NOM removal by ultrafiltration membranes : enhancement of filtration performance

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**NOM REMOVAL BY ULTRAFILTRATION
MEMBRANES
– ENHANCEMENT OF FILTRATION
PERFORMANCE**

**WEI XI
SCHOOL OF CIVIL & ENVIRONMENTAL ENGINEERING
2007**

NOM Removal by Ultrafiltration Membranes – Enhancement of Filtration Performance

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School of Civil & Environmental Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Ph. D

2007

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	I
TABLE OF CONTENTS	II
SUMMARY	VII
PUBLICATION	IX
LIST OF TABLES	X
LIST OF FIGURES	XI
LIST OF SYMBOLS	XVIII
CHAPTER 1. INTRODUCTION	1
1.1 Background	1
1.2 Objectives and cope of the thesis	2
1.3 Organization of this thesis	4
CHAPTER 2. LITERATURE REVIEW	7
2.1 Nature organic matter (NOM)	7
2.1.1 Impact of NOM on surface water quality	7
2.1.2 Composition and fractionation of NOM	8
2.1.3 Extraction of NOM from surface water	10
2.1.4 Characteristics of NOM	13
2.1.5 Interaction between NOM and other contaminants	17
2.2 Membrane Filtration Processes and NOM Fouling	20
2.2.1 Introduction	20
2.2.2 Membrane processes	20
2.2.3 Ultrafiltration and microfiltration	21
2.2.4 Modes of operation	23
2.2.5 Membrane modules	25
2.2.6 Fouling and polarization	26

2.2.7 Review of NOM membrane fouling studies	32
2.2.8 Techniques to reduce NOM fouling	49
2.3 Conclusions	57

CHAPTER 3. INFLUENCE OF IONIC STRENGTH ON NOM SIZE AND REMOVAL BY ULTRAFILTRATION 59

3.1 Introduction	59
3.2 Materials and methods	61
3.2.1 Model NOM and other chemicals	61
3.2.2 Solution preparation	61
3.2.3 Membranes and filtration protocol	62
3.2.4 Analysis	63
3.3 Results and discussion	64
3.3.1 Effect of Na ⁺ interaction with NOM	64
3.3.2 Effect of Ca ²⁺ interaction with the NOM	69
3.3.3 Effect of solution pH	72
3.3.4 Ultrafiltration study	75
3.4 Conclusions	78

CHAPTER 4. CHARACTERIZATION OF TROPICAL NOM AND ITS INFLUENCE ON UF MEMBRANE FOULING 80

4.1 Introduction	80
4.2 Material and methods	82
4.2.1 Water Source	82
4.2.2 NOM isolation process	82
4.2.3 Solution preparation	83
4.2.4 Membranes and filtration protocol	84
4.2.5 Analysis methods	84
4.2.6 Membrane fouling parameters	85
4.3 Results and discussion	86
4.3.1 Interaction of multivalent ions with NOM in the NOM isolation	86
4.3.2 Composition of tropical NOMs	86
4.3.3 Characteristics of tropical NOMs	88

4.3.4 Filtration performance of tropical NOMs	90
4.4 Conclusions	95
PREAMBLE TO CHAPTERS 5, 6, and 7	97
CHAPTER 5. IMPACT OF OPERATING CONDITIONS ON NOM REMOVAL AND MEMBRANE FOULING IN ULTRAFILTRATION PROCESSES	98
5.1 Introduction	98
5.2 Materials and methods	100
5.2.1 Source water and NOM	100
5.2.2 Membranes	100
5.2.3 Filtration protocols	101
5.2.4 Analysis methods	101
5.2.5 Theory of NOM fouling	102
5.3 Results and discussion	105
5.3.1 Characteristics of source water and NOM	105
5.3.2 NOM retention	105
5.3.3 NOM fouling	109
5.3.4 Membrane morphologies	118
5.4 Conclusions	119
CHAPTER 6. HYBRID SYSTEM OF MIEX WITH LOW-PRESSURE MEMBRANES: EFFECTS OF MIEX PRETREATMENT ON NOM REMOVAL AND MEMBRANE FOULING	121
6.1 Introduction	121
6.2 Materials and methods	123
6.2.1 Singapore NOM and other chemicals	123
6.2.2 MIEX Resins	123
6.2.3 Membranes and filtration protocol	123
6.2.4 Analytical methods	124
6.2.5 Membrane fouling parameters	124
6.3 Results and discussion	125

6.3.1 Characterization of Singapore NOM	125
6.3.2 NOM removal by MIEX & membrane filtration	126
6.3.3 Impact of MIEX on the membrane filtration performance	131
6.3.4 Fouling morphology studies	137
6.4 Conclusions	139

CHAPTER 7. DEVELOPMENT OF A NOVEL ELECTROPHORESIS-UV GRAFTING TECHNIQUE TO MODIFY PES UF MEMBRANES USED FOR NOM REMOVAL

7.1 Introduction	141
7.2 Materials and methods	144
7.2.1 Materials	144
7.2.2 Methods	146
7.3 Results and discussion	148
7.3.1 Grafting yield and surface properties of modified membranes	148
7.3.2 MWCO and pure water flux (PWF)	151
7.3.3 NOM filtration performance	155
7.3.4 NOM fouling study	156
7.3.5 Membrane morphologies	158
7.4 Conclusions	161

CHAPTER 8. CONCLUSION AND RECOMMENDATIONS

8.1 Overall conclusions	162
8.1.1 Influence of ionic strength on NOM size and removal by ultrafiltration	162
8.1.2 Characteristics of tropical NOM and its influence on UF membrane fouling	163
8.1.3 Impact of operating conditions on NOM removal and membrane fouling in ultrafiltration processes	165
8.1.4 Hybrid process with MIEX and low-pressure membranes: effects of MIEX pretreatment on NOM removal and membrane fouling	165
8.1.5 Development of a novel electrophoresis-UV grafting technique to modify PES UF membranes used for NOM removal	166

8.2 Recommendations and future work	167
APPENDIX I	170
REFFERENCES	174

SUMMARY

Raw water supplies in Singapore tend to contain high levels of natural organic matter (NOM) and other contaminants. The effective removal of NOM from surface water is a great challenge to the water industry. This work aims to study novel techniques to improve NOM filtration performance of UF membranes with low fouling tendency and high permeability through various approaches, not only from an engineering perspective, but also from the view of UF membrane characteristics.

In order to achieve this target, as the first step, a comprehensive literature review has been conducted which focuses on the nature of NOM and its influence on the water, water treatment and membrane process especially membrane fouling. Since detailed characterizations are necessary due to the variation of NOM from different sources, the relevant characterization techniques were described. In addition, ultrafiltration membrane technology for NOM removal has been reviewed and a general description of NOM fouling has also been presented.

The experimental study was commenced with water sample collection and NOM isolation from Singapore local reservoirs. Two types of tropical NOM were isolated using a RO system. The water samples and isolated NOM were characterized in terms of pH, conductivity, turbidity, ionic strength, TOC, UV/Visible absorbance spectra and molecular weight distribution of NOM by HPSEC. The experimental results indicated that NOM concentration varied with different reservoirs, and that solution conditions such as ionic composition, ionic strength and pH are important in determining the conformation of the NOM species and subsequent filtration performance.

Membrane filtrations of the natural water sample, reconstituted tropical NOMs and IHSS NOM through the UF membranes were conducted in order to understand the impact of the characteristics of tropical NOM on UF membrane fouling. It was found that cake layer formation on the membrane surface was the main fouling mechanism of tropical NOMs during UF filtration.

To improve UF membrane performance for NOM removal, a systematic study was carried out using different UF membranes operated over a full spectrum of operating conditions, which included constant pressure and constant flux modes with and without stirring. It was found the UF membrane exhibited a higher NOM retention under the stirring conditions for either the constant pressure or constant flux modes. The membrane fouling also decreased with the provision of stirring, especially for the hydrophobic membrane. The optimal operating condition recommended for NOM removal is the constant flux mode with a stirring speed of 300-400rpm.

Another approach to improve NOM removal was to develop a hybrid system. The hybrid membrane process with MIEX and low pressure membranes has been evaluated for a NOM-laden water from the tropical source. Experiments were performed with both MF and UF membranes, operated at various modes and conditions. It was found that MIEX pretreatment allowed about 85 % removal of NOM, compared with only 10 to 15 % removal by the membranes alone. However, the MIEX pretreatment could be beneficial or detrimental in terms of fouling control. In particular, stirring with UF at constant flux was beneficial.

Finally, a novel technique which combines controlled deposition by electrophoresis of charged moieties, with UV grafting on the membrane surface has been applied to modify Poly(ether sulfone) membranes with several different monomers. The molecular weight cut-off, pure water flux, wettability, surface charge and surface morphology were measured for modified/unmodified membranes. The filtration and fouling performance were also tested and compared. It was found that the modified membrane surfaces exhibited more hydrophilic and negatively charged features, which gave them possess lower fouling tendency than the unmodified membranes when filtering NOM. With electrophoresis assistance, the modified membrane exhibited more homogeneous properties than that modified without electrophoresis.

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LIST OF TABLES

Chapter 2

Table 2.1	Function groups present in different river NOMs (Schafer, 1999).....	14
Table 2.2	A general overview of membrane processes and solute dimensions	19
Table 2.3	Membrane processes and characteristics for water treatment	21
Table 2.4	Module types and characteristics for water treatment	26
Table 2.5	NOM and other foulant species in raw water	31
Table 2.6	Summary of selected NOM membrane fouling studies	34

Chapter 3

Table 3.1	The NOM retention of different membranes with timing difference.....	63
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Chapter 4

Table 4.1	Mass balance on tropical NOM after isolation	87
Table 4.2	FTIR analyses of S-NOM I and S-NOM II	88
Table 4.3	Characteristics of tropical NOMs and the IHSS NOM aqueous solutions	89

Chapter 5

Table 5.1	Characteristics of Membranes tested	106
-----------	---	-----

Chapter 6

Table 6.1	Characteristics of Membranes tested	124
-----------	---	-----

Chapter 7

Table 7.1	Characteristics of tropical NOM in MilliQ water	145
Table 7.2	Properties of modified PW-PES membrane	149

Table 7.3	Contact angle (degree) of membranes modified by UV grafting and electrophoresis-UV grafting	150
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LIST OF FIGURES**Chapter 1**

Figure 1.1	Schematic description of the ‘NOM removal using UF membranes’ research scope	4
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Chapter 2

Figure 2.1	Outline of raw water fraction procedure	9
Figure 2.2	Schematic illustration of the XAD-8 resin isolation technique	11
Figure 2.3	Schematic illustration of the RO isolation method	12
Figure 2.4	Schematic of humic acid model structure (Zularisam <i>et al.</i> , 2006) ...	14
Figure 2.5	Schematic of fulvic acid model structure (Zularisam <i>et al.</i> , 2006) ...	14
Figure 2.6	Mode of operation: crossflow vs deadend; Constant pressure vs constant flux	25
Figure 2.7	Schematic of fouling mechanisms	29
Figure 2.8	Typical flux histories during membrane fouling	29
Figure 2.9	Schematic depiction of the effect of solution conditions on the conformation of NOM macromolecules in the solution and on the membrane surface	44

Chapter 3

Figure 3.1	Flow sheet of a dead-end cell filtration system – constant pressure	62
Figure 3.2	Particle size analysis of Singapore NOM with different NaCl concentrations	65
Figure 3.3	Particle size analysis of IHSS NOM with different NaCl concentrations	65
Figure 3.4	Particle size analysis of Biohumic with different NaCl concentration	65
Figure 3.5	Molecular Weight Distribution of Singapore NOM with different NaCl concentrations	66

Figure3.6	Molecular Weight Distribution of IHSS NOM with different NaCl concentrations	67
Figure3.7	Molecular Weight Distribution of Biohumic NOM with different NaCl concentrations	68
Figure3.8	Particle size analysis of Singapore NOM (52.14ppm) with different Calcium Concentrations	70
Figure3.9	Particle size analysis of IHSS NOM (60 ppm) with different Calcium Concentrations	70
Figure 3.10	Particle size analysis of Biohumic NOM with different CaCl ₂ concentrations	71
Figure 3.11	Molecular Weight Distribution of IHSS NOM with different CaCl ₂ concentrations	71
Figure 3.12	Molecular Weight Distribution of Biohumic NOM with different CaCl ₂ concentrations	72
Figure 3.13	Size Distribution of IHSS Humic Acid under different pH	73
Figure 3.14	Size Distribution of IHSS Fulvic Acid under different pH	73
Figure 3.15	Size Distribution of IHSS NOM under different pH	74
Figure 3.16	Size Distribution of Biohumic NOM under different pH	74
Figure 3.17	Retention of PBGC Membrane for Singapore NOM Solutions with different Sodium Concentration (10 ppm NOM)	75
Figure 3.18	Retention of PBGC Membrane for Biohumic NOM Solutions with different Sodium Concentrations (100 ppm NOM)	76
Figure 3.19	HPSEC chromatograms of the permeate solution collected after Ultrafiltration of Biohumic NOM (200ppm)	76
Figure 3.20	Retention of PBGC Membrane for Singapore NOM Solutions with different Calcium Concentrations (10 ppm NOM)	77
Figure 3.21	Retention of PBGC Membrane for Biohumic NOM Solutions with different Calcium Concentrations (20 ppm NOM)	77
Figure 3.22	Retention of PBGC Membrane for different IHSS Solutions; Solution A: IHSS; Solution B: IHSS+NaCl 20mM+CaCl ₂ 0.5mM	78

Chapter 4

Figure 4.1	Flow sheet of TECSW RO system with microfiltration cartridge for the NOM isolation	86
Figure 4.2	FTIR results of isolated tropical NOMs: (a) S-NOM I; (b) S-NOM II: (i) $-\text{CH}_2-$, (ii) ; (iii) $-\text{OH}$; (iv) $\text{C}-\text{OH}$; (v) $\text{C}=\text{O}$; (vi) $\text{C}=\text{C}$	91
Figure 4.3	Molecular weight distributions of tropical NOMs and IHSS NOM	93
Figure 4.4	Retentions of NOM solutions through the PBGC Membrane	94
Figure 4.5	Retentions of NOM solutions through the YM10 Membrane	94
Figure 4.6	Flux decline during the PBGC membrane filtration: (a) S-RW; (b) S-NOM I; (c) S-NOM II; (d) IHSS NOM	95
Figure 4.7	Total additional resistance R_c during the PBGC membrane filtration: (a) S-RW; (b) S-NOM I; (c) S-NOM II.....	96
Figure 4.8	NOM irreversible resistance during the PBGC membrane filtration: (a) S-RW; (b) S-NOM I; (c) S-NOM II.....	96
Figure 4.9	Flux decline during the YM10 membrane filtration: (a) S-RW; (b) S-NOM I; (c) S-NOM II; (d) IHSS NOM	97
Figure 4.10	Total additional resistance during the YM10 membrane filtration: (a) S-RW; (b) S-NOM I; (c) S-NOM II.....	97

Chapter 5

Figure 5.1	Mode of operation: crossflow vs deadend; constant pressure vs constant flux	99
Figure 5.2	Flow sheet of a constant pressure stir cell filtration system	101
Figure 5.3	Flow sheet of a constant flux stirred cell filtration system	102
Figure 5.4	Schematic of the concentration profiles and the mass balance	104
Figure 5.5	Molecular weight distribution of NOM	107
Figure 5.6	TOC/ UV-Vis Retention of (a) YM3, (b) YM10, (c) PT membranes	108
Figure 5.7	NOM retention under (a) constant pressure conditions, (b) constant flux conditions	108

Figure 5.8	Fouling performances during NOM filtration for different membranes (a) constant pressure, (b) constant flux	110
Figure 5.9	Fouling performances during NOM filtration for YM3 membrane-constant pressure	111
Figure 5.10	Fouling performances during NOM filtration for YM10 membrane-constant pressure	112
Figure 5.11	Fouling performances during NOM filtration for PES-PT membrane-constant pressure	113
Figure 5.12	Fouling performances during NOM filtration for YM3 membrane-constant flux	114
Figure 5.13	Fouling performances during NOM filtration for YM10 membrane-constant flux	115
Figure 5.14	Fouling performances during NOM filtration for PT membrane-constant flux	116
Figure 5.15	Comparison of fouling resistance between constant pressure vs. constant flux mode for YM3 membrane	116
Figure 5.16	Comparison of fouling resistance between constant pressure vs. constant flux mode for YM10 membrane	117
Figure 5.17	Comparison of fouling resistance between constant pressure vs. constant flux mode for PT membrane	117
Figure 5.18	NOM fouling –YM3 membrane at constant pressure (a) dead end; (b) 100rpm; (c) 200rpm; (d) 300rpm	118
Figure 5.19	NOM fouling –YM10 membranes at constant flux (a) dead end; (b) 200rpm	119
 Chapter 6		
Figure 6.1	Molecular weight distribution of NOM after MIEX treatment	125
Figure 6.2	MIEX Jar tests	126
Figure 6.3	Fouling performances during NOM filtration- constant pressure (50kPa), no MIEX	128
Figure 6.4	Fouling performance during NOM filtration- constant pressure (50kPa, 200rpm), no MIEX.....	128

Figure 6.5	Fouling performances during NOM filtration- constant flux (60/m ² .h), no MIEX	129
Figure 6.6	Fouling performance during NOM filtration- constant flux (100l/m ² .h), no MIEX	130
Figure 6.7	Fouling performance during NOM filtration- constant flux (150l/m ² .h), no MIEX	130
Figure 6.8	Effect of MIEX pretreatment on the fouling of GVVP membrane –Constant Pressure 50kPa	132
Figure 6.9	Effect of MIEX pretreatment on the fouling of GVHP membrane –Constant Pressure 50kPa	132
Figure 6.10	Effect of MIEX pretreatment on the fouling of PBHK membrane –Constant Pressure 50kPa	133
Figure 6.11	Effect of MIEX pretreatment on the fouling of membranes –Constant flux 60l/m ² .h: (a) HVLP, (b) GVVP, (c) GVHP, (d) PBHK	134
Figure 6.12	Effect of MIEX pretreatment on the fouling of membranes –Constant flux, 100l/m ² .h: (a) HVLP, (b) GVVP, (c) GVHP, (d) PBHK	135
Figure 6.13	Effect of MIEX pretreatment on the fouling of membranes –Constant flux, 150l/m ² .h: (a) HVLP, (b) GVVP, (c) GVHP, (d) PBHK	135
Figure 6.14	Effect of MIEX pretreatment on the fouling of GVVP membrane –Constant flux 100L/m ² .h	136
Figure 6.15	Effect of MIEX pretreatment on the fouling of GVHP membrane –Constant flux 100L/m ² .h	137
Figure 6.16	Effect of MIEX pretreatment on the fouling of PBHK membrane –Constant flux 100L/m ² .h	137
Figure 6.17	NOM fouling without MIEX pretreatment – HVLP CP	138
Figure 6.18	NOM fouling after MIEX pretreatment – HVLP CP	138
Figure 6.19	NOM fouling without MIEX pretreatment – GVVP CP	139
Figure 6.20	NOM fouling after MIEX pretreatment – GVVP CP	139

Chapter 7

Figure 7.1	Chemical structure of different monomers used for electrophoresis-UV grafted polymerization of PES membranes	144
Figure 7.2	Schematic diagram of the combined electrophoresis-UV grafting system	146
Figure 7.3	The effects of monomer concentration and electrophoresis on the degree of grafting during the modification of PES membranes ...	148
Figure 7.4	Molecular weight cut-off (MWCO) of membranes modified with different monomers at 1wt%	152
Figure 7.5	Pure water flux of the PW/PT membranes modified with different monomers at 1wt%	153
Figure 7.6	Pure water flux of the PW membranes modified with MA at different concentrations	154
Figure 7.7	Retentions of NOM solutions through the modified membranes...	155
Figure 7.8	Fouling performances during NOM filtration using the PT membranes	156
Figure 7.9	Fouling performances during NOM filtration using the PW membranes	157
Figure 7.10	Surface of the PW membrane with MWCO of 56kDa (magnification: 40k)	158
Figure 7.11	Surface of the AAG modified PW membrane (magnification: 40k)	159
Figure 7.12	Surface of the HEMA modified PW membrane (magnification: 40k)	159
Figure 7.13	Surface of the fouled unmodified PW membrane after NOM filtration (magnification: 3k)	160
Figure 7.14	Surface of the fouled PES-PW membrane modified by 2% MA after NOM filtration (magnification: 3k)	160

LIST OF SYMBOLS

A	the membrane surface area (m^2)
C_B	the concentration in the bulk feed (mol.L^{-1})
C_b	the bulk humic acid concentration (mol.L^{-1})
C_{permeate}	Organic carbon concentration of permeate (ppm)
$C_{\text{retentate}}$	Organic carbon concentration of retentate (ppm)
D_g	the degree of grafting
D_S	the solute diffusivity
F_b	the pore blockage parameter (m^2/kg)
θ	the fraction of humic acids in the bulk solution (-)
J_o	the initial volumetric flux ($\text{L}/\text{m}^2.\text{h}$)
J_v	volumetric flux of permeate ($\text{L}/\text{m}^2.\text{h}$)
k_s	the solute mass transfer coefficient (m/s)
Δp	the pressure drop imposed across the fouling layer and membrane (Pa)
Δp_{pure}	pressure drop imposed across the membrane (Pa)
R_c	the cake resistance (m^{-1})
R_{co}	the resistance of the first layer of the humic acid deposit (m^{-1})
R_i	the various additional resistances during the filtration process (m^{-1})
R_m	the resistance of clean membrane (m^{-1})
S_a	actual membrane sieving coefficient
S_o	the observed membrane sieving coefficient
TOC	Total organic carbon (ppm)
T	temperature (K)
t	the time (min)
W_g	the dried membrane weight after grafting with different monomers (g)
W_o	the original membrane weight before modification (g)
V	the total volume of permeate (L)

Greek letter

α_c	the specific resistance of the cake layer (m/kg)
δ	boundary layer thickness (mm)

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ε_s	the extent of superimposed resistance ($\text{m}^{-1}\text{mg}^{-1}$)
η	the viscosity of the permeate ($\text{kgm}^{-1}\text{s}^{-1}$)
τ	the fouling time constant

1.

INTRODUCTION

1.1. Background

Natural Organic Matter (NOM) present in natural water sources is a complex mixture of organic compounds derived from the degradation and decomposition of biological organisms. With a broad spectrum of functional groups, sub-structures and molecular weight distribution, the composition of the mixture is strongly dependent on environmental sources, and the concentrations of NOM are found to vary widely in natural water sources.

Raw water supplies in Singapore tend to contain high NOM and other contaminants, particularly in 'imported' surface waters. The significant removal of NOM is important, as NOM affects odour, colour and taste of the water, forms complexes with heavy metals and pesticides, and reacts with chlorine, the most widely used oxidant for water disinfection. The chlorinated disinfection by-products have been recently recognized to be human carcinogens.

Membrane processes are increasingly used in drinking water treatment to meet stringent water quality regulations. For the removal of NOM, in general, the choice of reverse osmosis (RO) or nanofiltration (NF) membranes would reach a high removal to more than 90%, but extensive pre-treatment is necessary and filtration flux is relatively low. Ultrafiltration (UF) membranes have proven to be a valuable and effective technique in terms of removal efficiency of water contaminants such as turbidity and pathogens. However, UF membranes have a limitation for the

1. Introduction

retention of NOM due to their generally larger molecular weight cut-off (MWCO) compared to the relative molecular weight of NOM. NOM removal is very pore size dependent showing a transition at about 6nm pore size. The commercial UF membranes only typically achieve partial removal of NOM in the range of 20-50%.

