes NF90, NF270 and XLE were measured with an Electro Kinetic Analyzer (EKA) (Anton Paar, Graz, Austria). The membranes were thoroughly rinsed and soaked in Milli-Q water for 24 hours prior to analysis.

Figure D. 3. Zeta potential (as a function of pH) of virgin RO and NF membranes used in current study. pH was adjusted by NaOH and HCl, ionic strength of 10 mM (by addition of NaCl), and temperature at ~23 °C.

Table A. Foulant mass deposition and specific cake layer resistance for LYS-alginate fouling. Test conditions: ionic strength of 10 mM, and temperature at 20 ± 1 °C. Standard deviations were based on the analysis of 2-3 membrane samples.

Conditions					Mass deposition, m_f ($\mu\text{g}/\text{cm}^2$)			$J_0/J_{00}-1$	R_f (m^{-3})	$r_f R_f/m_f$ (m/g)
LYS (%)	pH	Ca^{2+} (mM)	J_0 ($\text{L}/\text{m}^2\text{-h}$)		Alginate	LYS	Total			
0	7	0	75		97.7 ± 7.3	0	97.7 ± 7.3	0.47	$1.40\text{E}+13$	$1.45\text{E}+13$
5	7	0	75		140	157	297	0.98	$3.00\text{E}+13$	$1.01\text{E}+13$
30	7	0	75		107	339	458	4.16	$1.30\text{E}+14$	$2.90\text{E}+13$
50	7	0	75		93	345 ± 10.8	438 ± 10.8	4.05	$1.50\text{E}+14$	$3.48\text{E}+13$
70	7	0	75		94	310	404	4.69	$1.60\text{E}+14$	$3.97\text{E}+13$
100	7	0	75		0	11.5 ± 1.3	11.5 ± 1.3	0.24	$8.10\text{E}+12$	$7.07\text{E}+13$
50	5	0	75		153 ± 10.8	305 ± 20.5	458 ± 10	3.88	$1.10\text{E}+14$	$2.47\text{E}+13$
50	7	0	75		93.2	344 ± 10.8	438 ± 10.8	4.05	$1.50\text{E}+14$	$3.48\text{E}+13$
50	7	1	75		237 ± 10.5	263 ± 2.0	500 ± 12.7	6.14	$1.90\text{E}+14$	$3.83\text{E}+13$
50	7	1	120		254 ± 20.3	287	542	10.2	$2.90\text{E}+14$	$5.44\text{E}+13$
50	7	1	75		237 ± 10.5	263 ± 2	500 ± 12.7	6.14	$1.90\text{E}+14$	$3.83\text{E}+13$
50	7	1	50		201 ± 21.9	227	428	3.75	$1.20\text{E}+14$	$2.83\text{E}+13$
50	7	1	28		159 ± 10.1	179	338	1.86	$6.40\text{E}+13$	$1.89\text{E}+13$
50	7	1	15		106 ± 7	129	235	0.61	$1.70\text{E}+13$	$7.33\text{E}+12$

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