Membrane fouling by NOM is another problem. The efficiency of NOM removal by UF membranes is also highly dependent on the adverse fouling effect. Membrane fouling is influenced by the characteristics of NOM such as structure (aromatic/aliphatic, or hydrophobic/hydrophilic), size (average relative molecular mass and its distribution), and charge density, the chemical composition of the feed water and the hydrodynamic conditions. In addition, membrane properties such as pore size, porosity, charge, and hydrophobic/hydrophilic nature of the membrane are important factors that could influence fouling by NOM.

The effective removal of NOM is a great challenge in the water industry and many researchers have devoted their efforts in this area. A Strategic Research Program on 'Membrane Technology for Sustainable Water' funded by ASTAR was launched in September 2002. The research program included a project "NOM and contaminant removal by ultrafiltration membranes ---- enhancement of filtration performance", which is the topic of this thesis.

1.2. Objectives and scope of the thesis

The objectives of this thesis are as follows:

- To evaluate the influences of various factors such as environmental conditions, NOM status, membrane properties and operating conditions on the membrane fouling caused by NOM in the filtration process.
- To isolate NOM from the raw water of a Singapore reservoir to prepare a tropical NOM for Singapore, and to compare the tropical NOM ultrafiltration fouling performance with that of IHSS NOM as a reference

1. Introduction

- To evaluate a full spectrum of operating strategies, which include constant pressure and constant flux modes with and without stirring, in order to identify optimal operating conditions to enhance UF membrane performance and control NOM fouling
- To combine UF membrane filtration with other processes such as adsorption, and identify the most suitable membranes and optimize the operating strategies favoring NOM removal and minimizing fouling.
- To develop a novel method of UF membrane modification to make membrane surfaces exhibit more hydrophilic and negative charged features for more effective NOM removal with lower fouling tendency

In order to achieve these targets, extensive and systematic studies were conducted. The effects of the ions in the water on the NOM removal efficiency were studied over a wide range of ionic strengths. Several types of membranes were used to study the influences of membrane MWCO and membrane surface properties on the NOM filtration performance. In addition, tropical NOM was isolated from a Singapore water source and characterized by a range of techniques. The impact of the characteristics of the tropical NOM (reservoir-based) on UF membrane fouling was investigated and the results were compared with standard humic substances IHSS NOM (river-based standard) and a commercially produced NOM (soil-based). In addition, various operating modes and factors were compared in terms of NOM removal efficiency and their effect on fouling performance. A hybrid system which combined MIEX pretreatment and low-membrane filtration was studied. The effects of MIEX pretreatment on NOM removal and membrane fouling were evaluated.

1. Introduction

Finally, a novel technique which combines controlled deposition by electrophoresis of charged moieties, with UV grafting on the membrane surface was applied to modify Poly(ether sulfone) membranes with several different monomers to improve the membrane filtration performances for the NOM removal. The scope of the work is summarized schematically in Figure 1.1.

Figure 1.1 Schematic description of the ‘NOM removal using UF membranes’ research scope

1.3. Organization of this thesis

Chapter 1 provides an introduction to the background of NOM and membrane technologies for NOM removal as well as description of the research objectives and scope.

The literature review presented in Chapter 2 covers the definition and discussion of NOM properties and matters related to the application of membrane technologies to

1. Introduction

drinking water production such as UF membrane characteristics, NOM fouling and membrane modification.

Chapter 3 focuses on the influence of ionic (Na^+ and Ca^{2+}) interactions with the NOM on the apparent molecular size distribution of the species and the NOM removal efficiency. The investigation was conducted over a wide range of ionic strengths. This is the first reported detailed assessment of Singapore NOM, which is typical of a tropical catchment.

In Chapter 4, two types of tropical NOM were isolated using a RO system and characterized by a series of analyses. Membrane filtration of the natural water sample, reconstituted tropical NOMs and IHSS NOM through two types of UF membrane were conducted in order to understand the impact of the characteristics of tropical NOM on UF membrane fouling.

Chapter 5 presents a systematic study to evaluate different operating strategies, including constant pressure and constant flux modes with and without stirring, in terms of NOM removal efficiency and their fouling performance using different UF membranes with MWCOs around 10-30 kDa.

In Chapter 6, the hybrid membrane process with MIEX and low pressure membranes has been evaluated for a NOM-laden water from a tropical source. Experiments were performed at the bench-scale with both MF and UF membranes, operated deadend (unstirred) and stirred, at constant pressure and constant flux. Guidelines for optional conditions were identified.

Chapter 7 describes the first reported attempt to control the surface properties of UF membranes by the combined application of electrophoresis and UV grafting. Three types of PES UF membranes were modified by this approach and used for NOM removal. With electrophoresis assistance, the modified membrane exhibited more homogeneous properties than without electrophoresis.

1. Introduction

Chapter 8 summarizes the overall research, presents conclusions and provides suggestions for future work.

2.

LITERATURE REVIEW

2.1 Nature organic matter (NOM)

2.1.1 Impact of NOM on surface water quality

Natural organic matter (NOM) present in surface water is a complex mixture of organic compounds derived from the degradation and decomposition of biological organisms. A large number of studies, which investigate the nature of NOM and its influence on water quality, can be found in the literature. The presence of NOM may have an adverse effect on the water quality for three main reasons (Stevenson, 1982; Aiken, 1985; Edzwald *et al.*, 1985; Thurman, 1985; Amy *et al.*, 1987; Gjessing *et al.*, 1999; Schaefer, 1999):

- Increasing the transport and distribution of inorganic and organic micro-pollutants;
- Promoting the formation of potentially harmful disinfection by-products;
- Serving as a substrate for undesired biological growth in distribution systems.

Studies of NOM have shown that these compounds are the precursors of chlorination disinfection by-products, such as trihalomethanes, haloacetic acids and chlorophenols. The by-products have been recognized to be human carcinogens. This suggests that it is safer to remove the natural organics during treatment and

2. Literature review

prior to disinfection. Further problems associated with natural organics are taste and odors, and their association with pollutants such as hydrophobic organics (e.g. pesticides) and heavy metals.

2.1.2 Composition and fractionation of NOM

The major fractions of dissolved NOM in aquatic environments are humic substances. In general, the humic substances are macromolecules that contain aromatic and aliphatic components with carboxylic and phenolic groups attached to aromatic rings.

Two main compounds can be identified, humic acid (HA) and fulvic acid (FA). The quantitative amount of each fraction is very case specific. An average organic composition of natural water is listed below (Thurman, 1985; Schaefer, 1999; Aoustin *et al.*, 2001):

- 10% humic acid (HA)
- 40% fulvic acid (FA)
- 30% hydrophilic acid (Hyd)

Humic acid and fulvic acid are anionic polyelectrolytes with carboxyl functional groups and phenolic groups. They are mainly responsible for the color in natural water. The non-humic fractions of NOM are composed of transphilic acids, proteins, amino acids and carbohydrates; they are less hydrophobic than the humic fractions (Peuravuori and Pihlaja, 1997; Maartens *et al.*, 1998; Frimmel and Abbt-Braun, 1999; Hem and Efraïmsen, 1999; Nissinen *et al.*, 2001; Baker, 2002; Maurice *et al.*, 2002).

In order to understand the nature and reactivity of NOM in water treatment processes, the isolation of the complex NOM into more homogeneous fractions is a useful approach. The resin fraction method by XAD-8 resin and XAD-4 resin can

2. Literature review

be used for this purpose as described in the following (Maurice *et al.*, 2002). An outline of the raw water fractionation procedure is shown in Figure 2.1.

Figure 2.1 Outline of raw water fraction procedure

- The raw water concentrate is filtered through a 0.45µm membrane, adjusted to pH 2, and fed onto a XAD-8 non-functionalized resin which retains strongly hydrophobic organic matter attributed to humic acids and fulvic acids. This fraction is eluted with NaOH and acid on an IRC-120 cation exchange resin.
- The unabsorbed concentrate from the XAD-8 resin is fed onto an XAD-4 resin, which retains weakly hydrophobic (or transphilic) organic matter. This fraction is also eluted with NaOH, and separately acid on an IRC-120 resin.
- The unadsorbed concentrate from the XAD-4 resin, which consists of hydrophilic (non-humic) organic matter attributed to proteins, amino acids, and carbohydrates, is fed onto an IRA-958 anion exchange resin, which retains charged materials. This fraction is eluted with a NaOH/NaCl

2. Literature review

mixture. The remaining neutral materials are not retained by any of the resins.

Thus, the fractionation according to this procedure yields the following four fractions (Alberts and Takacs, 1999; Frimmel and Abbt-Braun, 1999; Nissinen *et al.*, 2001):

- Hydrophobic acids (HA)-adsorbed by XAD-8.
- Transphilic acids (TA)-adsorbed by XAD-4.
- Hydrophilic charged compounds (Charged) - adsorbed by IRA-958.
- Hydrophilic neutral compounds (Neutral) - passed through all resin columns.

2.1.3 Extraction of NOM from surface water

Previous studies have shown that the properties of NOM vary with different water sources. Although some characterization methods for dissolved NOM can be applied to raw filtered samples, isolation and concentration are required for many processes. Ultraviolet/visible absorbance and fluorescence, ICP and organic acidity can analyze NOM with a low concentration of less than 10ppm (Alberts and Takacs, 1999; Ratnaweera *et al.*, 1999; Wang *et al.*, 2001; Baker, 2002; Her *et al.*, 2002). However, a sample solution with 100ppm is required for elemental composition study. Furthermore, HPSEC with a commercial RI detector working on a solution with a concentration around 10ppm does not produce reliable results regularly. To get a clear understanding of NOM properties, it is necessary to extract NOM from the treated water source.

Processes available for the extraction of natural organics from water include resin adsorption (typically XAD), ultrafiltration, reverse osmosis (RO), low temperature evaporation and others. Among these methods, the ion exchange resin and the hybrid membrane processes (MF+RO) are the most common methods for the

2. Literature review

processing of large samples. It is important to minimize the loss of certain fractions, such as small compounds which are difficult to treat.

(i) XAD resin and Ion Exchange Resin

XAD resin, the acrylic-ester resin, is considered as the most commonly used isolation method for NOM extraction from surface water. The XAD-8 is an excellent sorbent for humic substances at low pH(around 2), resulting in the extraction of humic substances without other organic and inorganic constituents. The XAD-8 isolation method requires samples to be acidified to pH 2 with concentrated HCl and desorbed from the resin with 0.1M NaOH. It may be used to isolate NOM from large quantities of water. The recovery is about 40-60%. This resin, however, mainly retains hydrophobic acids, whereas hydrophilic acids are better retained by XAD-4 and are lost if only a XAD-8 resin is used. Figure 2.2 shows schematically the XAD-8 isolation procedure (Peuravuori and Pihlaja, 1997; Frimmel and Abbt-Braun, 1999; Schaefer, 1999; Baker, 2002; Maurice *et al.*, 2002).

It is evident that the XAD isolation method, although widely used, has its limitation. The acid/base extremes could potentially alter the NOM structure. It is also very time consuming due to the long resin preparation procedure. Recoveries are also not stable and are low for low molecular weight compounds.

Figure 2.2 Schematic illustration of the XAD-8 resin isolation technique

2. Literature review

(ii) Reverse osmosis isolation with MF pretreatment

RO membranes have a very small molecular weight cut-off (MWCO) and are expected to retain a large fraction of low molecular weight compounds. Unlike the XAD resin, RO system is not designed to isolate humic substances. The use of membranes for NOM concentration was first reported by Serkiz and Perdue (Serkiz and Perdue, 1990; Hem and Efraïmsen, 1999; Aoustin *et al.*, 2001). Then the use of a potable RO system to extract NOM from the raw water became more and more common. Several groups report the recovery of NOM to be around 90%. That means most compounds in surface water may be concentrated using RO with only a minimal loss of very small organics during concentration and freeze drying. Compared with the XAD method, this method appears to be well suited for NOM removal (Peuravuori and Pihlaja, 1997; Alberts and Takacs, 1999; Baker, 2002). The problem arises with other compounds such as SO_4^{2-} and silica which often

Figure 2.3 Schematic illustration of the RO isolation method

concentrated along with the NOM and are difficult to remove from the RO isolate without causing unwanted NOM fractionation. This generally results in a product of high ash content and the salt can lead to precipitation in the concentrate. It is not yet known whether the concentration of inorganic components and the accompanying ionic strength changes over the RO procedure alter the

2. Literature review

characteristics of NOM or not. Figure 2.3 shows the schematic illustration of the RO isolation method.

(iii) Desalting and Purification

It may be necessary to desalt the isolated NOM. Desalting can be difficult since inorganic and organic ions having a similar size need to be separated. The method applied to desalt the concentrate is cation exchange, which unfortunately either decreases the pH or only exchanges multivalent for monovalent ions. Ions which are complex by the organics cannot be exchanged. There was a report on the decrease in cation resin exchange efficiency at a lower pH (Schaefer, 1999; Wang *et al.*, 2001). It can also be expected that some organics will be lost in the cation exchange process.

2.1.4 Characteristics of NOM

NOM properties include structure (aromatic/aliphatic, or hydrophobic/hydrophilic), size (average molecular weight and weight distribution), and charge density. They play an important role to lead the interaction between NOM and membranes, colloids and other contaminants in the raw water.

(i) Functional groups

Functional groups determine the chemical origin of NOM, which is related to characteristics such as chemical binding, UV absorption, charge, hydrophobic interactions and solubility. Major functional groups of NOM are carboxylic acids, phenolic hydroxyl, carbonyl and hydroxyl groups. The fraction of these functional groups exhibited much difference because of the variation of the raw water source. Table 2.1 presented an example provided by Schaefer *et al* (Schaefer, 1999; Clair *et al.*, 1996). Aliphatic, Carbohydrate, Aromatic and Carboxyl were considered of

2. Literature review

the main functional group of four different NOMs, and these functional groups presented different percentage in these kinds of NOM.

Table 2.1 Function groups present in different river NOMs (Schaefer, 1999)

Organic Type	Aliphatic	Carbohydrate	Aromatic	Carboxyl	Other
Suwannee FA	31	19	23	18	9
Suwannee HA	23	19	37	14	7
NOM least aromatic	38	42	5	13	2
NOM most aromatic	37	27	12	19	5

Recently, the studies on the characteristics of NOM presented the variation of NOM functional groups in more details. Zularisam et al. (Zularisam *et al.*, 2006) characterized different kinds of NOM and summarized that NOM was composed of humic substance, polysaccharides, amino acids, proteins, fatty acids, phenols, carboxylic acids, quinines, lignins, carbohydrate, alcohols, resins and inorganic compounds such as silica, alumino-silicates, iron, aluminium, suspended solids and microorganisms. The Schematic model structures of HA and FA are shown in Figure 2.4 and Figure 2.5, respectively (Kim *et al.*, 2006; Thacker *et al.*, 2005)

Figure 2.4 Schematic of humic acid model structure (Zularisam *et al.*, 2006)

Figure 2.5 Schematic of fulvic acid model structure (Zularisam *et al.*, 2006)

2. Literature review

Basically, NOM could be classified into two groups: Aliphatic and Aromatic. The fraction of aromatic group of the NOM determined the tendency to form the potentially harmful disinfection by-products and the membrane fouling performance. It is important to define the fraction of the aromatic groups. The specific UV absorbance ($SUVA = UVA_{254}/TOC$) of NOM is ascribed exclusively to aromatic chromophores. It is considered as a measure of the humic fraction (the relative aromatic content) of NOM. However, UV measures the aromatic compounds preferentially and does not give correct results if the aromaticity is altered.

(ii) Hydrophobicity/hydrophilicity

The major fraction of NOM is composed of humic substance which exhibited hydrophobicity with larger molecular weights. Different NOMs contain different fractions of humic substance and perform different hydrophobicity. It is well known that hydrophobicity describes how much a molecule ‘dislikes’ water, which is linked to its solubility. A hydrophilic compound is highly soluble in water, whereas a hydrophobic compound is more soluble in an organic solvent. Consequently, the partitioning coefficient of the organics between organic solvents and water can be used to measure hydrophobicity. The phenolic groups are more soluble in organic solvent, whereas the hydroxyl, amine or carboxylic acid groups are more soluble in water (Chin *et al.*, 1994; Alberts *et al.*, 2002; Kohler *et al.*, 2002; Schafer *et al.*, 2002). Thus hydrophobic interactions and electrostatic exclusion between NOM and the membrane surface vary with different NOM sources and it is important to define the hydrophobicity of the NOM.

(iii) Size (average molecular weight and weight distribution)

Size and molecular weight are interrelated and they are important factors in water treatment, especially for membrane processes. As a mixture of species, the molecular weight ranges of NOM change batch to batch. In general, the molecular

2. Literature review

weight range of humic acid is 200-100,000Da; the range of fulvic acid is 2,000-10,000Da. However, the variation of NOM leads to different molecular weights and distributions, some studies report that the molecular weight of NOM ranges from 5,000 to 50,000Da (Zularisam *et al.*, 2006). These results are often dependent on the method afforded and the standards used. The methods often used for determining the size and molecular weight include ultra-centrifugation, viscosimetry, small-angle X-ray scattering, size exclusion chromatography, ultrafiltration and others (Chin *et al.*, 1994; Schafer, 1999). The most extensively used method is apparently size exclusion chromatography -- at present, almost solely the High-Pressured Size Exclusion Chromatography (HPSEC). This method reveals not only the molecular size distribution but also number-averaged and weight-averaged molecular weights, a major advantage compared to other methods. Another advantage is the possibility to carry out analysis without a prior isolation of NOM. However, the results of HPSEC change with different techniques, detectors, standards and eluents, this makes the comparison of results difficult (Cai, 1999; Pelekani *et al.*, 1999; Nissinen *et al.*, 2001; Egeberg *et al.*, 2002; Parlanti *et al.*, 2002).

(iv) Charge Density

The charge of natural organic matter is an important factor to determine the interaction between NOM and membranes, cations and solubility. Charge is therefore a very relevant characteristic for water treatment, and the distinction between the charges of functional groups could explain the pH effects on membrane rejection and fouling. As a mixture, NOM contains several carboxylic groups and some phenolic functional groups. These groups give the molecules charge, which increases in negativity with increasing pH. Among the NOM fractions, humic acid has more phenolic groups than fulvic acid and is more hydrophobic. Fulvic acid has a higher carboxylic acidity than humic acid and therefore has a higher charge (Wang *et al.*, 2001; Schafer *et al.*, 2002)

2. Literature review

2.1.5 Interaction between NOM and other contaminants

(i) Cations

The interaction between cations and NOM is summarized in two major classes; site specific strong binding and weak binding. The strong binding is very organic specific and is not always present with various NOM. However, the weak binding is caused by the electrostatic attraction or the presence of counter-ions in the vicinity of the organic molecule. The weak binding presents in all NOM sources and increases with functional groups (carboxylic groups, phenolic groups) and the structural arrangement of these groups. It was also well known that the mechanisms of both bindings are not independent of each other. (Kim *et al.*, 2002; Lu and Allen, 2002; Schmitt *et al.*, 2003)

The interaction of natural organics with cations results in various species. Numerous investigations on complexation between them have been conducted. It has been reported that Fe^{3+} , Cu^{2+} and Al^{3+} perform a greater extent for the available binding site than Ca^{2+} and Mg^{2+} . However, the effect of Ca^{2+} and Mg^{2+} get more important aspect to consider the complexation of the organic elements with the cations due to the abundance of Ca^{2+} and Mg^{2+} in most natural waters. The complexation of the organic elements with the ions may lead to the formation of stable complexes or aggregation brought about by the chelating effect of the divalent cations. This results in an increase in both size and apparent molecular weight of the humic substances (Vilge-Ritter *et al.*, 1999; Pinheiro *et al.*, 2000; Schmitt *et al.*, 2003; Lu *et al.*, 2002; Cheng and Allen, 2006).

(ii) Inorganic Colloids

A colloid or colloidal dispersion is a substance with components of one or two phases. Inorganic Colloids in a natural environment include the oxy/hydroxides of Fe, Al, Si and Cu as well as clays and carbonates. A colloid particle size is between 1 nm and 1000 nanometers in diameter. The high specific surface area of the

2. Literature review

colloids allows the adsorption of many reactive species. Several mechanisms including electrostatic interaction, specific chemical affinity, and hydrophobic interactions predict the interaction between colloids, organics, and multivalent ions (Mousley *et al.*, 2003, Wilkinson and Buffle, 1997).

In general, colloids in the natural environment have a negative surface charge due to an adsorbed layer of NOM, which can lead to stabilization of the colloids. It is because NOM contains many acidic functional groups (mainly carboxyl and phenolic-OH), its adsorption produces a uniformly negative surface charge on the colloid surface. The NOM can adsorb at the colloid surface in loops or tails, depending on the solution chemistry, and thus alter the surface morphology of the inorganic colloids (Schaefer, 1999; Schmitt *et al.*, 2003). The stability of the colloids depends on colloid charge and steric effects. The negative charge brought by NOM imparts the colloids stability by producing repulsive electrostatic double-layer forces. In addition, much NOM has a high molecular weight and thus could impart colloids stability through repulsive steric force. On the other hand, the stability of colloids could be broken and the aggregation will occur while the environment conditions such as pH, ionic strength, primary colloid size, and stirring change. Thus the interactions among colloids, organics, and multivalent ions suggest the importance of these phenomena in the membrane filtration behavior of natural waters containing colloids and organics.

(iii) Other compounds

Except for cations and colloids, many studies have been conducted concerning the interaction between NOM and trace metals, organic or inorganic toxins. It is believed that most of the trace metals in the aquatic systems could form soluble complexes with organic ligands, and others associate with organics as colloids. And they could be transported associating with NOM and colloidal materials. The toxins occurred in natural water also perform the binding effect to NOM and transport with the NOM. It has been proved that hydrophobic and amphipathic micropollutants, such as herbicides and pesticides could bind to NOM and cause the

2. Literature review

problem once they are released (Wilkinson *et al.*, 1997). This pollutant uptake brings an important effect in water treatment, where the retention of such colloids and the resulting stress could cause a release of such pollutants.

Table 2.2.A general overview of membrane processes and solute dimensions

	Atomic Force Microscopy		Electron Microscope		Optical Microscope		Visible	
	Dissolved Matter		Colloids		Suspended Matter		Macroparticles	
	Ions	Molecules	Macromolecules	Colloids	Microparticles	Macroparticles	Macroparticles	
Molecular Weight [Da]	100	1000	10000	100000	1	10	100	1000
Size [µm]	0.001	0.01	0.1	1	10	100	1000	
Solute/Particle Dimension	Mineral Salts		Proteins		Algae Protozoa			
	Fumaric Acid				Red Blood Cells			
	Humic Acid		Pyrogens		FeCl ₃ Flocs			
			Virus		Bacteria, Micro Algae			
	Metal Ions		Colloids					
	Pesticides							
	Amino Acids							
Membrane Separation Process	RO	NF	UF	MF				
	Dialysis							
	Electrodialysis							
Physico-Chemical Separation Process					Ultrafiltration	Centrifugation		
					Coagulation / Flocculation Decantation / Sedimentation			
					Media Filtration			
Separation Process with Change of Phase	Distillation / Gel Concentration							
Chemical Separation Process	Ion Exchange							
	Solvent Extraction							
	Macroporous Resin							
	Activated Carbon							

2. Literature review

2.2 Membrane filtration processes and NOM fouling

2.2.1 Introduction

Until relatively recently the major application of membrane technology to produce drinking water has been for desalination of saline waters by reverse osmosis. However since about 1990 technical advances in the lower pressure membrane processes coupled with more stringent water quality standards has seen these methods increasingly applied to the production of drinking water from 'traditional' non-saline sources. The major reasons favoring this trend are,

- Membrane technologies are capable of removing a wide range of contaminants from particulates, including pathogens, to ionic species. (Table 2.2)
- The technology only requires modest energy usage (no phase change).
- Membranes are modular allowing small (decentralized) to large (centralized) facilities.

Most importantly, the economics of water treatment by membranes has become increasingly competitive with conventional processes.

2.2.2 Membrane Processes

The pressure-driven membrane processes applied to water treatment make use of finely microporous membranes, usually polymeric, in the form of sheets, tubes or hollow fibers. Table 2.3 summarizes the key features of these processes.

For non-saline water treatment the methods used are MF, UF and NF. All three processes remove turbidity, bacteria and protozoa. Virus removal can be achieved by UF and NF. Substantial removal of NOM requires NF or low pressure MF or UF coupled with coagulants or adsorbents. RO is applied if the raw feed water is saline. Because of their different pore sizes and applications the various membrane processes respond in different ways to foulants in raw water, as discussed in section 2.2.6 below.

2. Literature review

2.2.3 Ultrafiltration and Microfiltration

As mentioned previously, membrane porosity, morphology and surface properties (hydrophobicity and surface charge) play an important role in determining NOM rejection and associated fouling during the filtration process, in addition to the membrane material itself. Generally, UF membranes have following characteristics:

Table 2.3 Membrane processes and characteristics for water treatment

Membrane Process	Pore Size (nm)	Species retained	Typical fluxes (litres/m ² hr)**
Microfiltration (MF)	100-1000	Bacteria, turbidity, particles	50-200
Ultrafiltration (UF)	5-50	Virus, colloids, macrosolutes	50-100
Nanofiltration (NF)	2-5	NOM, sugars, divalent ions	10-50
Reverse Osmosis (RO)	< 1*	Monovalent ions, low MW org.	10-30

* No detectable pores ** For water treatment applications

- All membranes have quite rough inside surfaces;
- The surface pores are circular in shape or slit shaped;
- The membranes have moderate surface porosity (more than 10%);
- The pore diameters range from 1 to 100 nm.

Techniques to characterize membrane properties are detailed below (Schock *et al.*, 1989; Ludwig *et al.*, 1997; Maartens *et al.*, 2000; Yuan *et al.*, 2002; Chang and Benjamin, 2003; Rao *et al.*, 2003).

(i) Membrane pore size – MWCOs analysis

In general, membrane pore size in UF is characterized by the molecular weight cut-off (MWCO) value, which is the molecular weight above which rejections are

2. Literature review

expected to be higher than 90%. Many manufacturers provide the membrane MWCO information by measuring the retention of solutes of various macromolecular weights. The solute retention is the most common method to characterize the membrane pore size. Other methods include bubble-pressure breakthrough, mercury porosimetry, and electron and atomic force microscopy.

Standard test procedures are not yet defined. Various solutes are chosen for retention tests: salts, sugars, proteins, dextrans, polyethyleneglycol etc. The test should run under conditions where concentration polarization is minimized. This can be achieved by testing at a low solute concentration, high agitation or feed flow rate, and low pressure. The measurement methods include TOC analysis and HPSEC analysis. However, the MWCO becomes imprecise if fouling occurs.

(ii) Hydrophobicity – contact angle analysis

The contact angle value indicates the hydrophobicity of the membrane surface. Several methods are currently available to measure contact angles, including capillary rise, sessile drop or captive bubble, Wilhelmy balance, laser goniometry, and others. The conventional method to measure contact angle is the captive bubble and sessile drop method. The contact angle of membrane surfaces is not easy to accurately measure because of the effects of surface texture and porosity, but it is still regarded as a convenient semi-quantitative index of membrane hydrophobicity/hydrophilicity. Comparisons of contact angle value between material surfaces are more meaningful if the entire protocol is kept consistent for each sample.

(iii) Surface charge – zeta potential analysis

The membrane charge plays an important role in solute rejection, and charge effects become more important for tighter membranes. The membrane charge is measured by the zeta potential (the potential at the shear plane in the diffuse layer), which can be estimated by the streaming potential method. Streaming potential can be measured through pores and along the surface. However the pore streaming

2. Literature review

potential is difficult to be determined and the calculation often results in underestimation.

(iv) Membrane morphology – Field emission scanning electron microscopy (FE-SEM)

Scanning electron microscopy can be used directly only with dry membranes to measure total surface porosity and pore size. This method is limited in resolution power to pore size greater than 50nm. Membrane specimen was prepared for morphological observation using a Hitachi S520 scanning electron microscope. The SEM was operated at 20keV accelerating voltage to determine the pore diameters of membranes.

2.2.4 Modes of operation

There are important operational modes that need to be considered as these influences the type of module used and the kinetics and degree of fouling; understanding the basic differences between the modes may help us interpret apparently conflicting data. Figure 2.6 introduces these concepts, which are,

- *crossflow*: in this situation surface shear is applied as the feed moves across the surface of the membrane, usually pumped in tangential flow but it could be stirred (lab systems) or induced by bubbles or other agents (vibrations, rotations etc). The surface shear provided by crossflow operation encourages back-transport of retained species and this helps to minimize surface interactions and fouling. Crossflow is typically used for NF and RO and for feeds with high solids content in MF and UF. In theory this mode can achieve steady-state, and with very idealized systems it does so, but in practice some degree of fouling tends to occur, so that flux (Figure 2.6(c)) or transmembrane pressure (TMP) (Figure 2.6(d)) continue to change with time. It is important to note that ‘batch concentration’ with crossflow will

2. Literature review

not achieve steady state as the feed concentration increases, but polarization will be controlled to some extent by the crossflow.

- *deadend*: operation without surface shear which allows retained species to accumulate at the membrane and then to be removed by intermittent backwash etc (Figures 2.6(a) and (b)). Thus deadend operation inevitably accepts the deposition of potential foulants but it tends to require less energy and is favored by feeds with low solids content. Nowadays it is frequently used in water treatment with low pressure (MF and UF) membranes
- *constant pressure operation*: as depicted in Figure 2.6(c) with a fixed, constant, pressure and crossflow the flux is initially high and drops rather rapidly to a pseudo ‘steady state’ as cake or retained species (particles or solutes) build up. For constant pressure and deadend operation (Figure 2.6(a)) the flux can effectively decline to zero if the cake is not backwashed. Laboratory studies have tended to favour experiments at constant pressure. It is obvious that with constant pressure operation the initial rate of fouling would be high, due to the high flux, but that eventually the rate of fouling can slow down considerably (although it may not reach a zero rate).
- *constant flux operation*: is more typical of large-scale plant where the system is required to produce a given amount of permeate each day. Figure 2.6(d) shows that for crossflow operation the steady flux will lead to a gradual rise in the required TMP if fouling occurs. This cannot continue indefinitely and occasional cleaning will be required. For deadend mode, Figure 2.6(b) shows that the TMP steadily increases until backwash occurs and a new filtration cycle commences. With constant flux the initial rate of fouling can be relatively slow, but foulants continue to arrive at the same rate over time, unlike constant pressure operation.

2. Literature review

2.2.5 Membrane modules

Membranes are housed in modules that serve to support the membranes and facilitate ‘fluid management’. Table 2.4 lists the various modules and refers to their typical mode of operation. More detailed descriptions of module types and their characteristics can be found in Fane (Fane, 2004). Crossflow modules are typically housed in a pressure vessel, such as the Spiral Wound Module which is the standard for large scale NF and RO. The modules commonly used in water treatment for MF and UF are hollow fibres (contained in pressure vessels or submerged in tanks); tubular systems tend to have niche applications in water treatment.

Figure 2.6: Mode of operation: crossflow vs deadend; Constant pressure vs constant flux

The stirred and dead-end cells are the modules usually used in the lab-scale studies. The stirred cell is almost the same as the dead-end cell except that the stirred cell has a magnetic stirrer, which is controlled by a tachometer. The constant pressure and constant flux modes can be operated in these cells by controlling the feed pressure and the permeate flux. The details can be found in section 5.2.3 of Chapter 5 in this thesis.

2. Literature review

Table 2.4 Modules types and characteristics for water treatment

Module Type	Module features	Advantages	Disadvantages	Mode of operation
Tubular (C)*	Tubes (5-25mm) in series /parallel	Dirty feeds with no pretreatment	High energy cost. Low packing density.	Crossflow**
Hollow fibre (C)	Contained in a pressure vessel	Low energy. High packing d.	Pretreatment may be required.	Dead end or Crossflow***
Hollow Fibre (S)*	Submerged fibres in a tank	Low energy. High packing d.	Hydrodynamics and flow distribution may be poor.	Dead end
Spiral Wound (C)	Flat sheets and spacers wrapped in pressure vessel	High packing d. Good hydrodynamics	Pretreatment may be required. Moderate energy cost.	Crossflow

*C=Pressure Vessel, S=Submerged **Deadend possible ***Crossflow if turbidity rises

2.2.6 Fouling and polarization

(i) Definitions

Fouling: is the deposition of material on or within the structure of membranes that is not readily reversed by simply releasing the pressure or by backwashing. Some foulants may be removed by physical or chemical cleaning but some may be irreversible. The effect of fouling is to decrease membrane permeability (flux declines at constant pressure, or pressure rises at constant flux), and to alter solute retention (tends to increase for MF and UF, and decrease for NF and RO). Thus membrane fouling deteriorates membrane performance, increases operating cost and ultimately shortens membrane life.

The fouling effect can be described by Darcy's law as follows,

$$J_v = \frac{dV}{A dt} = \frac{\Delta p}{\eta (R_m + \sum R_i)} \quad (2.1)$$

where J_v is the volumetric flux of permeate, V the total volume of permeate, A the membrane surface area; Δp the pressure drop imposed across the fouling layer and membrane, η the viscosity of the permeate, R_m the resistance of clean membrane,

2. Literature review

and R_i the various additional resistances during the filtration process as a result of the polarization (see below) and subsequent fouling. The pressure drop, Δp , is frequently referred to as the transmembrane pressure or TMP. It is often convenient to lump the deposit resistances into a 'cake' resistance, R_c , so equation (2.1) is written,

$$J_v = \frac{\Delta p}{\eta (R_m + R_c)} \quad (2.2)$$

Equations (2.1) and (2.2) apply to all modes of operation (crossflow, deadend, constant pressure or flux). For conditions where there is a significant osmotic pressure ($\Delta \pi$) the driving force in equations (2.1) and (2.2) becomes ($\Delta p - \Delta \pi$).

Polarisation: is the accumulation of retained species adjacent to the membrane and is known as Concentration Polarisation (solutes) or Particle Polarisation (particles). By definition, polarization is a reversible phenomenon (for example by stopping flux) and once it becomes irreversible it is fouling. Due to concentration polarization the concentration at the membrane surface (C_w) will be greater than in the bulk feed (C_B). The well-known film model provides a useful relationship for C_w in crossflow operation,

$$C_w = C_B \exp(J_v / k) \quad (2.3)$$

Where J_v is flux and k is the boundary layer mass transfer coefficient (increases with crossflow and decreases with molecular weight). This equation is important as it shows that the surface concentration, C_w that can determine fouling, is very dependent on the J_v/k ratio. For constant pressure crossflow tests, the ratio J_v/k will not be constant and this may complicate interpretation.

For particles and colloids in the $> 0.5\mu\text{m}$ range crossflow produces shear-induced 'back transport' from the membrane (Fane and Fell, 1987); the effect decreases as size decreases and small particles tend to deposit first. Colloids $< 0.1\mu\text{m}$ tend to behave as Brownian species with backtransport decreasing as size increases. Around 0.1 to $0.2\mu\text{m}$ the mechanisms crossover and colloids of this size tend to

2. Literature review

have the lowest ‘backtransport’ and become foulants. This could be modified if electrokinetic interactions are significant, and this is dependent on the materials and solution chemistry (pH, ionic content etc).

For deadend operation ‘polarisation’ is inevitable and since it usually applies to MF and UF the polarization is particulate, forming a cake. However, with mixed feeds, like raw water, fine colloids, macro and microsolutes, can pass into the cake and either be partially retained (modifying the cake), or pass into and through the membrane.

(ii) Fouling mechanisms and interpretation

Fouling can take three ‘generic’ forms (depicted in Figure 2.7),

- pore restriction: a reduction in pore diameter due to adsorption/deposition (small changes in d_{pore} have significant effect as membrane permeability varies with $[d_{\text{pore}}]^4$);
- pore plugging/blocking: a loss of pore density due to species, such as colloids or aggregates, blocking the entrance or internal passageway of pores;
- cake formation / surface deposition of individual particles, aggregates and precipitates, (including deposition favored by the raised concentration at the membrane surface, such as inorganic scale formation, crosslinking of hydrogels, and aggregation of colloids). A fourth type of fouling is,
- biofouling: a type of surface deposition due to bacterial adhesion and biofilm growth, where the ‘cake’ comprises bacterial colonies and expressed biopolymer.

2. Literature review

Figure 2.7 Schematic of fouling mechanisms

The biofouling mechanism is more prevalent in wastewater processing, due to the availability of nutrients. The other three mechanisms can be found in water treatment, with (a), (b) and (c) occurring in MF and UF, either in sequence or simultaneously, and (c) most likely for NF (the very small pore size tends to lead to surface deposition). For MF and UF membranes, which have a distribution of pore sizes around a mean, the effect of colloids and macrosolutes may vary locally.

Figure 2.8 Typical flux history during membrane fouling (Fane and Fell 1987)

During operation a membrane may go through several fouling stages. Figure 2.8 depicts the flux history of a membrane operated under constant pressure conditions; for constant flux conditions the history would be TMP change which would tend to

2. Literature review

mirror as shown in Figure 2.8. Four phases are possible. Phase I is a possible change during water flux testing of the new membrane. Phase II is the initial flux drop when put into use, and this will be due to concentration polarization, pore plugging and adsorptive interactions. Phase III is the longer term operation where flux will usually still continue to decline, and phase IV is the recovery phase during membrane cleaning. The measured water fluxes, $J_{W1,2,3}$ will provide some evidence of fouling (see below).

Fouling data are presented in various ways which include the following:

- Flux decline ratio (J_v/J_o), where J_o is the initial flux at the start of the filtration process. This ratio is illustrative but potentially misleading, as it is not linearly related to fouling resistance. Typically J_v/J_o drops sharply and then changes more slowly, but this could still correspond to a steady increase in fouling resistance. When membranes are compared, based on J_v / J_o , a membrane with an initially high flux will ‘look’ more fouling prone than one with an initially low flux.
- Fouling resistance (R_c) can be obtained from flux and TMP data by applying Darcy’s equation (2.2). This is a better measure of analysis and comparison of different membranes and protocols. Comparing resistances after washing and cleaning allows estimation of ‘easily reversible’ and ‘irreversible’ foulant.
- Transmembrane pressure (TMP) for constant flux processing the parameters $dTMP/dt$ or $dTMP/dV$ are useful and direct measures of fouling effect (TMP is proportional to (R_m+R_c) via equation (2.2)).

(iii) Foulant species

Any species in the feed water is a potential foulant and its impact will depend on its characteristics and concentration as well as membrane properties (pore size, charge, and hydrophobicity), module properties, mode of operation and applied flux.

2. Literature review

Table 2.5 NOM and other foulant species in raw water

Foulant Species	Characteristic	Comment
Particles (POM)	Colloidal ($< 1\mu\text{m}$ $> 0.45\mu\text{m}$)	Bacterial cell wall residues (polysaccharides/proteins)
Dissolved Organic Matter (DOM)	Colloidal and macromolecular ($< 0.45\mu\text{m}$ $> 3.5\text{kD}$)	Bacterial cell wall residues (polysaccharides/proteins)
Humics ($< 3.5\text{KD}$)	Hydrophobic – Neutral – Charged Transphilic Hydrophilic – Neutral – Charged	Proteins, aminosugars, polysaccharides, polyhydroxyaromatics, organic acids
Inorganic ions	Divalent cations (particularly calcium)	Aggregates NOM species. Bridges/binds NOM to membrane surface.

The potential membrane foulants in raw waters include colloidal and suspended particles as well as microorganisms, dissolved macromolecular organic substances and inorganic compounds. Natural organic matter (NOM) with a broad spectrum of molecular weights and size distributions, functional groups and sub-structures has been shown to be the major foulant in the membrane filtration of natural waters (Hong, 1996; Amy and Cho, 1999; Costa and de Pinho, 2002; Jarusutthirak, 2002; Makdissy, 2004; Her *et al.*, 2004). Table 2.5 illustrates the range of species found in river water by Croue *et al.* (Makdissy *et al.*, 2004), based on the fractionation protocol of Leenheer *et al.* (Leenheer *et al.*, 2000). The term NOM covers the particulate colloids (POM), ‘dissolved’ colloids and macrosolutes (DOM), and the humics. In Table 2.5 humics are indicated as $< 3.5\text{kDa}$ (based on Leenheer), but this is arbitrary and the literature refers to humics with molecular weights ranging from 200 to 100 kDa. Since NOM is from bacterial origin its composition is highly variable both in space and time, which makes comparisons rather difficult. Many studies have used the IHSS standards for comparative purposes, but these presumably exclude the POM fraction. In actual raw water the POM fraction ($< 1\mu\text{m}$, $> 0.45\mu\text{m}$) can be significant, and Croue *et al.* (Makdissy *et al.*, 2004) found it to be 30-40% of the organic colloid fraction ($> 3.5\text{kDa}$). It was also a very significant foulant (see section 2.2.7 (ii), (a) below).

2. Literature review

One of the major groups in NOM is humic substances, which include a complex mixture of organic compounds such as humic acids, fulvic acids and other hydrophilic compounds. As noted above humic substances have been found to vary in different water sources. In general, humic substances have characteristic lengths around 1nm to 10nm and molecular weight from few hundreds to approximately 100kDa. They contain both aromatic and aliphatic components with carboxylic and phenolic groups attached to the aromatic rings. As a result, humic substances can be negatively charged as well as having hydrophobic and hydrophilic (humic and non-humic) components (Amy and Cho, 1999; Seidel and Elimelech, 2002; Her *et al.*, 2004). The importance of the charge character is that it can lead to significant interactions with the membrane and with divalent cations, such as calcium which is usually present in raw water (see section 2.2.7(ii), (b)). As indicated in Table 2.4 the humics fraction also has neutral components.

2.2.7 Review of NOM membrane fouling studies

(i) Mechanisms of NOM fouling

From the above it is obvious that NOM fouling of membranes is a complex process for example (Lahoussine-Turcaud *et al.*, 1990; Bersillon, 1998; Seidel and Elimelech, 2002) with many influencing factors, not least being the variable nature of raw waters. This section reviews the extensive literature that has evolved over the past two decades. At the outset it should be noted that not one single component of NOM has been identified as the chief culprit for membrane fouling, and there are apparent conflicts in the literature. However some components are clearly implicated. In order to aid the discussion Table 2.6 attempts to summarize a number of studies and gives details of the key features, such as membrane process, mode of operation etc. From Table 2.6 it is evident that the types of NOM studied vary widely from 'standard' IHSS material, to local NOM samples to soil-derived NOM (Aldrich). It is also apparent that for MF the mode of operation in research studies is usually crossflow (stirred) and constant pressure, whereas the industry tends to operate at deadend and constant flux, with backwash. For UF and NF the

2. Literature review

preponderance of studies have used constant pressure, and again the industry favors constant flux (constant production rate).

As a general statement, NOM fouling on membranes can be caused by several interacting phenomena. As an example, Seidel and Elimelech *et al.* (Seidel and Elimelech, 2002) found that permeation drag controlled by the permeate flux and calcium binding to NOM were the major causes for the development of a densely compacted fouling layer on the membrane surface in the process of NOM nanofiltration. NOM fouling and filtration performance were governed by the *coupled* influence of chemical hydrodynamic interactions. For these reasons researchers such as Amy *et al.* (Amy and Cho, 1999; Her *et al.*, 2004) report fouling at controlled values of J_v/k (see equation 2.3).

The study of Lahoussine-Turcaud *et al.* (Lahoussine-Turcaud *et al.*, 1990) on the ultrafiltration of natural water with different organic and inorganic macromolecules indicated that organic matter had a much greater effect on the flux decline than inorganic colloids. Similar results were reported by Bersillon *et al.* (Bersillon, 1998) in the analysis of the deposited cake formed on the membrane surface after natural water filtration. This heterogeneous process can be generally attributed to the various mechanisms discussed in section 2.2.6 including pore restriction and plugging as well as cake/surface deposition. Fouling by NOM adsorption is proposed as a significant factor and is a consequence of the interactions between the organic compounds and membranes either at the membrane surfaces or within the pores. The interactions include chemical, physical and electrostatic effects. Chemical adsorption of organic compounds on the membrane materials is generally irreversible because of the relatively high strength of attachment, and recovering the permeate flux is difficult. However physical adsorption shows a weak attachment to the membrane surface and the flux decline due to this mechanism is reversible. The electrostatic interaction between the membrane materials and NOM may be either attractive or repulsive, depending on their charged functional groups. Ionic species, such as calcium may play a role.

2. Literature review

As Table 2.6 shows there have been many studies of the mechanisms of membrane fouling by NOM. Mallevialle et al. (Mallevialle et al. 1989) examined the fouling layer formed during the microfiltration (MF) and ultrafiltration (UF) of natural waters. They reported that NOM served as a 'glue' for the inorganic clays in the fouling layer, this is analogous to the proposed role of extracellular polymeric substances (EPS) in biofouling of membranes. Kaiya et al. (Kaiya *et al.*, 1996) pointed out that organic matter was a major component of the fouling layer deposited on a MF membrane after the filtration of eutrophic lake water.

Table 2.6 Summary of selected NOM membrane fouling studies

Membrane Process	Mode* of Operation	Feed properties and preparation	Factors** influence fouling	Proposed fouling species and mechanism	Ref.
1. MF	Xf/CP	Aldrich NOM solution	(i), (iii)	Aldrich NOM, cake formation, pore blocking, Adsorption, calcium role	[14],[16],[35], [49]
	Xf/CP	Surface water, filter< 0.45µm	(i),(ii), (iii)	Hydrophilic neutral compounds, hydrophobic acids, transphilic acids, hydrophilic charged compounds Colloidal material, Adsorption, cake formation, calcium role	[25], [71]
	De/CP	River water	(i),(ii), (iii)	Colloidal material, NOM ,small, neutral,hydrophilic	[32],[62]
2. UF	De/CP	Surface water, River water , filter< 1µm ;	(i), (ii), (iii), (iv)	Organic Colloids (hphilic) Polysaccharides/proteins & aromatics;	[7], [8], [26]
	Xf/CP	River water, Reservoir water<0.2µm, ground water, Lake water; Aldrich NOM, IHSS NOM	(i), (ii), (iii), (iv)	Hydrophilic NOM, Adsorption, cake formation; Steric and electrostatic exclusion Humic acid adsorption, concentration polarization, aggregate deposition	[5],[18], [21],[23], [27],[28], [31], [37], [42], [60]
	Xf/CF	Reservoir Water, ground water	(i), (ii), (iii), (iv)	Hydrophilic NOM, Hydrophobic NOM; Cake Layer formation	[17], [26], [39], [53], [61],
3. NF					
	Xf/CP	River water, Reservoir Water, IHSS NOM; Aldrich humic acid	(i), (ii), (iii), (iv)	Hydrophilic NOM, Hydrophobic NOM; Adsorption, cake formation Permeation drag, electrostatic double layer interactions Calcium binding	[9], [15], [28],[34], [40],[42], [45],[46] [47]
	Xf/CF	Lake Water River water	(ii),	NOM adsorption	[38], [72]

De – Dead end; Xf – Cross flow; CP –Constant pressure; CF – Constant flux;

(i) NOM properties; (ii) Membrane type; (iii) Solution conditions; (iv) Operating conditions

2. Literature review

The study of Yuan et al. (Yuan and Zydney, 1999; Yuan *et al.*, 2002) on the microfiltration of NOM indicated that large humic acid aggregates collected on the membrane surface initially and a cake layer of humic acid began to form with relatively little internal fouling within the membrane pores.

Subsequent humic acid fouling was accelerated by this initial humic acid deposit. Intra- and intermolecular electrostatic repulsions were thought to be responsible for the increased fouling. Additionally, the solution properties such as pH and salt have significant effects on the fouling behavior. The repulsions were reduced at low pH and the presence of divalent calcium caused an increase in the adsorption and aggregation of humic acids. It should be noted that Yuan et al. used NOM derived from soils, rather than natural waters in most of their studies. It has been shown that NOM derived from soils contains some organic compounds of larger molecular weight than aqueous NOM, and there are also differences in functional groups, and hydrophobic /hydrophilic character between the NOM derived from soils and aqueous NOM.

In other studies, the mechanisms of ultrafiltration membrane fouling have been shown to be cake formation, pore restriction by adsorption and pore plugging. Crozes et al. (Crozes *et al.*, 1997) observed that both reversible and irreversible fouling could be found in the treatment of natural river water with UF membranes. Taniguchi et al (Taniguchi *et al.*, 2003) examined the modes of NOM fouling during ultrafiltration and showed that cake formation was the dominant mechanism of UF fouling for large molecular weight cut-off (MWCO) ultrafiltration membranes. Cake formation was identified by a constant rate of increase in membrane resistance with permeate throughput and was independent of pore size over a range of 10kDa to 1000kDa MWCO. However, the lower MWCO membranes exhibited some irreversible fouling suggesting that low molecular weight species penetrated into the pore structure.

For NF membranes, several studies have shown that the combination of steric exclusion and electrostatic exclusion could be the main mechanisms for reducing

2. Literature review

NOM fouling. Hong and Elimelech (Hong and Elimelech, 1997) investigated the role of chemical and physical interactions in natural organic matter fouling of nanofiltration membranes. They recognized that the NOM fouling involved interrelationship (coupling) between the physical and chemical interactions. The rate of fouling was controlled by an interlay between permeation drag and electrostatic effects. Braghetta and DiGiano (Braghetta *et al.*, 1998) also indicated that neutralization of charge, electric double layer compression and the apparent shift in the conformation of charged NOM neutralization are the main reasons for inducing NOM fouling in NF membranes. The influence of calcium, retained by NF, can also be important (see below).

(ii) Factors which influence NOM fouling

The nature of NOM such as size, hydrophobicity and charge density of species; the properties of the membrane such as MWCO, hydrophobic/hydrophilic character and surface charge (electrostatic repulsion), the chemistry of the water solution such as pH and ionic environment, and the operating conditions of the system all have impacts on membrane fouling (Yuan and Zydney, 2000; Jones and O'Melia, 2001; Chen and Seidel, 2002; Teixeira and Rosa, 2003). The following sections highlight the effects of some of these factors.

(a) Impact of NOM properties

Extensive studies have been conducted to evaluate the roles of NOM properties in fouling [for example, (Nilson and DiGiano, 1996; Maartens *et al.*, 1998; Fan *et al.*, 2001)]. The relevant NOM properties include bulk NOM concentration, size and molecular mass distribution, the structure (aromatic/aliphatic, hydrophobic /hydrophilic), and charge density.

Although NOM rejection is anticipated to be mainly dependent on the NOM molecular sizes when other factors are excluded, NOM has a wide range of sizes and structures, and since membranes normally have a pore size distribution, it is not

2. Literature review

straightforward to illustrate NOM rejection simply by size exclusion effects (Nilson and DiGiano, 1996; Fan *et al.*, 2001). It is commonly believed that a fraction of NOM with molecular weights smaller than the membrane pores can be adsorbed on the membrane surface and reduced the cross sectional area for permeation, while larger fractions can block pore entrances and contribute to cake or gel formation (Maartens *et al.*, 1998; Yuan and Zydney, 2000).

Nilson and DiGiano (Nilson and DiGiano, 1996) reported that only the large molecular weight fraction of NOM contributed to the formation of a fouling layer during NF filtration. Kaiya *et al.* (Kaiya *et al.*, 1996) found that compounds larger than 100kDa were the major foulants in a MF system. Fan and Harris (Fan *et al.*, 2001) also indicated that the higher molecular weight fractions of NOM (>30 kDa) were responsible for the greater flux decline on a hydrophobic MF membrane. In recent work on NOM removal by a charged hydrophobic UF membrane, Cho *et al.* (Cho *et al.*, 1998) suggested that the larger size NOM compounds played a major role in influencing NOM fouling during the membrane filtration process. However, Maartens *et al.* (Maartens *et al.*, 1998) observed that a mixture of small and large organic compounds exhibit a greater fouling effect than a fraction of only large organic compounds for a UF filtration system. It is likely that all three mechanisms depicted in Figure 2.5 occur to some extent, and that internal fouling is more irreversible.

The hydrophobicity/hydrophilicity of NOM is also found to be one of the main factors in influencing membrane fouling in natural water treatment. A vast amount of research regarding this aspect has been presented in the literature in recent decades [for example, (Jucker and Clark, 1994; Cho *et al.*, 1998). There is strong evidence that the hydrophobic components in NOM are mainly responsible for the fouling of hydrophobic membranes due to the interaction between the hydrophobic NOM and the hydrophobic membrane surface. For instance, Nilson and DiGiano (Nilson and DiGiano, 1996) evaluated the filtration performances of hydrophobic NF membranes and found that the hydrophobic fraction of NOM significantly affects the flux decline. The hydrophobic NOM was more highly removed by the

2. Literature review

membranes than hydrophilic fractions. Jucker and Clark (Jucker and Clark, 1994) demonstrated that humic macromolecules adsorbed more favorably onto hydrophobic membranes. The hydrophilic components were thought to impact water quality less than the hydrophobic components.

Cho et al (Cho *et al.*, 1998) suggested that flux decline resulting from hydrophobic NOM adsorption on a relatively hydrophilic membrane surface was greater than that with hydrophilic-NOM feed-water. In another study on the retention of NOM by a negatively charged hydrophobic UF membrane, Cho et al. (Cho *et al.*, 2000) concluded that the retention of hydrophobic compounds of NOM were higher than that for the hydrophilic compounds because of the combined hydrophobic interaction and electrostatic exclusion between NOM and the membrane surface.

The components of NOM can be divided into the following four fractions by pyrolysis-GC/MS (Speth *et al.*, 1996): polysaccharides, proteins, polyhydroxy-aromatics, and amino sugars. It was found that the fouling potential of these fractions could be ranked in the order of polyhydroxy-aromatics, proteins, polysaccharides and amino sugars. The polyhydroxy aromatics, which were thought to be the main foulants for negatively-charged NF membrane surfaces, are probably hydrophobic acids with phenolic groups, which exhibit no negative charge at a neutral pH. Base proteins were also found to be foulants for the NF membrane. Polysaccharides and amino sugars were other foulants and are derived from high polyhydric alcohols and have neutral characters. These observations are supported by a recent study by Croue et al (Makdissy *et al.*, 2004) who tested NOM fractions from river water on polyethersulfone UF membranes. They introduced the concept of a biopolymer mixture of polysaccharides, proteins and amino sugars which is made more fouling prone in the presence of polyhydroxy-aromatics.

However, a contrary view concerning the importance of NOM hydrophobicity has been provided by several researchers. Fan et al. (Fan *et al.*, 2001) isolated NOM into four fractions; hydrophilic neutral, hydrophobic acids, transphilic acids, and hydrophilic charged. It was found that the order of the fouling potential of the

2. Literature review

individual fractions during microfiltration with PVDF membranes was hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. It was suggested that the hydrophilic neutral fraction exhibited the greatest fouling potential because of its size (>30kDa) and due to interactions with calcium in the water. It was postulated that fouling was within the internal pore structure. Interestingly, hydrophobic PVDF membranes were significantly more fouling prone than hydrophilic PVDF. Recently, Cho et al (Cho *et al.*, 2000) suggested that NOM hydrophobicity was not an influential factor except for extremely hydrophobic NOM-source water, as hydrophobic NOM comprises a relatively high fraction of ionizable hydrophobic acids. For a typical NOM-source water, hydrophilic NOM was found to be the major membrane foulant, due to its non-charged character, thereby promoting easier adsorption onto the membrane surface. Lin et al. (Lin *et al.*, 2000) studied the effects of the characteristics of fractionated humic acids on the performance of a negatively charged hydrophobic ultrafiltration membrane. Again it was observed that the hydrophilic fraction induced the most rapid flux decline despite little retention of DOC. Carroll et al. (Carroll *et al.*, 2000) also concluded that the major foulants were the hydrophilic neutral components of NOM while the fractions comprising humic acid and fulvic acids have less effect on membrane fouling in their study on the NOM fouling of a hydrophobic MF membrane treating a single water source. Recent results from the same group (Gray *et al.*, 2004) using two different waters and polypropylene MF membranes found that the hydrophilic components were the major foulants for one water and the hydrophobic components were the major foulants for the other. In this study the authors also noted that short term tests did not correspond well to long term trials. The lack of consensus in the literature with regard to hydrophobic vs hydrophilic components of NOM may be due to subtle variations in source waters and the molecular weights of the dominant foulants.

According to some researchers, electrokinetic interactions could dominate fouling (Speth *et al.*, 1996; Hong and Elimelech, 1997; Taniguchi *et al.*, 2003). For example, electrostatic repulsion may take place between a negatively charged hydrophobic membrane and NOM components with negative charge density. In

2. Literature review

addition the adsorbed species could change the properties of the membrane. For example, Yoon et al. (Yoon *et al.*, 1998) performed zeta potential measurements at different pH values (3.45-7.2) with and without humic acids. They verified that over the entire range of pH studied, the membrane was positively charged in the absence of humic acids. However, when the zeta potential was measured in the presence of humic acids, it became negatively charged for all pH values, except at pH 4.5. This phenomenon was attributed to the adsorption of negatively charged humic acids onto the membrane surface. Conversely if there is no net surface charge on the membrane the hydrophobic and hydrophilic neutrals could be easily adsorbed and this may explain the observed fouling and flux decline with these species.

Finally, the role of particulate organic matter (POM, $< 1\mu\text{m}$, $>0.45\mu\text{m}$, – see Table 2.5) should not be overlooked. Croue et al. (Makdissy *et al.*, 2004) found these to be very significant foulants for their two river water samples. In their study the POM contributed from 63 to 86% of the colloidal fouling; only 37 to 14% were due to the dissolved colloids. However it is possible that the effect of the POM was exaggerated in their experiments which used a constant pressure protocol that would have had a J_o in the region of $700\text{l/m}^2\text{hr}$, potentially giving rapid pore plugging and cake formation. Nevertheless POM, which may not be detected in standard TOC analysis (usually involves prefiltration at $0.45\mu\text{m}$), could be a major foulant, particularly for which MF and UF in the absence of chemical addition (see section 2.2.8 (i))

(b) Impact of membrane properties

Membrane properties include pore size and distribution, MWCO, hydrophobicity, surface/pore charge (electrostatic repulsion), as well as the morphology of the membrane surface. These characteristics play different roles that affect NOM filtration performance during various processes ranging from nanofiltration to microfiltration.

In the MF filtration of natural water, NOM fouling can result in flux decline and NOM retention, even though the large pores of the MF membranes are expected to

2. Literature review

cause minimal retention of the humic substances. This behavior is related to the permeability of the cake or 'gel' layer formed by organic/inorganic compounds on the membrane surface and to the effective size of the membrane pores, which become smaller due to the adsorption of dissolved compounds. Pore blockage caused by the physical deposition of large organic compounds on the membrane surface induces the initial NOM fouling. These aggregates appear to serve as nucleation sites for the subsequent deposition of humic acids on the membrane surface.

For example, Yuan and Zydney (Yuan and Zydney, 1999) investigated the extent and mechanisms of humic acid fouling with a 0.16 μ m hydrophilic MF membrane. They observed that the flux decline was due to the convective deposition of large humic acid aggregates/particles on the membrane surface followed by the subsequent deposition of macromolecular humic acids, which was accelerated by the initial step of humic acid fouling. It was also found that the three classical filtration models, i.e., the pore blockage, pore restriction, and cake filtration models were unable to provide an accurate description of the experimental data over the full course of the microfiltration. The modified model of Zydney and coworkers is described below [(iii) Modeling NOM fouling]

There are various opinions on NOM fouling during microfiltration. Nystrom et al (Nystrom *et al.*, 1996) found a dramatic flux decline during humic acid microfiltration through inorganic capillary membranes. This rapid decline in flux caused by the nearly complete blockage of the membrane pores was attributed to electrostatic interaction between the negatively charged humic acids and the positively charged inorganic membrane. This phenomenon is less likely with polymeric MF membranes that are more typically negative.

For UF membranes, the main mechanisms responsible for NOM fouling are the interactions between NOM and the membrane surfaces. These interactions include pore adsorption and plugging which are most likely to be the initial, and even longer term, fouling mechanisms for UF membranes. Therefore, the low molecular

2. Literature review

weight molecules smaller than the membrane pore sizes could lead to significant membrane fouling due to adsorption on or within the pores. Larger humic acid aggregates/particles would tend to form surface cake layers. Kulovaara *et al.* (Kulovaara *et al.*, 1999) reported that surface water fouling of a 50kDa polysulfone membrane was largely irreversible due to the formation of a strongly adherent deposit on the membrane surface. As for the fouling of ultrafiltration membranes by a lake surface water, Cho *et al.* (Cho *et al.*, 1999) found that most of the flux decline was attributed to the weak NOM adsorption on the membrane surface along with a small contribution from gel layer formation, while concentration polarization was only important for polysulfone membranes with the largest pore size of 10kDa. In their later study, Cho *et al.* (Cho *et al.*, 2000) compared three types of UF membrane, in terms of their characteristics of flux decline, retention of NOM, and the adsorbed foulants, with two very different (relatively hydrophilic and relatively hydrophobic) NOM-containing source waters. They came to the conclusion that the humic components were either excluded by the membrane or passed through the pores; they were not selectively adsorbed (weak adsorption) onto the membrane surface. The adsorbed components (which could not be differentiated between surface and pore sorption) were predominantly neutral and basic NOM species.

In the NF filtration process, the mechanisms of NOM retention and fouling are believed due to a combination of steric and electrostatic exclusion, thus the hydrophobicity and surface charge of the NF membrane plays an important role in NOM fouling. Generally, hydrophilic NF membranes with negative charge exhibit high retention with low NOM fouling tendency (Her *et al.*, 2000). In contrast, Jucker and Clark (Jucker and Clark, 1994) found that hydrophobic membranes were severely fouled by humic substances adsorption in their static (zero flux) adsorption analysis. More recently, Lee *et al.* (Lee *et al.*, 2002) analyzed the relationship between the flux declines of NF membranes with NOM transport characteristics. They concluded that diffusion and convection contributed to NOM transmission. The membrane surface charge (in terms of zeta potential) was also found to be an important factor associated with NOM removal and membrane fouling by Braghetta *et al.* (Braghetta *et al.*, 1998).

2. Literature review

(c) Impact of solution conditions

The chemical composition of source water, which includes pH, ionic strength, and the concentration of divalent ions such as Ca^{2+} , is another important factor influencing NOM fouling. Braghetta (Braghetta *et al.*, 1998) found a substantial flux decline at low pH and high ionic strength and attributed this observation to the conformational changes of NOM during NF fouling experiments with aquatic NOM. In contrast Ruohomaki *et al.* (Ruohomaki *et al.*, 1998) observed that fouling was higher at neutral pH than at acid or alkaline pH when the pH effect on humic acid retention was evaluated using polyethersulphone membranes. The possible reason was shown to be the formation of compact humic acids under the conditions of lower or higher pH values. Nilson and DiGiano (Nilson and DiGiano, 1996) found that flux decline was relatively significant at pH 4 and 7 but negligible at pH 10, probably due to the fact that the acidic components of NOM and the membrane have a higher negative charge density at higher pH values thus inhibiting NOM adsorption on the membrane surface.

Divalent cations are also believed to increase NOM fouling of membranes. The mechanisms involved are aggregation of humics and acting as a 'chelating' bridge between negative membrane surfaces and negative humic species. The role of calcium in UF membrane fouling has been described by Jucker and Clark (Jucker and Clark, 1994) and in NF fouling by , for example Schaefer *et al.* (Schaefer *et al.*, 1998; Lee *et al.*, 2004) and Yoon *et al.* (Yoon *et al.*, 1998). However, under some conditions the presence of calcium could be beneficial, as described by Schaefer *et al.* (Schaefer *et al.*, 2000) for the addition of coagulant in a hybrid MF/UF removal processes. Calcium enhanced the coagulation to produce more filterable floc.

NOM would be expected to change conformation in different ionic environments. According to the polyelectrolyte solution theory, charged macromolecules undergo coil-to-globule conversion in response to a change in solution conditions. The roles of ion concentration and pH are schematically depicted in Figure 2.7.

2. Literature review

Figure 2.9 Schematic depiction of the effect of solution conditions on the conformation of NOM macromolecules in the solution and on the membrane surface.

When an ion salt is added to a NOM solution, the NOM solubility is likely to be affected. NOM could contract to small globules to adjust to the change in its environment.

The NOM transition could be expected in two ways: as a polyelectrolyte chain, the transition would pass through a series of intermediate conformations, which consist of chains bearing several sub-globules along the chain; the number of these globules would decrease with increasing the salt concentration. On the other hand, NOM is a complex mixture which consists of different macromolecules. These macromolecules would show different responses with increasing salt level. The coil-to-globule transition would be faster for some components (Fan *et al.*, 2001).

Unlike indifferent monovalent cations, divalent cations such as Ca^{2+} , Mg^{2+} interact specifically with NOM and form metal-humic complexes (Crozes *et al.*, 1997). The complexation of divalent cations with NOM changes the electro-kinetic properties of the NOM. The extent of complex formation is strongly dependent on the solution chemistry and on the characteristics of the NOM. Wei *et al.* (Wei *et al.*, 2004) demonstrated that increasing Ca^{2+} showed competing effects on the size of NOM. At relatively low concentrations of Ca^{2+} the size of the NOM was reduced, due to charge shielding. However as the concentration of Ca^{2+} increased there was an

2. Literature review

increase in NOM size, presumably due to aggregation or chelating between NOM and Ca^{2+} .

Clearly, the chemistry of the feed water affects the electrostatic properties of the dissolved organic compounds and the membrane and influences NOM interactions with the membrane surface. As a consequence the fouling potential of NOM may be changed. This thesis describes the effect of ionic environment on NOM properties and membrane filtration (see Chapter 3).

(d) Impact of operating conditions

As noted above, from Table 2.5 it is apparent that for MF, UF and NF the mode of operation in research studies is, with few exceptions, crossflow (pumped or stirred) and constant pressure. This differs from typical industrial operation which tends to use constant fluxes, with crossflow (NF or UF) or in deadend mode (MF or UF). There appears to be a need to develop standard fouling protocols for lab scale studies.

The relevance of controlling the crossflow /flux ratio has been pointed out in discussion of the J/k ratio in equation 2.3. Some studies (for example (Amy and Cho, 1999)) have examined the influence of the J/k ratio on fouling, and shown that as this ratio is increased so is the rate of fouling. This points to the means of controlling fouling by limiting flux or improving the mass transfer coefficient k (typically increased by increasing crossflow). A similar approach was demonstrated in hollow fiber operation by Crozes et al.(Crozes *et al.*, 1997).

The strategy used for submerged MF or UF is to add some coagulant and then operates on a cycle at constant flux in deadend mode with regular backwash. The benefit of deadend is that with relatively low solids content the energy usage can be minimized. Choice of imposed flux is dictated by the frequency of backwash, irreversible fouling, and capital costs (inversely related to flux). Further analysis of

2. Literature review

the effect of operating conditions in NOM membrane filtration is given in Chapter 5 of this thesis.

(iii) Modeling NOM fouling

Several researchers have explored theoretical approaches to describe the membrane fouling and flux decline associated with NOM source water. A number of mathematic models have been developed with system parameters, material balance equations plus appropriate boundary conditions and flow dynamics, such as the modified fouling index, the membrane resistance-in-series model, the gel resistance model, and the fouling kinetic model etc (Champlin, 2000; Ho and Zydney, 2000; Tansel *et al.*, 2000; Yuan *et al.*, 2002).

Normally, the fouling effect is described by Darcy's law (equation (2.1) in 2.2.6 (i)) and the fouling resistance R_c (in equation (2.2)) lumps together the various components of resistance. Ho and Zydney (Ho and Zydney 2000) developed a fouling model for the MF of macrosolutes where simultaneous pore blockage and cake formation were accounted for. It was assumed that the cake layer only formed over those regions of the membrane that have been blocked by the physical deposition of initial large aggregates. The model is different from most previous pore blockage models, since it also assumes that the aggregates might allow some fluid flow through the blocked pores. Based on these assumptions, R_c in equation (2. 2) can be rewritten as:

$$R_c = (R_m + R_{co}) \sqrt{1 + \frac{2f'\alpha_c\Delta PC_b t}{\eta(R_m + R_{co})^2}} - R_m \quad (2. 4)$$

where R_{co} is the resistance of the first layer of the humic acid deposit, C_b the bulk humic acid concentration, f' the fraction of humic acids in the bulk solution that contributes to the growth of the existing deposit, α_c the specific resistance of the cake layer, η the solution viscosity and t the time. The filtration flux through the

2. Literature review

fouled membrane was then a combination of the flow rates through the open and blocked pores:

$$\frac{J}{J_o} = \exp\left[-\frac{F_b \Delta PC_b}{\eta R_m} t\right] + \frac{R_m}{R_m + R_c} \left\{ 1 - \exp\left[-\frac{F_b \Delta PC_b}{\eta R_m} t\right] \right\} \quad (2.5)$$

where J_o is the initial flux through the clean membrane, R_c is evaluated from equation (2.4). and F_b is the pore blockage parameter (m^2/kg). The two terms on the right hand side of equation (2.5) are the flow rates through the open and blocked pores, respectively. The first term is derived using the classical pore blockage model.

This model was evaluated by measuring the flux decline in the microfiltration of an Aldrich humic acid solution through 0.2 μm pore size membranes (Yuan *et al.*, 2002). It was found that the theoretical results were in good agreement with experimental data of the filtration flux as a function of time under different solution conditions. A possible limitation of this model is that it was compared with data obtained with Aldrich NOM, a soil-based material which has a higher proportion of high MWt components. The constant pressure protocol was also applied.

In a study of NOM fouling kinetics in ultrafiltration systems, Tansel *et al.* (Tansel *et al.*, 2000) proposed a simple flux model based on the resistances-in-series approach to estimate the characteristic fouling time, τ . Assuming the overall resistance to flow is the combined result of two types of resistances namely a time-dependent resistance and a constant resistance, the relationship is;

$$(R_m + R_c)_{t=t} / (R_m + R_c)_{t=0} = (1 - X_f) + X_f \exp\left(t/\tau\right) \quad (2.6)$$

where X_f indicates the extent of fouling and τ is the fouling time constant. This relationship can be used to correlate the normalized flux data and predict the critical

2. Literature review

fouling time when the flux decreases to a specified fraction of the initial flux. Again this model applies to the constant pressure mode.

Braghetta (Braghetta *et al.*, 1998) also used the resistances-in-series model to describe the accumulation of NOM at NF membrane surfaces. They assumed that the membrane fouling associated with NOM occurred in three stages: concentration polarization, cake layer accumulation on the membrane surface and adsorption of NOM components on the membrane surface and/or within the pores. The summation term of R_i in equation 2.1 was then expanded to be a number of different resistances, as follows:

$$J_v(t) = \frac{\Delta p - \Delta \pi}{\eta(R_m + R_{cp} + R_e + R_c)} \quad (2.7)$$

where R_{cp} , R_e , R_c denoted the additional resistances during the filtration processes due to concentration polarization, internal pore fouling, and external deposition or cake/gel formation respectively.

A parameter, called the specific foulant mass resistance ε_s was also defined (Braghetta *et al.*, 1998) to evaluate the value of R_{chem} associated with the amount of NOM removed from the membrane surface by chemical cleaning:

$$\varepsilon_s = \frac{\sum R_{chem}}{NOM \text{ recovered}} \quad (2.8)$$

where ε_s has units of $m^{-1}mg^{-1}$. The physical meaning of ε_s is related to the extent of superimposed resistance offered per unit mass of foulant associated with the membrane surface. According to Braghetta (Braghetta *et al.*, 1998), the specific foulant mass resistance ε_s can be used to quantify the extent of membrane fouling. Relatively high ε_s would suggest a densely compacted layer of foulant that superimposed a large resistance to filtration per unit mass of foulant. In contrast, a low ε_s would suggest a loosely connected layer of foulant that contributed little additional foulant-related resistance to the filtration. The parameter ε_s is obviously related to specific cake resistance α_c (resistance per mass load of membrane area).

2. Literature review

2.2.8 Techniques to reduce NOM fouling

Preventing or reducing NOM fouling would significantly cut down the cost of the raw water treatment process, extend the membrane life and reduce the energy demand. By doing so, the additional costs associated with frequent cleaning operations and membrane replacement would also be reduced. Much effort has been made in this area and the techniques developed to minimize NOM fouling include hybrid membrane processes, the pretreatment of NOM raw water, the optimization of hydrodynamic parameters, the modification of the membrane surface and cleaning of the membrane system. These techniques are briefly reviewed below.

(i) Hybrid membrane processes

The combination of coagulation/flocculation, or sorbents, such as powdered activated carbon (PAC) or polyaluminium chloride (PAC) with membrane processes is a common practice in water and wastewater treatment. For example, coagulants such as alum, ferric salts and cationic polymers are often used prior to membrane units to assist removal of insoluble metals, proteins and bio-organics from industrial wastewater. Recently, the application of the hybrid membrane processes for NOM removal has received attention.

In general, the hybrid membrane processes can improve the removal of NOM and some other contaminants from the water, but their effects on membrane fouling are not always beneficial. Thus membrane fouling can be reduced or enhanced by adding particulate species. Vickers *et al.* (Vickers *et al.*, 1995) concluded that without pretreatment, MF/UF can achieve only nominal (~10%) removal of NOM, whereas these processes can be used in combination with coagulation chemistry or PAC to achieve a higher NOM removal. Zhang *et al.* (Zhang *et al.*, 2003) investigated the behavior of UF processes to which powdered activated carbon (PAC), heated iron oxide particles (HIOPs), or (nonadsorbent) SiO₂ particles were added. The NOM removal efficiency was found to be in the order of PAC > HIOPs > SiO₂. They also studied the fouling tendency of these introduced particles

2. Literature review

and found that in the case of both PAC and SiO₂, increasing the dosage of solids led to a steady increase in fouling, but the opposite trend applied when HIOPs were added. Interestingly, in the absence of NOM, none of the solids fouled the membrane significantly. Lin et al (Lin *et al.*, 2000) reported that the use of PAC in a combined PAC/UF membrane system increased the membrane fouling even though the NOM removal efficiency increased. Schaefer et al. (Schafer *et al.*, 2000) also observed that, under certain conditions, the addition of ferric chloride to solutions containing humics can significantly increase the fouling of MF/UF membranes. Carroll et al (Carroll *et al.*, 2000) found that small molecular weights, non-ionics, hydrophilic NOM that were poorly removed by coagulation were responsible for the fouling after the coagulation process.

To understand these phenomena, it is important to understand the interactions between the membrane, the NOM and the adsorbent particles. One explanation for the more severe fouling after the addition of the particles is that the NOM residue and the flocs form a 'composite' cake layer at the membrane surface, with NOM filling the interstices between particles. These cakes become compressed and distorted due to transmembrane pressure, forming a low permeability layer and blocking the pores on the membrane surface.

In order to reduce membrane fouling in the process of NOM removal, it is necessary to reduce the adsorption in the membrane pores and surface, increase cake porosity and reduce the interaction between NOM and the membrane surface. For example, the heated iron oxide particles (HIOPs) have a much higher tendency to bind with NOM than the membrane surface, which reduces the tendency of either the NOM or the HIOPs to interact with the membrane surface and leaves enough porosity in the cake layer for water to reach the membrane surface (Zhang *et al.*, 2003). It was noted by Carroll et al. (Carroll *et al.*, 2000) that the selection of coagulant would define the size, permeability and stability of flocs on the membrane surface and thus affect the NOM fouling. The filtration resistance of alum treated NOM was significantly less than that of the residual NOM, but this observation was not repeated for other coagulants because of the differences in the

2. Literature review

interactions between the NOM, membrane surfaces and coagulants. However it should be noted that alum may not be a panacea as it tends to slowly foul some MF membranes, and is not easily backwashed.

Recently Cabane et al.(Cabane *et al.*, 2002) reported that the aggregates produced under sweep flocc conditions were more compressible than under charge neutralization conditions, resulting in compaction when the membrane filtration system was pressurized. In practice, this effect will depend on the imposed fluxes or allowed TMPs. Choi and Dempsey (Choi and Dempsey, 2004) revealed that NOM removal was effective and fouling was reduced by 'under-dosing' the coagulation (relative to conventional coagulation) in a UF membrane filtration process. The most appropriate under-dose conditions would likely depend on the nature of the raw water and on the operational requirements. This indicates that the control of water chemistry and optimization of operating conditions are important strategies to minimize NOM fouling.

MIEX is an anion exchange resin capable of removing relatively low molecular weight negative organics from NOM. The combination of MIEX with low pressure membranes is of interest (Morran *et al.*, 2001), and can achieve good removal of TOC. It has been shown by Galjaard et al (Galjaard *et al.*, 2004) that by using MIEX to remove organics < molecular weight cut off of a UF membrane which is hydrophilic and positively charged leads to very low fouling. Interestingly in this study the feed was chemically softened so the detrimental effects of calcium were obviated. The operating mode was deadend and constant flux (range, 50 to 100 L/m²hr).

(ii) Water chemistry control and optimization of operating conditions

The chemical composition of source water, which includes pH, ionic strength, and the concentration of divalent ions such as Ca²⁺, is one of the main factors influencing NOM fouling. Therefore, the adjustment of the pH and ionic strength could help to reduce NOM fouling. Maartens et al.(Maartens *et al.*, 1999) showed

2. Literature review

that the pH of the raw water had a significant effect on the adsorption of NOM onto a polysulfone UF membrane surface. Since the lowest adsorption occurred at pH 7, adjusting the pH of the feed solution to 7 should minimize the membrane fouling caused by the interaction between NOM and the membrane surface. Hong and Elimelech (Hong and Elimelech, 1997) suggested that pretreatment was necessary to prevent NF membrane fouling by NOM. For hard water, it was evident that the removal of calcium and magnesium ions via a pretreatment step could substantially reduce NOM fouling. Cleaning with strong chelating agents such as EDTA to remove free and NOM-complexed calcium ions was the most effective way to eliminate the fouling layer and restore permeate flux.

It is also useful to conduct optimization on the operation conditions to minimize membrane fouling caused by the NOM. This involves consideration of the options for 'mode of operation' (section 2.2.3(ii)). Thus, for NF in spiral wound modules and other systems with significant solids load crossflow operation at a controlled flux (constant J/k) is recommended. The importance of this is illustrated by Hong and Elimelech (Hong and Elimelech, 1997) who investigated the distribution of the NOM fouling layer due to strong hydrodynamic shear at high cross flows. Although they did not operate at constant flux they found that NOM fouling was controlled by the interplay between fouling drag and electrostatic double layer repulsion. For hollow fibre UF of surface water Crozes et al. (Crozes *et al.*, 1997) investigated the impact of flux (and TMP), crossflow velocity and backwash frequency on fouling. In their case they found an optimum flux of 75 l/h.m^2 with 0.9 m/s crossflow velocity to limit fouling by particulates (turbidity). This 'optimum' would be specific to the module used and the condition of the feed. Some hollow fibre systems treating surface waters operate in deadend (no crossflow) for low turbidity feed and switch automatically to crossflow when turbidity increases. In all cases backwash would apply.

(iii) Membrane surface treatments

2. Literature review

In general, hydrophilic membranes, with hydroxyl, amine or carboxylic acid groups, have been found to be less prone to fouling than hydrophobic membranes when treating natural water containing NOM. Unfortunately, most commercially available UF and MF membranes are made from relatively hydrophobic materials with low surface energies such as polypropylene, polysulfone, polyethersulfone and polyvinylidene fluoride as they offer better chemical, thermal and biological stabilities. However it is possible to combine the lower fouling potential of hydrophilic surfaces with the stability of hydrophobic membranes by surface modification (Li *et al.*, 1996; Hester *et al.*, 1999; Pieracci *et al.*, 1999; Lee *et al.*, 2001; Kim *et al.*, 2003; Marchese *et al.*, 2003; Meier-Haack *et al.*, 2003).

The successfully modified membranes should have a high degree of coverage to the internal pore channels and the separation surface with long-term stability and high membrane permeability. They should also minimize the impact on the bulk membrane properties. In addition, the costs of the modification technique should be compensated for by reduced costs of materials (cleaning) and operation (reduced fouling).

Surface modification can be achieved simply through the adsorption of surfactants and soluble polymers onto the membrane surface to change the hydrophobicity and surface charge of the membranes used in order to enhance the membrane performance. Several surface modification techniques for commercially available UF membranes have been developed, which are described below. A novel approach is also presented in Chapter 7 of this thesis.

(a) Coating a hydrophilic thin layer onto the surface of the membrane (Li *et al.*, 1996; Pieracci *et al.*, 1999; Hester and Mayes, 2002)

Forming a hydrophilic monolayer onto a support membrane surface will give the hydrophobic membrane hydrophilic character, which is the so-called surface functionalization of membranes. According to previous studies, this approach can be realized by several techniques such as the lamination of a pre-formed film,

2. Literature review

chemical dip coating, and in-situ polymerization, etc. For example, Fane and Fell (Fane and Fell, 1987) confirmed that a reduction in foulant adsorption by hydrophobic membranes can be achieved by forming a hydrophilic monolayer on the membrane surface, as it gave the membrane a hydrophilic character with fewer hydrophobic sites for foulant adhesion. Maartens et al (Maartens *et al.*, 2000) found that pre-coating membranes with hydrophilic surfactants significantly reduced the adsorption of foulant species in NOM and improved initial color retention of the membranes to above 96%, but the flux through the membranes was marginally reduced.

(b) Initiating polymerization by radiation and grafting reactions onto a support membrane to impart hydrophilic properties (Kilduff *et al.*, 2000; Carroll *et al.*, 2002; Taniguchi and Belfort, 2004)

Photochemical modification has distinct advantages in simplicity, cost and breadth of application. This simple method increases membrane surface wettability and shifts the membrane pore size distribution to smaller sizes. The results of previous studies suggested that the selective UV excitation of a photo-initiator adsorbed onto the polymer surface causes a heterogeneous hydrogen abstraction and subsequent initiation by polymer mechanisms for polymer surface modification. In this way, the surface modification is achieved by applying a very simple, inexpensive graft polymerization technique. Recently, this method has been widely used to increase NOM retention and reduce NOM fouling.

Carroll et al. (Carroll *et al.*, 2002) studied the surface modification of a polypropylene hollow fiber membrane with charged and non-charged hydrophilic polymers. They showed that non-ionic and cationic hydrophilic grafts reduced the flux decline due to NOM fouling by up to 50% compared with the ungrafted polypropylene. In contrast, anionic hydrophilic grafts had initial flux increases up to 140% at high graft yields due to multi-valent ions in the natural water, although the pure-water flux was substantially lower than that of the ungrafted membrane. Kilduff et. al. (Kilduff *et al.*, 2000) investigated photochemical modification of

2. Literature review

poly(ether sulfone) and sulfonated poly(sulfone) nanofiltration membranes for fouling control of natural organic matter, with N-vinyl-2-pyrrolidinone (NVP) grafting. They concluded that the fouling by NOM was reduced significantly after surface grafting, but solute retention was also decreased. Taniguchi et al. (Taniguchi and Belfort, 2004) revealed that photochemical grafting increased membrane surface wettability and shifted the membrane pore size distribution to smaller sizes, which consequently increased natural organic matter retention.

(c) Deposition of a hydrophilic layer from a glow discharge plasma onto the membrane (Kim *et al.*, 2002)

Plasma-induced polymerization is another technique that has been successfully used for surface modification of polymeric membranes. The capability of plasma to alter the physical and chemical properties of polymeric surfaces without affecting the bulk properties (especially mechanical properties) of the base material is advantageous for the design and development of surface modified polymer membranes. With plasma treatment, specific surface chemistries can be created for increasing NOM retention and reducing membrane fouling. However, a limitation of plasma treatment is its temporal instability such as the gradual loss of surface chemical properties with time (Kim *et al.*, 2002).

(d) Chemical attachment of selected polymer and/or monomers (Ling and Chen, 1995; Belfer *et al.*, 1998; Maartens *et al.*, 2000)

Concentrated emulsion polymerization and blending have been developed as one of the approaches for the preparation of hydrophobic-hydrophilic composite membranes. With this method two types of membrane structure have been developed: the asymmetric structure obtained by the phase inversion technique and the composite one formed by over-coating a porous substructure with a thin top layer acting as the barrier. The latter is made of an interfacial polymerized polyamide supported on a micro porous polysulfone and has gained importance because of the improved performance characteristics.

2. Literature review

The choice of the specific surface modification techniques depends on the chemical structure of the given support membrane and the desired characteristics of surface modification required. Several patents have been issued to membrane manufacturers for modifying well-known polymers or precast porous films in this regard, such as photo-induced graft polymerization surface modification, surface modification by low-temperature plasma-induced graft polymerization and direct microemulsion polymerization using polymerizable surfactants.

(iv) Membrane cleaning

The techniques mentioned above focus on reducing the membrane fouling caused by NOM. Nevertheless, membrane fouling inevitably occurs over a long period of operation, resulting in loss of membrane permeability, manifesting as flux decline or increase in required TMP. To recover the fouled membranes, hydraulic backwash and chemical cleaning is needed. Of course backwash is only applied to hollow fiber membranes. Cleaning agents include acid and caustic agents, as well as alkaline solutions. Many studies have been conducted to investigate the efficiency of these chemical cleaning agents and hydraulic wash procedures. A full survey is beyond the scope of this thesis.

An example is provided by Lee et al (Lee *et al.*, 2001) who investigated various cleaning strategies for the UF membranes used to treat source waters containing different NOMs. They found that high ionic strength cleaning (with 0.1M NaCl) was more effective in promoting flux recovery for the membrane fouled with relatively hydrophilic NOM than acid, caustic or surfactants solutions. They also showed that increased cross-velocity and prolonging cleaning time influenced the cleaning efficiency of caustic solution, but did not influence the effectiveness of high ionic strength cleaning. Maartens et. al. (Maartens *et al.*, 1999) found that a 0.1% Triton X100 solution with NH_3 was successful to remove the NOM foulant on their UF membranes. The treated membrane flux increased even to levels higher than that of unfouled membranes. However, the chemical cleaning agent not only

2. Literature review

removed the foulants, but also absorbed onto the membrane surface and interacted with the membrane.

Interaction between the chemical cleaning agent and the membrane surface may not be good for the membrane system. Repeated chemical cleaning may affect the membrane life. Chemical cleaning is also typically cumbersome and requires shutdown of the unit being washed for several hours. This results in a reduction of the overall plant capacity, and produces a waste that may be difficult to dispose of. Chemical cleaning should thus be limited to a minimum.

2.3 Conclusions

A comprehensive literature review has been conducted with focuses on the nature of NOM and its influence on the water, water treatment and membrane processes. Detailed characterizations are necessary due to the variation of NOM from different sources. The relevant characterization techniques have been described.

The application of membrane technology to drinking water production continues to grow. However, the ability to control fouling by NOM and other species has not been perfected because of the complexity of the feed and the potential surface interactions. We have some clear insights, such as the benefit of hydrophilic membranes, the adverse effects of colloids and the detrimental role of calcium. The significances of other foulants are still moot. This is possibly due to local variations in NOM and also the lack of standard fouling protocols to make a fair comparison.

The literature provides a basis of this study which involves,

- Study on the influence of ionic strength on NOM size and removal by ultrafiltration;
- Characterization of tropical NOM and its influence on UF membrane fouling;

2. Literature review

- Impact of operating modes and factors on NOM removal and fouling performance in ultrafiltration;
- Evaluation of a hybrid system of MIEX with low-pressure membranes: effects of MIEX pretreatment on NOM removal and membrane fouling;
- Development of a novel electrophoresis-UV grafting technique to modify PES UF membranes used for NOM removal.

3.

INFLUENCE OF IONIC STRENGTH ON NOM SIZE AND REMOVAL BY ULTRAFILTRATION *

3.1 Introduction

It is well recognized that the presence of the NOM in surface water has an adverse effect on the water quality. As a result the removal of NOM from drinking water has been extensively studied [for example (Bowen *et al.*, 1995; Chang and Benjamin, 1996; Maartens *et al.*, 1998; Frimmel and Abbt-Braun, 1999; Gjessing *et al.*, 1999; Hem and Efraimsen, 1999; Aoustin *et al.*, 2001; Chang and Benjamin, 2003)]. Among the various removal technologies, membrane ultrafiltration (UF) has the advantages of low pressure operation and relatively good removal efficiency, especially when the “tightest” UF membranes are employed (Kulovaara *et al.*, 1999; Cho *et al.*, 2000; Majewska-Nowak *et al.*, 2002). Whilst NOM removal can be improved by addition of coagulant (Aoustin *et al.*, 2001) there are benefits if chemical addition can be limited. However, NOM removal by UF not only depends on the membrane pore size but also on the hydrodynamic size of the NOM components. The source of NOM and solution conditions such as ionic composition, ionic strength and pH are important in determining the conformation of NOM species and subsequent filtration performance.

Previous studies have shown that multivalent ions such as Ca^{2+} and Mg^{2+} interact strongly with the humic substances, as the functional groups of the humic substances exhibit a wide range of affinities for the metal ions. The complexation of

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3. Influence of ionic strength on NOM size and removal by ultrafiltration

the organic elements with the ions may lead to the formation of stable complexes or aggregation brought about by the chelating effect of the divalent cations. This results in an increase in both size and apparent molecular weight of the humic substances (Vilge-Ritter *et al.*, 1999; Pinheiro *et al.*, 2000; Schmitt *et al.*, 2003). For instance it is reported that Ca^{2+} enhanced the aggregation of an NOM at a critical coagulation concentration of 2 to 3mM CaCl_2 .

The ionic environment can also have an impact on the molecular size of the humic substances which may become smaller at a high ionic strength or low pH. It has been postulated that neutralization of anionic carboxylic acid and phenolic groups by the cations of the salts makes their conformation change from linear to spherical (Ghosh and Schnitzer, 1980) For example it was suggested that the molecules of the humic substances tended to be linear at a low ionic strength of 1mM NaCl, whereas the structure was fully spherical at 50 to 100mM NaCl (Andersen *et al.*, 2000). In natural waters that typically have low ionic strength, the molecules of fulvic and humic acid were found to be very large. The hydrodynamic diameters of the humic substances were found to decrease from 15 to 1.7nm when the concentration of NaCl changed from 0.4mM to 1M (Margarida and Maria, 2003).

The solubility of humic substances also varies with the concentration of multivalent ions and the pH. The multivalent ions can decrease the solubility of humic substances under certain pH conditions because of charge neutralization or complexation effects. Humic acid is insoluble at a $\text{pH} < 2$ while fulvic acid is soluble over the pH range (1-14) (Margarida and Maria, 2003).

In this Chapter, the effects of Na^+ and Ca^{2+} interaction with NOM on the apparent molecular size distribution of the species and the NOM removal efficiency by UF is described over a wide range of ionic strengths. This is the first reported assessment of Singapore NOM, which is typical of a tropical catchment. It is compared with IHSS NOM (typically temperate) and Biohumic NOM (soil derived). The particle sizes and molecular size distributions of the NOM before and after the addition of ions were analyzed using light scattering particle size analysis and HPSEC,

3. Influence of ionic strength on NOM size and removal by ultrafiltration

respectively. The filtration performance was evaluated in a dead-end filtration cell fitted with UF membranes. This study is an attempt to obtain a better understanding of solute-solute interactions for further optimization and enhancement of UF for NOM removal.

3.2 Materials and methods

3.2.1 Model NOM and other chemicals

Three types of NOM were used in this study, namely Singapore NOM (a reservoir-based sample), IHSS NOM (a river-based standard) and Biohumic NOM (a soil-based sample). The Singapore NOM was collected from the Kranji reservoir at a concentration of about 5.02ppm TOC. It was then filtered by MF (Millipore 0.45 μ m) and concentrated to 52.1ppm by batch NF (Filmtec NF 270-400; measured retention of NOM was about 96%). The concentrated solution also contained 26.5ppm Ca²⁺, 3.2ppm Mg²⁺, 6.8ppm K⁺ and 16.2ppm Na⁺. IHSS 'NOM' was made by mixing equal amounts of IHSS humic acid (HA) and IHSS fulvic acid (FA), which were purchased from the International Humic Substances Society. The use of this well-defined material allows comparison of the results with other laboratories. Biohumic NOM was obtained from Bioiberica S.A. and, as it is soil-based may contain species different from those in the NOM collected from surface waters. The Biohumic NOM contained 11% humic acids with 200-300,000Da molecular weights and 4% fulvic acids with 2,000-3,000Da molecular weights. Other chemicals used, such as NaCl, CaCl₂, NaOH and HCl were purchased from Sigma-Aldrich at analytical grade.

3.2.2 Solution preparation

A series of NOM solutions containing the various NOMs and ions at different concentrations were prepared using high quality Milli-Q water. IHSS NOM solutions of 20 and 100ppm were used along with 100, 200, 500 and 1000ppm Biohumic NOM solutions for experiments. The Na⁺ strength in the solutions was

3. Influence of ionic strength on NOM size and removal by ultrafiltration

adjusted to 0, 5, 10, 20 and 50mM with 0.1M NaCl, while the Ca^{2+} concentration was adjusted to 0, 1, 2, and 5mM by adding 20mM CaCl_2 . The pH value of the solutions was adjusted to between 5-7 by adding 0.1M NaOH or 0.1M HCl solutions. All the solutions were stirred for 1 hour prior to the experiments.

3.2.3 Membranes and filtration protocol

The membranes used were flat-sheet PBGC UF membranes, manufactured by Millipore Corp. The PBGC membrane was asymmetric polyethersulfone membrane with 28 kDa MWCO, determined inhouse using Gel Permeation Chromatography and dextrans of various molecular weights (details of MWCO determination are given in Appendix I).

Prior to use, the membranes were washed thoroughly with MilliQ water to remove preservative and then compacted by permeation experiments with pure water at a pressure of 300kPa for a period of 3h. The operating temperature was kept at room temperature (25°C).

Figure 3.1 Flow sheet of a dead-end cell filtration system – constant pressure

The filtration experiments were carried out in a 110 ml dead end cell, which accommodated $12.6 \times 10^{-4} \text{m}^2$ of membrane as shown in Figure 3.1. The use of unstirred conditions was based on the objective of water treatment with dead end

3. Influence of ionic strength on NOM size and removal by ultrafiltration

operation to minimize energy usage. A feed reservoir of 1.5L was connected to the dead end cell to provide extended filtration volumes and a PC-controlled electronic balance was employed to weigh collected permeates. The transmembrane pressure applied was 300kPa using pressurized N₂.

The NOM retention exhibited as TOC was based on spot samples of retentate and permeate and defined by equation 3.1

$$\text{Retention}_{\text{TOC}} = (1 - C_{\text{permeate}} / C_{\text{retentate}}) \times 100 (\%) \quad (3.1)$$

It had been tested several times for different membranes and it was found that the TOC results exhibited variation in the first 10min and kept stable after 20min filtration as shown in Table 3.1. Thus the filtration testing protocol was decided to collect the sample for retention test after 20-30 minutes filtration.

**Table 3.1: TOC concentration (ppm) in the permeate streams
after different times of filtration**

	5min	10min	20min	30min
Feed	7.249	7.272	7.351	7.301
Membrane 1	5.941	6.127	6.318	6.302
Membrane 2	2.883	3.532	3.638	3.657
Membrane 3	5.434	4.942	3.957	3.767
Membrane 4	1.945	2.604	2.655	2.645

The membranes were cleaned by soaking in 0.1M NaOH for 30 minutes followed by soaking in MilliQ Water for 30 minutes two times; this protocol restored membrane permeability. The membranes were used up to five times and were stored in a 0.1M EtOH solution at 4 °C.

3.2.4 Analysis

The Total organic carbon (TOC) content was analyzed using a Shimadzu TOC-V_{CSH} Total Organic Carbon analyzer and the analysis was conducted within one day of sample collection to avoid any changes in the NOM.

3. Influence of ionic strength on NOM size and removal by ultrafiltration

The particle sizes of the NOM were analyzed using a 90plus/BI-MAS Multi Angle Particle Sizing Analyzer (Brookhaven Instruments Corporation USA). The light scattering particle size analyzer is capable of measuring concentrated suspensions of small particles or solutions of macromolecules over the range of 2nm to 3 μ m. The sizes reported are the mean particle sizes.

The relative molecular weight distribution of NOM was determined using a High Pressure Size Exclusion Chromatography (HPSEC) with a RI detector which was manufactured by Waters. Ultrahydrogel columns types 120, 250 and 500 from Waters and a Shodex standard P-82 were used for HPSEC analysis. Prior to HPSEC measurement, water samples were filtered by a 0.45 μ m microfiltration membrane to remove large particles and colloids. The filtered samples were then concentrated by low pressure RO membrane to more than 50ppm for analysis. The MilliQ water was used as the mobile phase to carry the analysis to avoid the influence of ions in the mobile phase. The molecular weight distribution of NOM was presented by the HPSEC analysis based on the linear relationship between the NOM concentration and the area of the peak.

3.3 Results and discussion

3.3.1 Effect of Na⁺ interaction with NOM

The influence of sodium concentration on the size of Singapore NOM is shown in Figure 3.2. The Na⁺ concentration varied over the range of 0-50mM. It was found that the particle size of Singapore NOM reduced significantly from about 700nm to 80nm when the concentration of Na⁺ increased to 50mM. A similar trend was observed for IHSS NOM, HA and FA and Biohumic NOM, as shown in Figures 3.3 and 3.4. This phenomenon was mirrored by the HPSEC analysis of the NOM solutions. It should be noted that the NOM is particulate-free fraction after 0.45 μ m microfiltration. Figures 3.5, 3.6 and 3.7 illustrate the apparent molecular weight distributions of Singapore NOM, IHSS NOM and Biohumic NOM with different NaCl concentrations, respectively.

3. Influence of ionic strength on NOM size and removal by ultrafiltration

Figure 3.2 Particle size analysis of Singapore NOM with different NaCl concentrations

Figure 3.3 Particle size analysis of IHSS NOM with different NaCl concentrations

Figure 3.4 Particle size analysis of Biohumic with different NaCl concentrations

3. Influence of ionic strength on NOM size and removal by ultrafiltration

Figure 3.5 Molecular Weight Distribution of Singapore NOM with different NaCl concentration

3. Influence of ionic strength on NOM size and removal by ultrafiltration

Figure3. 6 Molecular Weight Distribution of IHSS NOM with different NaCl concentrations

3. Influence of ionic strength on NOM size and removal by ultrafiltration

Figure 3. 7 Molecular Weight Distribution of Biohumic NOM with different NaCl concentrations

3. Influence of ionic strength on NOM size and removal by ultrafiltration

The original NOMs without Na⁺ addition had broad molecular weight distributions. With the addition of Na⁺ to the solutions, the distributions for all the NOMs shifted gradually to narrower bands and the smaller NOM molecules accounted for the bulk. The effect of Na⁺ on Singapore NOM was found to be more pronounced than for IHSS or Biohumic NOM when comparing these results.

The observed effect of Na⁺ on NOM may be mainly due to coil-to-globule conversion and polyelectrolyte interaction, which changes the conformation of NOM from linear to spherical as suggested previously (Ghosh and Schnitzer, 1980; Jucker and Clark, 1994; Andersen *et al.*, 2000). Based on Flory's average field theory (Kayaman *et al.*, 1999; Kirwan *et al.*, 2004), soft polymer chains can change from coils to globules when the conditions of the solution are altered. This conversion could be attributed to either ion addition or temperature change. For instance, the size of Poly-*N*-isopropylacrylamide (PNIPAM) can be reduced by 99% when the temperature is adjusted to 32°C. NOM, being a mixture of macromolecules or polymer, is normally in a state of random coils in a water solution. When an ion salt is added into the NOM solution, the NOM solubility would be affected. NOM could contract to small globules to adjust for this change in its environment.

An alternative view point is that the NOM contains polar compounds which can be ionized in a water solution. The electrostatic forces of repulsion would result in an “open” conformation. With the addition of salts the interactions would become shielded resulting in a smaller effective size.

3.3.2 Effect of Ca²⁺ interaction with the NOM

The influence of calcium concentration on the size of Singapore NOM is presented in Figure 3.8. An opposite trend to the case of Na⁺ was found as the size of Singapore NOM increased with an increase in Ca²⁺ concentration. However, as shown in Figure 3.9, IHSS HA and IHSS FA responded differently to Ca²⁺ addition. Increasing Ca²⁺ showed competing effects on the size of IHSS HA. When 5mM

3. Influence of ionic strength on NOM size and removal by ultrafiltration

Ca^{2+} was added to the 60ppm IHSS HA solution, the size was reduced from 400nm to 180nm. However, with a further increase in Ca^{2+} concentration to 10mM, the size of IHSS HA increased significantly to 1800nm. In contrast, the size of IHSS FA consistently decreased with Ca^{2+} loading over the range of concentrations. For IHSS NOM, being a mixture of IHSS HA and IHSS FA in equal portions, the effect of Ca^{2+} loading on the size of IHSS NOM followed the pattern of IHSS HA as the change in IHSS HA size was then more significant.

Figure 3. 8 Particle size analysis of Singapore NOM (52.14ppm) with different Calcium Concentrations

Figure 3. 9 Particle size analysis of IHSS NOM (60 ppm) with different Calcium Concentrations

3. Influence of ionic strength on NOM size and removal by ultrafiltration

Biohumic NOM response to Ca^{2+} addition was similar to IHSS NOM. As indicated in Figure 3.10, Biohumic NOM size was reduced at relatively low concentrations of Ca^{2+} (1mM), while there was an increase in Biohumic NOM size from 100nm to 2000nm, when the concentration of Ca^{2+} in the solution was increased (>2mM). It was observed in the experiments that there were aggregated particles suspending in the solutions, which lends support to the observed NOM size increase.

Figure 3.10 Particle size analysis of Biohumic NOM with different CaCl_2 concentrations

Figure 3.11 Molecular Weight Distribution of IHSS NOM with different CaCl_2 concentrations

These observations were also verified using HPSEC analyses. The molecular weight distributions of IHSS NOM and Biohumic NOM with low Ca^{2+} concentrations shown in Figures 3.11-3.12, respectively, confirmed that there was a

3. Influence of ionic strength on NOM size and removal by ultrafiltration

decrease in the NOM size at low concentration of Ca^{2+} , as the original broad molecular weight distributions narrowed in the range of low molecular weights. However, this type of spectrum could not be obtained for Singapore NOM and other NOM solutions with higher Ca^{2+} loading, because the aggregated particles in the solutions tended to clog the guard column in the HPSEC leading to operational problems. Thus the sizes of the aggregated particles had exceeded the limitation of the guard column, which pretreated the solutions with a $0.45\mu\text{m}$ microfilter.

It is presumed the same mechanism observed in the case of Na^+ played a role in the case of Ca^{2+} interaction with IHSS NOM and Biohumic NOM at relatively low concentrations. However as the concentration of Ca^{2+} in the solution was increased, the size increase could be due to aggregation or chelation between the phenolic groups in humic acid and Ca^{2+} becoming a dominant factor. Similar mechanisms have been proposed in the literature [35].

Figure 3. 12 Molecular Weight Distribution of Biohumic NOM with different CaCl_2 concentrations

3.3.3 Effect of solution pH

Figure 3.13 shows the size distribution of IHSS HA at different pH obtained by HPSEC. It was found that although there was no difference in the effective molecular size distribution of IHSS HA over the pH range 4-10, its measured size decreased significantly at low pH values (≤ 2) (lower molecular weights are to the right of the figure). However, IHSS FA was not very sensitive to the pH change as shown in Figure 3.14. For the IHSS, combining IHSS HA and FA, the measured

3. Influence of ionic strength on NOM size and removal by ultrafiltration

size shifts to lower values at pH2 (Figure 3.15) which is in line with IHSS HA. Figure 3.16 illustrates that the pH influence on biohumic NOM is in a similar manner to IHSS NOM.

Figure 3. 13 Size Distribution of IHSS Humic Acid under different pH

Figure 3. 14 Size Distribution of IHSS Fulvic Acid under different pH

3. Influence of ionic strength on NOM size and removal by ultrafiltration

Figure 3.15 Size Distribution of IHSS NOM under different pH

Figure 3.16 Size Distribution of Biohumic NOM under different pH

3. Influence of ionic strength on NOM size and removal by ultrafiltration

3.3.4 Ultrafiltration study

In addition to the above studies, the impact of ion interactions with NOM on NOM removal in an ultrafiltration process was investigated. As noted above, the measurements were done in unstirred conditions to more closely simulate the dead end mode typically used in the water industry. As a result the reported retentions are likely to be significantly lower than the intrinsic retention of the membranes used. The influence of hydrodynamic conditions on retention is presented in Chapter 5. Figures 3.17 and 3.18 show the retentions of Singapore NOM and Biohumic NOM solutions with/without NaCl addition, respectively using the PBGC membrane. With the introduction of Na^+ , the Singapore NOM retention decreased from 52% to 29% and Biohumic NOM retention decreased from 45% to 29%. Moreover, the HPSEC chromatograms shown in Figure 3.19 demonstrate that the molecular sizes of Biohumic NOM permeates became smaller with Na^+ addition.

Figure 3. 17 Retention of PBGC Membrane for Singapore NOM Solutions with different Sodium Concentrations (10 ppm NOM)

3. Influence of ionic strength on NOM size and removal by ultrafiltration

Figure 3.18 Retention of PBGC Membrane for Biohumic NOM Solutions with 8 different Sodium Concentration (100 ppm NOM)

Figure 3. 19 HPSEC chromatograms of the permeate solution collected after Ultrafiltration of Biohumic NOM (200ppm):

For IHSS NOM, the combined effect of 20mM NaCl and 0.5mM CaCl₂ on the filtration was examined and the results are shown in Figure 3. 22. As the relative concentration of Ca²⁺ to NOM was quite low, the interactions of both Ca²⁺ and Na⁺ with the NOM resulted in a decrease in NOM size. As a consequence, the NOM

3. Influence of ionic strength on NOM size and removal by ultrafiltration

retention decreased from about 50% to 30% for the PBGC membranes. This result illustrates the complex interactions that can influence membrane performance.

Figure 3. 20 Retention of PBGC Membrane for Singapore NOM Solutions with different Calcium Concentrations (10 ppm NOM)

Figure 3. 21 Retention of PBGC Membrane for Biohumic NOM Solutions with different Calcium Concentrations (20 ppm NOM)

3. Influence of ionic strength on NOM size and removal by ultrafiltration

3.4 Conclusions

This Chapter deals with NOM sourced from a Singapore reservoir, which is compared with Standard humic substances and a commercially produced NOM. The influence of sodium and calcium concentrations as well solution pH on the NOM molecular size and removal efficiency in membrane ultrafiltration processes were investigated. The effective size of the NOM was significantly reduced by adding Na^+ to the NOM solution due to the coil-to-globule conversion and polyelectrolyte interaction. In contrast, increasing Ca^{2+} showed two possible effects on the size of the NOM. At relatively low Ca^{2+} concentrations, NOM size was reduced presumably by the same mechanism observed in the case of Na^+ . However when the concentration of Ca^{2+} in the solution was increased, there was an increase in NOM size, possibly due to an aggregation or chelation between the humic acid in NOM and Ca^{2+} . The NOM also reduced its size when the solution pH was below 2.

Figure 3. 22 Retention of PBGC Membrane for different IHSS Solutions; Solution A: IHSS; Solution B: IHSS+NaCl 20mM+CaCl₂ 0.5mM

These observations were further confirmed by NOM ultrafiltration experiments. The NOM retentions by the PBGC membranes decreased when Na^+ was added into the solution, whereas increasing Ca^{2+} concentration increased the NOM retentions of PBGC membranes. Therefore, it is important to have a good understanding of

3. Influence of ionic strength on NOM size and removal by ultrafiltration

solute-solute interaction to optimize and enhance NOM filtration performance. The next Chapter provides further characterization of Singapore NOM and its fouling of UF membranes.

4. Characteristics of tropical nom and its influence on UF membrane fouling

4.

CHARACTERISTICS OF TROPICAL NOM AND ITS INFLUENCE ON UF MEMBRANE FOULING

4.1 Introduction

Natural Organic Matter (NOM) is a complex mixture of organic compounds with a broad spectrum of functional groups and molecular weight distribution, NOM plays an important role in affecting water quality and inducing membrane fouling in water filtration processes (Hong, 1996; Amy and Cho, 1999; Jarusutthirak, 2002).

Generally, the NOM contains both aromatic and aliphatic components with carboxylic and phenolic groups attached to the aromatic rings. As a result, the NOM species are usually negatively charged or neutral and can be divided into hydrophobic and hydrophilic (humic and non-humic) components. The humic substances have characteristic lengths around 1nm to 10nm and molecular weights from a few hundreds to approximately 100kDa. However, the features of NOM have been found to vary in different water sources. The environmental conditions such as pH, ionic strength and the concentration of inorganic matter would also affect the NOM properties (Wang *et al.*, 2001; Wei *et al.*, 2004).

It is well known that multivalent ions, such as Ca^{2+} and Mg^{2+} , interact strongly with the NOM, as described in Section 3.1 Chapter 3 (page 56). Consequently, there is an increase in both size and apparent molecular weight of the humic substances (Cho *et al.*, 1998; Fan *et al.*, 2001).

4. Characteristics of tropical nom and its influence on UF membrane fouling

The reaction of multivalent ions with NOM can also result in a highly compacted fouling layer on the membrane surfaces, which may cause a severe permeability decline in the membrane filtration process. For example, flux decreased by about 90% with the increase of calcium concentration for a 100kDa ultrafiltration membrane due to the occurrence of an aggregation on the membrane surface, which formed a molecular bridge between the negatively charged NOM and the membrane surface in addition to increasing the electrostatic shielding (Cho *et al.*, 1999; Aoustin *et al.*, 2001).

In laboratory studies, NOM powders and various multivalent ions are often employed to make model aqueous solutions to simulate different water sources. The NOM powder used is preferably derived from source water which is high in dissolved organic compounds and low in salt content in order to minimize the influences caused by the salts during the NOM isolating process; this simplifies the subsequent analysis of the NOM reaction with the multivalent ions in the solutions. The common approach for NOM isolation is to use reverse osmosis (RO) membranes to conduct filtration (Alberts and Takacs, 1999). IHSS NOM powder from the International Humic Substances Society, which was extracted from Suwannee River by a RO system, for instance, is assumed to contain negligible multivalent ionic complexes after desalting treatment and thus is widely used to make NOM sample solutions. The details of the interaction between ions and IHSS NOM have been investigated in Chapter 3 and by others. (Borisover and Graber, 2002). However, tropical NOM collected from Singapore catchments contains higher concentration of calcium ions than the IHSS NOM derived from typically temperate environments (Aoustin *et al.*, 2001). As a result, the IHSS NOM solution with ions may not simulate the characteristics of the tropical NOM in the membrane ultrafiltration process. To make this NOM study applicable to tropical water sources and provide more relevant information for the Singapore water treatment, this study makes use of the tropical NOM rather than using only the IHSS NOM.

The objectives of this study were 1) to collect and concentrate NOM from the raw water of a Singapore reservoir to make a tropical NOM sample of Singapore; 2) to

4. Characteristics of tropical nom and its influence on UF membrane fouling

investigate the role of calcium in affecting NOM properties during the NOM isolating process; and 3) to study the tropical NOM ultrafiltration fouling performance with the IHSS NOM as a reference. The isolated NOM and water samples were analyzed using TOC, UV/Vis, HPSEC and FTIR. The filtration performance was evaluated in a dead-end filtration cell fitted with UF membranes. This study is an attempt to isolate a tropical NOM for the first time and get a better understanding of the impacts of calcium on the tropical NOM properties and fouling during the ultrafiltration process for NOM removal.

4.2 Material and methods

4.2.1 Water Source

Raw water and NOM isolates were collected from the Singapore Kranji reservoir, which is located at the northwest of Singapore Island. A total of 6,300L of raw water were used for NOM concentration and 40L of raw water was also used for comparison analysis.

4.2.2 NOM isolation process

A TECSW RO spiral wound thin film composite system built by MIZUTEC, USA was used to isolate the NOM from the raw water samples. In this process, water passed through the membrane and was purified by reducing total dissolved substances, such as organic materials, pyrogens, submicron colloidal matters, viruses and bacteria, up to 99%. A schematic diagram of the system is shown in Figure 4.1.

The raw water was pumped through a high-volume filter cartridge with 1 μ m pore size to eliminate particulate matter such as bacteria and inorganic particles, which were not part of the target material. This process was operated at a pressure of 300kPa at inlet, and the pressure decreased to 180kPa at the outlet of the microfiltration cartridge. The pretreated water was sent directly to the RO system.

4. Characteristics of tropical nom and its influence on UF membrane fouling

In each RO processing, the permeate solution was discarded, and the retentate solution was returned to the drum and combined with additional filtered raw water for processing. After 6,300L raw water was concentrated to about 50L, the concentrates were collected in a sealed bottle and stored at 4 °C for subsequent treatment.

Figure 4. 1 Flow sheet of TECSW RO system with microfiltration cartridge for the NOM isolation

In the concentrates, the concentration of organics was much higher than the inorganic ions such as calcium, parts of the concentrates reacted with the calcium to form coagulant. Thus the concentrates were further divided into two parts: the NOM solution without any calcium coagulum (denoted hereafter as S-NOM I) from the upper part of the container and the NOM solution mixed with calcium coagulum (denoted hereafter as S-NOM II) from the bottom of the container. Both portions were treated using an Alpha 1-4 LD-2 freeze dryer (Martin Christ). Quick freezing was applied to minimize structural damage of the molecules. After this operation the dried powders were stored in two dark bottles for further characterization and use.

4.2.3 Solution preparation

High quality Milli-Q water (Millipore USA) was used for the preparation of NOM solutions and for membrane fouling performance experiments. Other chemicals used were purchased from Sigma-Aldrich at analytical grade.

4. Characteristics of tropical nom and its influence on UF membrane fouling

Four types of NOM solution were used in the study of NOM properties and UF membrane fouling: the raw water collected from Kranji reservoir (denoted hereafter as S-RW), isolated S-NOM I, isolated S-NOM II and the IHSS NOM. The DOC concentration of the prepared solutions was kept the same as in the tropical raw water at around 10ppm. 1.5L of raw water (S-RW) collected from Kranji reservoir was pretreated by a 0.45 μ m microfiltration membrane to remove particulate matter.

4.2.4 Membranes and filtration protocol

Flat-sheet PBGC/YM UF membranes were applied in the study. The PBGC membrane with 28kDa MWCO exhibited mildly hydrophobic character (contact angle: 57.9 degree) and was almost neutral charge (zeta potential: -5.0mV at pH 7). The YM10 membrane was an asymmetric regenerated cellulose membrane with 49kDa MWCO. The membrane exhibited hydrophilic (contact angle: 10.9 degree) and neutral charged (zeta potential: -4.2Mv at pH 7) properties.

Filtration experiments were carried out in a dead end cell. The details have been described in Chapter 3, section 3.2.3. The permeates and retentates were sampled every 20 minutes.

4.2.5 Analysis methods

The Total organic carbon (TOC) content and UV/Visible absorbance spectra of NOM were analyzed. The details can be found in Appendix I.

A Perkin Elmer Optima 3000 Inductively Coupled Plasma Atomic Emission Spectroscope (ICP-AES) was used to measure cation concentrations of the samples. Solutions were diluted at a 1:1 ratio with MilliQ water.

The relative molecular weight distribution of NOM was determined using a High Pressure Size Exclusion Chromatography (HPSEC). The details had been described in Chapter 3, section 3.2.4.

4. Characteristics of tropical nom and its influence on UF membrane fouling

The functional groups of the isolated NOM were carried out by a Fourier Transform Infrared Spectrophotometer with Thermogravimetric Analyser (FTIR/TGA) which was supplied by Perkin Elmer. The isolated NOM powder was prepared into a 13mm KBr disc, and placed into the sample chamber for analysis.

4.2.6 Membrane fouling parameters

The fouling effect can be described by Darcy's law as follows,

$$J_v = \frac{1}{A} \frac{dV}{dt} = \frac{\Delta p}{\eta (R_m + R_c)} \quad (4.1)$$

where J_v is the volumetric flux of permeate, V the total volume of permeate, A the membrane surface area; Δp the pressure drop imposed across the fouling layer and membrane, η the viscosity of the permeating fluid, R_m the resistance of the clean membrane, and R_c the total additional resistances during the filtration process as a result of the accumulation of foulants on the membrane.

The hydraulic resistance of the clean membrane can be evaluated by measuring the flux of prefiltered MilliQ water as a function of applied pressure,

$$R_m = \frac{\Delta p_{pure}}{\eta J_{v,pure}} \quad (4.2)$$

where the subscript *pure* refers to operation with MilliQ water. Thus the total additional resistances R_c could be evaluated by

$$R_c = \frac{\Delta p}{\eta J_v} - R_m \quad (4.3)$$

The membrane was back washed after the filtration test. The irreversible fouling resistance R_{ir} can be described after back washing:

$$R_{ir} = \frac{\Delta p}{\eta J_{v,recover}} - R_m \quad (4.4)$$

where the subscript *recover* refers to operation after back washing. Therefore, the reversible fouling resistance R_{re} can be described as

$$R_{re} = R_c - R_{ir} \quad (4.5)$$

4. Characteristics of tropical nom and its influence on UF membrane fouling

4. 3 Results and discussion

4.3.1 Interaction of multivalent ions with NOM in the NOM isolation

The NOM isolation generated two samples of tropical NOM, i.e., the S-NOM I derived from the dissolved NOM in the aqueous solution and the S-NOM II from the mixture of the dissolved NOM and the calcium coagulum produced in the isolating process, as the raw water collected from Singapore Kranji reservoir tended to contain high concentration of calcium and magnesium, which reacted with the NOM.

Having observed the separation of the NOM concentrate into two “samples” (with and without coagulum), it was decided to analyze the two samples and compare their fouling tendency. Sample S-NOM II (with coagulum) represents an extreme condition for filtration.

As shown in Table 4.1, after the deduction of 4.7% NOM loss in the RO permeate, only 38.0% of the NOM remained in the concentrated product and 52.3% of the NOM reacted with the multivalent ions to form coagulum in the S-NOM II. 5% NOM loss in the operation was assumed. Similarly, the mass balance for the multivalent ions in the isolation process revealed that 36.2% of the calcium and 67.6% of the magnesium were kept in the concentrated solution while 55.1% of the calcium complexed with the NOM and 25.5% of the magnesium also participated in the reaction.

4.3.2 Composition of tropical NOMs

Figure 4.2 shows the FTIR analysis of the tropical NOMs and the main functional groups contained in the NOMs are summarized in Table 4.2. In Figure 4.2, the prominent peaks at 1428 cm^{-1} (i) and 874 cm^{-1} (ii) correspond to the aliphatic element of $-\text{CH}_2-$ and the aromatic element of respectively, which formed the

4. Characteristics of tropical nom and its influence on UF membrane fouling

main skeleton of the tropical NOMs. The NOMs also contained the –OH group, which was indicated by the peak around 3435 cm^{-1} (iii).

Table 4. 1 Mass balance on tropical NOM after isolation

		Volume (L)	NOM			Calcium			Magnesium		
			Average concentr ation (mgL^{-1})	Total mass (g)	Total (%)	Average concentrat ion (mgL^{-1})	Total mass (g)	Total (%)	Average concentra tion (mgL^{-1})	Total mass (g)	Total (%)
Raw water		6300	8.72	54.93	-	24.15	152.15	-	3.05	19.22	-
Concentrated NOM solution		50	417.50	20.88	38.0	1100	55.00	36.2	260	13.00	67.6
Loss during isolating process	Loss in RO permeate	5000	0.35	1.75	3.2	0.72	3.6	2.37	0.03	0.15	0.78
		1100	0.66	0.73	1.3	1.16	1.28	0.84	0.06	0.07	0.36
		150	0.74	0.11	0.2	5.91	0.89	0.58	0.84	0.13	0.68
	5% estimated loss	-	-	2.75	5.0	-	7.61	5.00	-	0.96	5.00
Coagulum in S- NOM II		-	-	28.71	52.3	-	83.77	55.1	-	4.91	25.5

However, the peak associated with C-OH bonding appeared at 1108 cm^{-1} in the S-NOM II but was shifted to 1144 cm^{-1} in the S-NOM I. This shift implies that the carbon connected with the hydroxyl group lost hydrogen and reacted with some other compounds. The C=O stretching peak at 1798 cm^{-1} was mainly attributed to carboxylic acid groups. The carboxylic acid groups retained their status in –COOH in the S-NOM I, but the asymmetric carboxylate stretch shifted to 1647 cm^{-1} in the S-NOM II, which indicated that an appreciable fraction of the carboxyls are deprotonated. The reason for this change may be due to the coagulation or chelating that occurred between the tropical NOM and the multivalent ions of calcium and magnesium. A peak around 1636 cm^{-1} for the S-NOM I represented the double bond of aromatic groups, which was split into two peaks at 1658 cm^{-1} and 1563 cm^{-1} in the S-NOM II. This phenomenon was also caused by the interaction between aromatic groups and multivalent ions to form π - π and p - π bonds, resulting in chelating or coagulation between NOM and multivalent ions. Clearly, the S-NOM I and S-NOM II are composed of almost the same main functional groups, but some groups appeared in a slightly different status due to the influence of the multivalent ions in the isolation process.

4. Characteristics of tropical nom and its influence on UF membrane fouling

Figure 4.2. FTIR results of isolated tropical NOMs: (a) S-NOM I; (b) S-NOM II:

(i) $-\text{CH}_2-$; (ii) $-\text{C}\equiv\text{C}-$; (iii) $-\text{OH}$; (iv) $\text{C}-\text{OH}$; (v) $\text{C}=\text{O}$; (vi) $\text{C}=\text{C}$

Table 4. 2 FTIR analyses of S-NOM I and S-NOM II

Sample	$\nu_{\text{as OH}}$ (cm^{-1})	$\nu_{\text{as COOH}}$ (cm^{-1})	$\nu_{\text{as COO}^-}$ (cm^{-1})	$\nu_{\text{as C}=\text{C}}$ (cm^{-1})	$\nu_{\text{as CH}_2}$ (cm^{-1})	$\nu_{\text{as COH}}$ (cm^{-1})	$\nu_{\text{as ph}}$ (cm^{-1})
S-NOM I	3436	1798	-	1636	1428	1144	874
S-NOM II	3435	-	1647	1658 1563	1428	1108	872

4.3.3 Characteristics of tropical NOMs

The characteristics of the tropical NOMs in MilliQ water, which include the aromatic fractions defined as SUVA ($\text{UV}_{254}/\text{DOC}$), pH and ion concentrations, are listed in Table 4.3 along with the IHSS NOM water sample as a reference. The

4. Characteristics of tropical NOM and its influence on UF membrane fouling

DOC of these four NOM solutions was kept at a similar level for comparison. The standard deviations of these measurements were less than 5%.

Table 4.3 Characteristics of tropical NOMs and the IHSS NOM aqueous solutions

	TOC (mgL ⁻¹)	SUVA (cm ⁻¹ mg ⁻¹ L)	pH	Na (mgL ⁻¹)	Ca (mgL ⁻¹)	Mg (mgL ⁻¹)	K (mgL ⁻¹)	Al (mgL ⁻¹)	Fe (mgL ⁻¹)	Mn (mgL ⁻¹)	Ni (mgL ⁻¹)
S-RW	8.06	0.034	7.1	14.3	27.1	5.9	2.69	0.001	0.011	0.01	0.001
S-NOM I	7.83	0.026	7.0	23.4	26.0	3.00	10.3	0.001	0.007	0.01	0.001
S-NOM II	8.76	0.053	7.4	44.0	42.8	3.06	23.0	0.074	0.054	0.02	0.001
IHSS NOM	11.63	0.032	7.1	0.11	0.15	0.01	0.03	0.04	0.06	0.001	0.006

It can be seen that for the NOM solutions with a DOC concentration around 8ppm, there was no much difference in pH value. However, SUVA was reduced from 0.034 in the S-RW sample to 0.026 cm⁻¹ mg⁻¹ L in the S-NOM I and increased to 0.053 cm⁻¹ mg⁻¹ L in the S-NOM II. These differences indicated that the relative amount of aromatic structures in the S-NOM I was less than in the raw water while the S-NOM II exhibited the highest aromatic fraction, implying that the aromatic elements tended to react with calcium to form calcium coagulum, which is in agreement with the FTIR results. This also suggests that high SUVA plus calcium could be important for fouling considerations.

Compared with the IHSS NOM, the tropical NOMs contained much higher concentrations of ions based on the ICP analysis. For example, the concentrations of Ca²⁺ and Na⁺ in the tropical NOMs were above 26ppm and 14ppm respectively, compared to the ion concentrations of less than 1ppm in the IHSS NOM. This difference may be one of the key causes to influence the NOM characteristics and their fouling performances in the membrane filtration.

Figure 4.3 shows the molecular weight distributions of the tropical S-RW, S-NOM I and the IHSS NOM. The S-NOM II was not included in Figure 4.3 as the calcium coagulum could block the column of the HPSEC. From Figure 4.3, all the NOMs were found to display a wide molecular weight ranging from a few Daltons to 1000kDa. Referring to Chapter 3, the difference between the tropical NOMs and the

4. Characteristics of tropical nom and its influence on UF membrane fouling

IHSS NOM was that the tropical NOMs contained more fractions of smaller molecular weights (less than 0.1kDa) and its molecular weight distribution was more dispersing than that of the IHSS NOM.

Figure 4. 3 Molecular weight distributions of tropical NOMs and IHSS NOM

Comparing the S-RW with the S-NOM I, it was noted that there were no NOM elements present in the range of 0.1 to 10kDa for the S-NOM I sample, while the molecular weights in this range occupied around 30% of the total NOM in the S-RW, suggesting that the NOM in this portion had a strong tendency to coagulate or chelate with the multivalent ions in the solution to form the coagulum left in the S-NOM II.

4.3.4 Filtration performance of tropical NOMs

Figures 4.4 and 4.5 show the retentions of different water samples through the PBGC and YM10 membranes, respectively. For the two membranes, the DOC retentions of the S-RW, S-NOM II and IHSS NOM were around 20%. These results could be expected because the molecular weights of about 80% of the tropical NOMs and 70% of the IHSS NOM were smaller than 50kDa as shown in Figure 4.4, and the measured MWCOs of the PBGC and YM10 membranes were 98kDa and 49kDa, respectively. There was not much difference in retention between the S-RW and S-NOM II.

4. Characteristics of tropical nom and its influence on UF membrane fouling

Figure 4. 4 Retentions of NOM solutions through the PBGC Membrane

In contrast, the membranes showed much higher retentions to the aromatic elements as indicated by the UV/Vis spectrum. The UV/Vis retentions of both the membranes reached above 40% for the S-RW, the S-NOM I and the IHSS NOM, and up to 70% for the S-NOM II. This demonstrates that the chelating of the aromatic elements with multivalent ions could result in a high retention of these species.

Figure 4. 5 Retentions of NOM solutions through the YM10 Membrane

a significant flux drop. Specifically, the flux of the S-NOM I dropped to 30% of pure water flux and was recovered to 58.6% after 0.1M NaOH washing. However, the S-RW and S-NOM II caused more severe flux drops than the S-NOM I, but the

4. Characteristics of tropical nom and its influence on UF membrane fouling

recovery of the S-NOM II was the highest to 75% of pure water flux. This result indicates that the presence of calcium coagulum in the S-NOM II solution tended to generate more severe fouling, but which was more reversible than the S-RW and S-NOM I. The possible reasons for this are that the formation of calcium coagulum might reduce the amounts of smaller molecular size NOM in the solution, resulting in reduction of the irreversible fouling caused by pore adsorption and pore plugging. Referring to the results of the IHSS NOM in Chapter 3 (section 3.3.4), it caused more severe flux decline but showed a much higher recovery than the tropical NOMs, probably due to its larger molecules than those in the tropical NOMs.

Figure 4. 6 Flux decline during the PBGC membrane filtration:

(a) S-RW; (b) S-NOM I; (c) S-NOM II; (d) IHSS NOM

The total additional resistance R_c introduced by the accumulation of foulants on the membrane versus filtration time is plotted in Figure 4.7. The S-NOM II and S-RW produced a much higher R_c than the S-NOM I. This shows that those NOM elements, which were removed from the isolated solution due to the reaction with calcium, play an important role in inducing NOM fouling during the UF filtration. By comparing the initial flux and the recovered flux after membrane filtration, the irreversible resistances could be calculated. Figure 4.8 shows the irreversible resistances of the S-RW, S-NOM I and S-NOM II solutions filtered through the PBGC membrane. The S-NOM II presented the lowest R_{ir} among the three NOM

4. Characteristics of tropical nom and its influence on UF membrane fouling

solutions, which was consistent with the results demonstrated in Figure 4.7. The dense compact fouling layer formed by the deposition of calcium coagulum may have formed a “precoat” that prevented the small molecules from penetrating into the membrane pores and being adsorbed, leading to the reduction of the irreversible fouling caused by pore blocking and plugging.

Figure 4. 7 Total additional resistance R_c during the PBGC membrane filtration:

(a) S-RW; (b) S-NOM I; (c) S-NOM II

Figure 4. 8 NOM irreversible resistance during the PBGC membrane filtration:

(a) S-RW; (b) S-NOM I; (c) S-NOM II

4. Characteristics of tropical nom and its influence on UF membrane fouling

Figures 4.9-4.10 illustrate the fouling behavior of the tropical NOMs on the hydrophilic YM10 membrane. As before, the S-NOM II showed the greatest flux decline because of the greater cake resistance compared with the other two NOMs, but the recoveries of all the NOMs were more than 90%. This implies that the irreversible fouling on the YM10 membrane caused by the tropical NOMs was negligible.

Figure 4. 9 Flux decline during the YM 10 membrane filtration:

(a) S-RW; (b) S-NOM I; (c) S-NOM II; (d) IHSS NOM

Figure 4. 10 Total additional resistance during the YM10 membrane filtration:

(a) S-RW; (b) S-NOM I; (c) S-NOM II

4. Characteristics of tropical nom and its influence on UF membrane fouling

The different filtration performances particularly in the flux recovery between the PBGC and YM10 membranes would be due to the different membrane properties. The YM10 membrane was an asymmetric regenerated cellulose membrane with a propylene support, which was considered hydrophilic in nature, whereas the PBGC membrane was made of more hydrophobic polyethersulfone materials. The greater fouling tendency of the PBGC membrane during NOM filtration confirms the general consensus that hydrophobic membranes would be more severely fouled with NOM species than hydrophilic membranes.

4. 4 Conclusions

This is believed to be the first effort to build and characterize a tropical NOM. Two types of tropical NOM were produced, i.e., the S-NOM I derived from the dissolved NOM and the S-NOM II from the mixture of the dissolved NOM and the calcium coagulum generated in the isolating process.

The S-NOM II contained more fractions of aromatic elements than the S-NOM I, as the high concentration of multivalent ions in the tropical water source tended to react with the aromatic elements to form calcium coagulum. The NOM component in the range 0.1 to 10kDa were also found to have a strong tendency to coagulate or chelate with the multivalent ions. The tropical NOMs contained much higher concentrations of ions and had a more disperse molecular weight distribution with a greater proportion of smaller molecules.

Filtration studies showed that the aromatic elements in the S-NOM II were retained the most effectively by either the PBGC or YM10 UF membranes, which demonstrates that the chelating of the aromatic elements with multivalent ions could result in a high retention. However, the presence of calcium coagulum in the feed water tended to generate more severe reversible fouling because of the cake formation on the membrane surface, but it also reduced the irreversible fouling caused by pore closure and pore plugging, as the formation of calcium coagulum reduced the amount of smaller molecules of NOM in the solution. Moreover, the

4. Characteristics of tropical nom and its influence on UF membrane fouling

cake layer may have prevented the small molecules of NOM from penetrating into the membrane pores and being adsorbed. Overall, cake layer formation on the membrane surface was the main fouling mechanism of tropical NOMs during this UF filtration study. The results also confirmed the better fouling tolerance of more hydrophilic membranes when filtering NOM solutions.

PREAMBLE TO CHAPTERS 5, 6, and 7

The current trend is to operate UF membranes in water treatment without crossflow, i.e. in dead-end mode. This helps to reduce energy and does not impact on removals of turbidity and pathogens. However this strategy is anticipated to be less suited to NOM removal. In this thesis the objectives are to explore how best to use UF for NOM removal. In the previous chapters the UF of Singapore derived NOM has been described with interest in NOM characterization, the effect of ions, inducing Calcium, and membrane properties. The remaining three chapters examine three strategies to enhance NOM removal and control fouling, as follows

- (i) Chapter 5: describes the effect of operating conditions, particularly crossflow versus dead-end operation, on NOM removal and UF fouling.
- (ii) Chapter 6: describes the application of MIEX resin to assist NOM removal and its effect on membrane fouling.
- (iii) Chapter 7: describes the surface modification of UF membranes to improve removal of NOM and fouling control.

5.

IMPACT OF OPERATING CONDITIONS ON NOM REMOVAL AND MEMBRANE FOULING IN ULTRAFILTRATION PROCESSES

5.1 Introduction

Previous studies have shown that reverse osmosis (RO) or nanofiltration (NF) membranes can achieve a high NOM removal to more than 90%, but pre-treatment usually is needed and relatively low filtration fluxes are obtained. Recently, Ultrafiltration (UF) membranes have been widely applied for the drinking water treatment, as the development in membrane technology has led to an improvement of low-pressure membrane properties and cost reduction of the low-pressure membrane treatment plants (Crozes *et al.*, 1997). Several operational advantages have been confirmed for the low-pressure membrane systems such as good removal efficiency of turbidity and pathogens, low energy requirement and limited use of chemicals as well as relatively low cost of maintenance.

However, the filtration performance of UF membranes exhibits a limitation for NOM removal. The rejection of NOM is lower due to the larger molecular weight cut-off (MWCO) compared to the relative molecular weight of NOM, and serious fouling caused by NOM has occurred (Lee *et al.*, 2004; Lee *et al.*, 2005). Membrane filtration performance in terms of flux and retention is highly depended

5. Impacts of operation conditions on NOM removal and membrane fouling...

upon the membrane properties and the operating conditions as well as the nature of the feed stream.

The impacts of flux and trans-membrane pressure (TMP), crossflow velocity and backwash frequency on NOM fouling have been studied for UF hollow fibers in surface water treatment. An optimum flux of 75 l/h.m^2 with 0.9 m/s crossflow velocity was found to limit fouling by particulates (turbidity) (Crozes *et al.*, 1997). The relevance of controlling the crossflow /flux ratio has been pointed out in Section 2.2.6 of Chapter 2 in the discussion of the J/k ratio. Some studies (for example (Amy and Cho, 1999)) have examined the influence of the J/k ratio on fouling, and shown that as this ratio is increased so is the rate of fouling. This pointed to the means of controlling fouling by limiting flux or improving the mass transfer coefficient k (typically increased by increasing crossflow velocity).

Figure 5.1 Mode of operation: crossflow vs deadend; Constant pressure vs constant flux

The important operating modes which influence the type of module used and the degree of fouling include constant flux vs constant pressure, crossflow vs. dead end. As shown in Figure 5.1, membrane filtration performance exhibits different features under different operating modes. In general, some hollow fiber systems used for

5. Impacts of operation conditions on NOM removal and membrane fouling...

treating surface water are operated in the dead-end mode for low turbidity feed streams and switched automatically to the crossflow mode when turbidity increases. However, MF, UF and NF membranes adopt the operating modes of crossflow (pumped or stirred) and constant pressure with few exceptions in research studies. This differs from typical industrial operations which tend to use the mode of constant flux with crossflow (NF or UF) or with dead-end (MF or UF). There is a need to conduct further study at the lab scale and to gain a deeper insight on the impact of the various operating modes.

In this Chapter, the impact of the operating conditions on the filtration was investigated over the spectrum of strategies: a) the constant pressure mode with crossflow; b) the constant pressure mode with dead-end; c) the constant flux mode with crossflow; d) the constant flux mode with dead-end. The flow was simulated by applying mechanic stirring in a dead-end cell. Several types of membranes were used to study the influences of membrane MWCO and membrane surface property on the NOM filtration performance. They include PES membranes with MWCOs of 28kDa and 100kDa, and cellulose membranes with MWCOs of 10kDa and 30kDa. The NOM retention and the fouling resistance were thoroughly evaluated. This study was an attempt to identify optimal operating conditions to enhance UF membrane performance and control NOM fouling.

5.2 Materials and methods

5.2.1 Source water and NOM

Raw water and NOM isolates were collected from Kranji reservoir, which has been described in Chapter 4, section 4.2.1 and 4.2.2. Details of the NOM characteristics also can be found in Chapter 4, section 4.3.3. Other chemicals used, such as NaCl, CaCl₂, NaOH and HCl were purchased from Sigma-Aldrich at analytical grade.

5.2.2 Membranes

5. Impacts of operation conditions on NOM removal and membrane fouling...

The membranes used included flat-sheet YM3 and YM10 UF membranes manufactured by Millipore Corp, and PT membranes by GE Osmonics, USA. The YM3 and YM10 series were asymmetric cellulose membranes with 10 and 30 kDa molecular weight cut-offs (MWCO), while the PT membranes were asymmetric poly(ether sulfone) membranes with 28kDa of MWCO, determined in-house and the details can be found in Appendix I.

5.2.3 Filtration protocols

The filtration facilities have been described in Chapter 3, section 3.2.3. Two systems were set up to give both constant pressure and constant flux operating modes, as shown in Figures 5.2 and 5.3 respectively.

Figure 5.2 Flow sheet of a constant pressure stir cell filtration system

The transmembrane pressure applied for the constant pressure system was 300kPa using pressurized N₂. The flux for the constant flux system was controlled at 30l/m²h. TOC retention was based on spot samples of retentate and permeates.

5.2.4 Analysis methods

The Total organic carbon (TOC) and the UV/Visible absorbance spectra of NOM were collected. The UV/Vis spectra was collected on a Hitachi U2000

5. Impacts of operation conditions on NOM removal and membrane fouling...

Spectrophotometer using a double beam and 1 cm quartz cells with MilliQ UV water as the reference. UV absorbance at 254nm (UVA254) was used to determine the humic content or aromaticity of the NOM.

Figure 5.3 Flow sheet of a constant flux stir cell filtration system

Cation concentrations of the samples were examined by the Perkin Elmer Optima 3000 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

The relative molecular weight distribution of the NOM was determined by HPSEC as described in Chapter 3, section 3.2.4.

Field emission scanning electron microscopy (FE-SEM) was used to examine fouled membranes. A JSM-6340F (Zeiss instrument, Leo, Germany) was used to observe membrane specimens at ultrahigh resolution in this study. Samples for FE-SEM were prepared according to the standard procedure, and covered with a thin (10–20 nm) Pt layer. Cross-sections were prepared using the technique of cryo-fracturing using liquid nitrogen. The FE-SEM was operated at 3 keV accelerating voltage to determine the membrane morphology.

5.2.5 Membrane fouling parameters

(i) Filtration resistance

5. Impacts of operation conditions on NOM removal and membrane fouling...

The fouling effect was described by Darcy's law which has been presented in details in Chapter 4, section 4.2.6. The hydraulic resistances R_m , the total additional resistance R_c and the flux of permeate were used to describe the membrane fouling performance.

(ii) Concentration Polarization

The accumulation of solute due to solvent convection through the membrane is called concentration polarization (Zeman and Zydney, 1996). It reduces permeate flux, either via an increased osmotic pressure on the feed side, or the formation of a cake or gel layer on the membrane surface. A laminar boundary layer is formed with mass conservation which is described by the stagnant film model:

$$J_v = k_s \ln \frac{(c_w - c_p)}{(c_b - c_p)} \quad (5.1)$$

where

$$k_s = \frac{D_s}{\delta} \quad (5.2)$$

c_b is the feed bulk concentration, c_w membrane surface concentration, c_p permeate concentration, D_s the solute diffusivity, k_s solute mass transfer coefficient and δ boundary layer thickness.

This classical stagnant film equation expresses the filtration flux in terms of the solute mass transfer coefficient and the concentration driving force, which is schematically shown in Figure 5.4. The solute mass transfer coefficient k_s is generally assumed to be independent of the solute concentration and flux J_v , but it changes with solute diffusion coefficient and the boundary layer thickness. Thus the introduction of crossflow could reduce the boundary layer thickness, resulting in reducing concentration polarization.

5. Impacts of operation conditions on NOM removal and membrane fouling...

Figure 5.4 Schematic of the concentration profiles and the mass balance

The diffusion coefficient can be expressed as

$$D_s = \frac{kT}{f} = \frac{kT}{6\pi\eta r_s} \quad (5.3)$$

where k is the Boltzmann constant ($k=1.38 \times 10^{-23} \text{ J/K}$), f the frictional coefficient, and r_s the solute radius, T temperature (K) and η viscosity. It can be found that the diffusion coefficient decreases with an increase in the solute size due to the solute-solute interaction. The implication of this is that for a mixture, such as NOM, the concentration polarization will vary according to solute size.

(iii) Observed sieving coefficient

The retention of the membranes can also be expressed as the actual membrane sieving coefficient, S_a , defined as the ratio of the solute concentration in the permeate C_p to that in the solution (boundary layer) at the membrane surface C_w , as shown in equation (5.4).

$$S_a = \frac{C_p}{C_w} \quad (5.4)$$

The accumulation of the retained solutes at the membrane surface can also have a dramatic effect on the observed (measured) membrane sieving coefficient S_0 as shown below:

5. Impacts of operation conditions on NOM removal and membrane fouling...

$$S_o = \frac{C_p}{C_b} = \left(\frac{C_w}{C_b} \right) S_a \quad (5.5)$$

The increase in C_w/C_b is associated with concentration polarization. The solute concentration at the membrane surface, C_w , can be evaluated using the stagnant film model (equation (5.1)), yielding the follow expression for the observed sieving coefficient in terms of the actual sieving coefficient S_a :

The observed sieving coefficient tends to the actual sieving coefficient at low permeate flux ($J_v < k$ or $C_w \rightarrow C_b$). As flux increases, S_o becomes greater than S_a . At very high permeate flux or very low k , S_o approaches the value of 1, that is $c_p \leq c_b$ as long as the membrane is at least partially permeable to the solution of interest.

$$S_o = \frac{S_a}{(1 - S_a) \exp\left(-\frac{J_v}{k}\right) + S_a} \quad (5.6)$$

5.3 Results and discussion

5.3.1 Characteristics of source water and NOM

The general characteristics of samples of Singapore water obtained from the reservoirs have been described in details in Chapter 4 (section 4.3.3). These characteristics include the NOM concentration indicated as total organic concentration (TOC), aromatic fractions defined as SUVA (UV_{254}/DOC), pH and ion concentrations present in the reservoirs. There were several ions in the raw water, particularly calcium, which would influence the status of the NOM.

5.3.2 NOM retention

The characteristics of the membranes used and their NOM filtration retentions at the operation mode of constant pressure (300kPa) in a dead-end cell without stirring are shown in Table 5.1. For YM3 and YM10 membranes, the TOC retentions were 66.5% and 25.2% respectively, indicating that the membrane retention of NOM was increased with the decrease of the membrane's MWCOs as expected. The retention

5. Impacts of operation conditions on NOM removal and membrane fouling...

of the PES-PT membrane was 59.2%. Since the relative molecule weight of the NOM covered a wide range from 1kDa to 100kDa, the membrane pore size plays a major role to define the retention. The membranes with the smaller pore size such as YM3 exhibited higher NOM retention than the membrane with larger pore size.

The membrane surface properties also affected the NOM retention. The YM10 membrane and PT membrane had a similar molecular weight cut-off around 30kDa but the NOM rejection was 25.2% for the YM10 and 59.2% for the PT membrane. As mentioned in the experimental section, the YM10 membrane was made of cellulose and exhibited hydrophilic surface property, while the PT membrane was made of poly (ether sulfone) which was more hydrophobic in nature. This difference led the YM10 membrane performing at a higher flux and a lower membrane resistance than the PT membrane.

Table 5.1 Characteristics of Membranes tested

Membrane tested	Specification	Pure water flux(l/m ² h)	Membrane resistance for MilliQ water (l/m)	Retention of NOM (TOC) (%)	Retention of Humic substance (UV) (%)
YM3	10KDa MWCO, Cellulose	19	5.23E+13	60.5	74.1
YM10	30KDa MWCO, Cellulose	182	5.78E+12	25.2	43.2
YM100	100KD MWCO, Cellulose	250	6.48E+11	9.7	38.7
PES-PT	28KDa MWCO, Polyethersulfone	79	1.36E+13	59.2	73.4
PES 100KD	100KDa MWCO, Polyethersulfone	450	3.96 E+11	15.7	37.8

Based on the definition of observed sieving coefficient S_o , the filtration flux and the membrane properties would affect the membrane retention. Therefore, the membrane was not just a porous barrier to filter NOM according to the nominal pore size, the hydrophobicity/hydrophilicity also played an role in determining membrane filtration behavior. The fouling appears to have reduced the pore size of the more hydrophobic PT membrane and decrease in the membrane sieving

5. Impacts of operation conditions on NOM removal and membrane fouling...

coefficient S_o , which made the NOM retention increase. Thus the dense fouling layer formed on the PT membrane surface helped to improve the NOM retention much more than that on the YM-10 membrane.

Figure 5.5 Molecular weight distribution of NOM

The NOM retention was also affected by the operating conditions during the filtration. The retentions of the YM3, YM10 and PT membranes in the dead end cell with different stirring speeds ranging from 100rpm to 400rpm are presented in Figure 5.6. Figure 5.7 shows these results depicted on another way. It was found that the NOM retention increased obviously when the filtration was operated at a higher stirring speed (more than 200rpm) for either operating mode. For YM3 membrane, the NOM retention increased from approximately 40% to 60%, and from 30% to 50% for the YM10 membrane. It was increased from about 60% to 80% for the PT membrane. According equation (5.2), the mass transfer coefficient k_s is determined by the diffusion coefficient and the boundary layer thickness. For the membranes filtering the same NOM samples, the (average) NOM diffusion coefficient was the same but the thickness of the boundary layer was decreased when the stirring speed was increased. As a result, the mass transfer coefficient k_s was increased with enhanced stirring, which made the observed sieving coefficient S_o reduced based on equation (5.6). In other words, the membrane retention increased while the stirring speed increased. Reducing concentration polarization

5. Impacts of operation conditions on NOM removal and membrane fouling...

can lead to a higher NOM retention, and if NOM removal without chemical addition is a goal, this would be important.

Figure 5.6 TOC/ UV-Vis Retention of (a) YM3, (b) YM10, (c) PT membranes
 CP: Constant pressure (300kPa), CF: Constant flux (100LMH)

Figure 5.7 NOM retention under (a) constant pressure conditions, (b) constant flux conditions

5. Impacts of operation conditions on NOM removal and membrane fouling...

increased while the stirring speed increased. Reducing concentration polarization can lead to a higher NOM retention, and if NOM removal without chemical addition is a goal, this would be important.

5.3.3 NOM fouling

(i) Impact of membrane materials

The membrane fouling studies were performed with the Singapore NOM and three different UF membranes of YM10, YM 30 and PT at the constant pressure and constant flux modes with several stirring speeds. The inherent resistance and pure water flux of the membranes are presented in Table 5.1. The YM10 membrane possessed the highest pure water flux around 182 L/m².h and lowest membrane resistance (R_m) because of its relatively larger pore size and hydrophilic surface. The pure water flux of the YM3 membrane and the PT membrane were 19 L/m².h and 79 L/m².h, respectively. The smallest pore size resulted in the YM3 membrane exhibiting much higher R_m than the YM10 membrane, and the hydrophobic surface made the PT membrane have higher R_m than the YM10 membrane even though both of them had similar MWCOs.

Figure 5.8 shows the fouling performance of these membranes as a function of time at the constant pressure and constant flux modes of operation. The transmembrane pressure was 300kPa for the constant pressure mode, and the flux was maintained at 30 L/m².h for the constant flux mode.

It can be seen that the fouling resistance R_c of all membranes slightly increased with time, but the YM3 membrane showed a much higher apparent R_c than the YM10 membrane under either operation mode due to its relatively smaller MWCO than the YM10 membrane. MWCO was the main factor to determine the membrane performance. Comparing the filtration resistance R_c of the PT membrane with that of the YM10 membrane under the same modes, it could be found that the R_c of PT membrane was slightly higher than that of the YM10 membrane at the constant

5. Impacts of operation conditions on NOM removal and membrane fouling...

pressure mode, but the former became much higher than the latter when operated at the constant flux mode. The difference between the PT and YM10 membranes was probably caused by their different surface properties, as the PT membrane was hydrophobic while the YM10 membrane was hydrophilic. This confirms that the surface hydrophobicity is a key property to affect the membrane fouling. However, this effect became self-limiting under the constant pressure operation mode as the flux declined to a very low level. In contrast, under the constant flux mode, the feed stream continued to convect NOM to the membrane. For the PT membrane which was hydrophobic in nature, the foulant tended to deposit or be absorbed on the membrane, leading to a higher extent of fouling than hydrophilic membranes with similar MWCOs. As a result, the PT membrane experienced a higher filtration resistance than the YM10 membrane at the constant flux mode of operation, whereas at constant pressure they were similar.

Figure 5.8 Fouling performances during NOM filtration for different membranes: (a) constant pressure, (b) constant flux

However, it is evident that the calculated resistance for constant pressure (CP) are about an order of magnitude higher than for constant flux (CF). This was probably because the initial fluxes for CP were much higher than for CF causing rapid interactions of NOM and the membrane. Another factor that deserves mention is the possible impact of osmotic pressure. Recently the potential effect of NOM osmotic pressure has been acknowledged. For the most retentive membranes (YM3), some of the apparent resistance could be due to the loss of driving force. A separate study

5. Impacts of operation conditions on NOM removal and membrane fouling...

to measure osmotic effect of NOM components is warranted but was outside the scope of this thesis.

(ii) Impact of operation conditions

To evaluate the effect of shear on the membrane fouling, the NOM filtration was carried out with different stirring speeds of 0, 100, 200, 300, and 400rpm at the constant pressure and constant flux modes. Figures 5.9-5.11 showed the fouling performance of the YM3, YM10 and PT membranes with the Singapore NOM solution, respectively.

**Figure 5.9 Fouling performance during NOM filtration for YM3 membrane
- constant pressure**

It can be seen that the filtration resistance for each membrane was much higher if the system was run without stirring, compared with stirring. The differences in the filtration resistance between non-stirring and stirring increased with an increase in the stirring speed. The R_c was reduced around 15% when the YM3 membrane was operated at 100 rpm instead of the dead end operation without stirring at the beginning of the filtration. The reduction reached about 20-25% if the stirring speed was increased to 400rpm as shown in Figure 5.9.

5. Impacts of operation conditions on NOM removal and membrane fouling...

However, the filtration fouling performance reached a similar level at the end of the filtration course. The hydrophilic YM3 membrane is unlikely to have suffered major fouling and the osmotic pressure effect may well apply. In support of this it can be seen that the stirring effect occurred at the start of the experiments at different stirring speeds. This would be typical of a concentration polarization effect, causing different osmotic pressure at the membrane surface.

For the YM10 membrane, according to Figure 5.10, the filtration resistances R_c was also reduced when the stirring speed was increased, but some different trends were observed. There was no much difference between the stirring and non-stirring conditions at the beginning of the filtration process, but the filtration resistance for non-stirring increased to much higher than those operated at stirring conditions. This slaver divergence of resistance than observed for the YM3 membrane suggests the effect was fouling rather than osmotic.

Figure 5.10 Fouling performances during NOM filtration for YM10 membrane- constant pressure

For the PT membrane shown in Figure 5.11, the filtration resistance was also reduced when the stirring was applied. The extent of reduction in R_c was increased with an increase in the stirring speed. For instance, the R_c reduction reached 10-20% at the stirring speed of 100-200rpm, compared to the case without stirring. It

5. Impacts of operation conditions on NOM removal and membrane fouling...

reached 80% when the stirring speed increased to 300-400 rpm and the fouling resistances increased slightly with the time lapsed.

Figure 5.11 Fouling performances during NOM filtration for PES-PT membrane- constant pressure

The above results can be explained by taking concentration polarization into consideration. From equations (5.1) and (5.2), the correlation between R_c and the concentration polarization could be derived as follows:

$$R_c = \frac{\Delta p}{\eta k_s \ln \frac{(C_w - C_p)}{(C_b - C_p)}} - R_m \quad (5.7)$$

The filtration resistance R_c is lower if the mass transfer coefficient k_s is larger. Stirring imposes the shear stress to the solution which helps reduce the build-up of a dense cake layer, and results in a reduction of the thickness of the boundary layer which causes the mass transfer coefficient to increase. According to equation (5.7), the filtration resistance should be increased when mass transfer coefficient k_s decreases while other conditions are maintained at a similar level.

However, the fouling difference between stirring and non stirring conditions was affected not only by the difference in concentration polarization, but also by membrane themselves. That was why the three kinds of the membranes performed rather differently. It is recognized that hydrophobic membranes would get more serious fouling than hydrophilic membrane during the NOM filtration process, as

5. Impacts of operation conditions on NOM removal and membrane fouling...

the hydrophobic fraction of the NOM are major foulants which can be easily attached onto the membrane surface. The membrane morphology also affects the membrane filtration performance; the fouling will be reduced while the membrane surface becomes smooth.

The stirring reduces the concentration polarization (C_w is reduced) and prevents the foulants from attaching on to the membrane surface. With a higher stirring speed, this effect becomes more significant.

The fouling performances of the membranes running in the constant flux mode are shown in Figures 5.12-5.14.

Figure 5.12 Fouling performances during NOM filtration for YM3 membrane- constant flux

A similar trend can be found as for the constant pressure mode. The filtration resistances were reduced when providing stirring instead of the non-stirring conditions, and the reduction increased as the stirring speed increased. It can be summarized that the influence of stirring speed had a more significant effect on the hydrophobic membrane than the hydrophilic membranes, either under constant pressure or under constant flux mode. These results can be explained by the same reasoning discussed in section 5.3.3 (i).

5. Impacts of operation conditions on NOM removal and membrane fouling...

(iii) Impact of operating modes

To compare the NOM fouling performance between the operations at constant pressure 300kPa and at constant flux 30L/m².h (operated around 300kPa), the filtration resistance R_c of the three UF membranes are presented in Figures 5.15-5.17. In general, the R_c of the membranes at the constant pressure mode was much higher than that at the constant flux mode at the dead end condition. For the YM3 and YM10 membranes, the R_c under the constant pressure mode was about 10 times that at the constant flux mode. However for the PT membrane, the difference was much less (only about 2 times) than the YM membranes.

Figure 5.13 Fouling performances during NOM filtration for YM10 membrane- constant flux

The initial flux was relatively high (around 100L/m².h) during the constant pressure filtration and ended at a very low flux (less than 10L/m².h). The significant flux drop was accompanied by a higher resistance increase and the filtration came to a semi stable status. On the other hand, the transmembrane pressure (around 300kPa) did not change too much during the constant flux filtration, which led to a slowly increased resistance while it reached the semi stable status.

Another interesting result can be observed in the Figure 5.17. The filtration resistance of the PT membrane at constant pressure became much lower (even less

5. Impacts of operation conditions on NOM removal and membrane fouling...

than at the constant flux mode) when it was operated at 400 rpm stirring. This effect was not seen for the YM3 and YM10 membranes. The hydrophobicity of the PT membrane may be attributed for such a result.

Figure 5.14 Fouling performances during NOM filtration for PT membrane- constant flux

Figure 5.15 Comparison of fouling resistance between constant pressure vs. constant flux mode for YM3 membrane

The NOM fouling is the combined result of interaction between the foulants and the membrane surface, and the impact of operating conditions. The hydrophobicity of the PT membrane tends to push the feed water away from the membrane surface,

5. Impacts of operation conditions on NOM removal and membrane fouling...

thus increasing the filtration resistance. On the other hand, stirring at 400rpm generated the force to push the feed water to the membrane surface, thus offsetting the force generated by hydrophobicity of the membrane. Consequently, the filtration resistance of the PT membrane at constant pressure with 400rpm stirring is much lower than that without stirring.

Figure 5.16 Comparison of fouling resistance between constant pressure vs. constant flux mode for YM10 membrane

Figure 5.17 Comparison of fouling resistance between constant pressure vs. constant flux mode for PT membrane

5. Impacts of operation conditions on NOM removal and membrane fouling...

5.3.4 Membrane morphologies

To assist in understanding the above experimental results, morphology studies of the fouled membranes were carried out. Figure 5.18 shows the dense cake layer formed on the YM3 membrane when operated at the constant pressure mode with different stirring speeds. The fouled membrane after the dead end filtration had a thick and rough layer on the membrane surface. With stirring speed increase, the layer became dense and smooth. These results were in accordance with the observation on the filtration resistance which altered with different stirring conditions. The FE-SEM images of the fouled YM10 membranes which operated at the constant flux mode are shown in Figure 5.19. A similar trend was found. The stirring made a thick and rough membrane surface become dense and smooth. The morphology studies have provided another approach to identify the impacts of the operating conditions on the membrane fouling during the NOM filtration.

Figure 5.18 NOM fouling –YM3 membrane at constant pressure (a) dead end; (b)100rpm; (c) 200rpm; (d) 300rpm

5. Impacts of operation conditions on NOM removal and membrane fouling...

5.4 Conclusions

To avoid high energy demand in the use of NF membranes, three UF membranes with MWCO around 10-30kDa were used for NOM removal from Singapore surface water. The membrane properties, filtration conditions and filtration modes were found to be important factors affecting the filtration performance.

Figure 5.19 NOM fouling –YM10 membrane at constant flux (a) dead end; (b)200rpm;

The hydrophobic membrane presented a higher NOM retention than the hydrophilic membranes. However, the heavy fouling that occurred led the hydrophobic membrane not to be the best choice for the NOM removal. In terms of stirring and non-stirring conditions, the NOM retention was improved with stirring in all the UF membrane filtrations, and it reached a relatively high retention (60 to 70%) when the stirring speed was increased. Moreover, stirring facilitated hydrodynamic movement and this helped to prevent the foulant from depositing onto the membrane surface and into the membrane pores. Consequently, the filtration resistance was reduced, especially for the hydrophobic membrane. The membrane morphology studies also confirmed that the fouling layer was thick and rough with non-stirring and it became dense and smooth when stirring was introduced.

Comparing the constant flux mode with the constant pressure mode, it was found the small pore size membranes running at constant flux exhibited much less fouling resistance than when operated at the constant pressure mode due to the high flux drop during the filtration process. It suggests that optimizing the filtration modes

5. Impacts of operation conditions on NOM removal and membrane fouling...

and filtration conditions is an effective way to reduce NOM fouling and improve retention, thus improve the filtration performance. The optimal operating condition recommended for the NOM removal is constant modest flux with 300-400rpm stirring speed. Whilst it is difficult to translate that to large-scale plant, the benefit of crossflow to improve NOM removal is clear cut. However it becomes a matter of economic comparison of UF membrane in crossflow versus dead-end operation of an UF-hybrid with chemical coagulation.

6.

HYBRID PROCESS WITH MIEX AND LOW-PRESSURE MEMBRANES: EFFECTS OF MIEX PRETREATMENT ON NOM REMOVAL AND MEMBRANE FOULING

6.1 Introduction

As a potential precursor of disinfection byproducts, Natural Organic Matter (NOM) has been recognized as an important compound to be removed from drinking water. Several techniques have been developed to remove NOM and membrane technology has become increasingly popular for this application. However, low-pressure membranes have an intrinsic limitation for retention of NOM due to their larger pore size relative to NOM. Thus the commercial low-pressure membranes only typically achieve around 20-50% removal of NOM. In addition the low-pressure membrane processes typically experience adverse fouling effects due to NOM present in surface waters (Hong, 1996; Costa and de Pinho, 2002; Her *et al.*, 2004).

Improvement of the filtration performance of low-pressure membranes could significantly cut the costs of the raw water treatment process, extend membrane life and reduce the energy demand. Efforts made to reach this goal include, development of hybrid membrane processes, raw water pretreatment, optimization of hydrodynamic parameters, membrane surface modification and membrane

6. Hybrid process with MIEX and low-pressure membranes...

system cleaning (Hong and Elimelech, 1997; Zhang *et al.*, 2003; Taniguchi and Belfort, 2004).

In recent years, the Magnetic Ion Exchange (MIEX) process for the NOM removal has been developed by Orica Watercare, South Australian Water Corporation and the CSIRO (Slunjski *et al.*, 1999). The rationale for MIEX is that since about 70-80% of the NOM species are weak organic acids that are ionized at pH range 6-8, up to 80% of the NOM can be removed by MIEX. Thus, the combination of MIEX with low-pressure membranes is of interest (Morran *et al.*, 2001), as it can achieve good NOM removal and potentially reduce membrane fouling. For example, it has been reported (Galjaard *et al.*, 2004) that using MIEX to remove organics that are less than the molecular weight cut off (MWCO) of a UF membrane, which is hydrophilic and positively charged, can lead to very low fouling. It should be noted that in that study, the feed was chemically softened so the detrimental effects of calcium were obviated. The operating mode used was dead end unstirred and constant flux, ranging from 50 to 100 L/m²h.

The purpose of this work was to investigate the effectiveness of the hybrid membrane system, combining the MIEX pretreatment and low-pressure membrane processes, for NOM removal and fouling control. In particular our target feed water was tropical, from a Singapore source. It is known from Chapter 3 that Singapore raw water contains relatively higher concentrations of calcium ions and NOM, and the NOM has a wide molecular weight distribution. The aim of this study is to measure the efficiency of the hybrid MIEX-membrane system, identify the most suitable membranes and optimize the operating strategies favoring NOM removal and minimizing fouling. To achieve this target, several low-pressure membranes were used for membrane filtration after MIEX pretreatment. The retention of the NOM and the permeability changes under the modes of constant pressure and constant flux were evaluated. Based on this study, an effective process is proposed to remove NOM with low fouling tendency.

6. Hybrid process with MIEX and low-pressure membranes...

6.2 Materials and methods

6.2.1 Singapore NOM and other chemicals

Raw water was collected from Singapore's Kranji reservoir. The isolation and preparation procedure are described in section 4.2.2 of Chapter 4. The treated water was collected in a sealed bottle and stored at 4 °C for the MIEX study.

Other chemicals used such as NaCl, CaCl₂, NaOH and HCl, were purchased from Sigma-Aldrich at analytical grade.

6.2.2 MIEX Resins

MIEX resins, provided by Orica Watercare, are acrylic, strong base anion exchangers. The magnetic property is achieved by incorporating permanently magnetized iron particles within the resin. Before use in this study all resins were regenerated several times with sodium chloride at 200g/L and residual salts were removed by rinsing with Milli-Q water prior to use.

6.2.3 Membranes and filtration protocol

The membranes used for the NOM filtration studies were flat-sheet MF or UF membranes, manufactured by Millipore Corp. HVLP was a hydrophilic PVDF microfiltration (MF) membrane with 0.45µm pores. GVVP and GVHP were also PVDF MF membranes with 0.22µm pores, but GVVP exhibited hydrophilic properties while GVHP was hydrophobic in nature. The YM100 and PBHK were Ultrafiltration (UF) membranes with reported MWCOs of about 100kDa. The YM100 was a regenerated cellulose membrane, (hydrophilic), and the PBHK was a poly(ether sulfone) membrane (relatively hydrophilic). The measured properties of these membranes are listed in Table 6.1. In particular it is evident that retention of NOM was less than 16% for all the membranes.

6. Hybrid process with MIEX and low-pressure membranes...

Table 6.1 Characteristics of Membranes tested

Membrane tested		Specification	Pure water flux(l/m ² h)	Membrane resistance for MilliQ water (l/m)	Retention of NOM (TOC) (%)	Retention of Humic substance (UV) (%)
UF	PBHK	100KD MWCO, Polyethersulfone	450	3.96 E+11	15.7	37.8
	YM100	100KD MWCO, Cellulose	250	6.48E+11	9.7	38.7
MF	GVHP	0.22Hydrophobic PVDF	3024	5.76E+10	9.8	25.3
	GVVP	0.22 Hydrophilic PVDF	3869	4.68E+10	13.9	34.3
	HVLP	0.45 Hydrophilic PVDF	7738	2.34E+10	9.8	15.6

The filtration processes has been described in Chapter 3, section 3.2.3. Two systems were set up, one for constant pressure and one for constant flux operation, as shown in Chapter 5, Figures 5.2 and 5.3. The transmembrane pressure applied for the constant pressure system was 50kPa using pressurized N₂. The flux for the constant flux system was controlled at 60, 100 and 150 l/m²h. TOC retention was based on spot samples of the retentate and permeate. All the filtration experiments were running for 2-3 times to confirm the data recording.

6.2.4 Analytical methods

The Total organic carbon (TOC), UV/Visible absorbance spectra and the relative molecular weight distribution of NOM were detected to evaluate the NOM removal performance. The details of the measurements can be found in section 4.2.5 of Chapter 4.

6.2.5 Membrane fouling parameters

The fouling effect was described by Darcy's law, which has been described in details in section 4.2.6 of Chapter 4. For constant pressure operation, the

6. Hybrid process with MIEX and low-pressure membranes...

transmembrane pressure (TMP) is fixed and flux declines with time. For constant flux operation, the flux is fixed and the TMP increases with time. Changes in either flux or TMP allow the calculation of R_c during a test.

The membrane fouling was also characterized by measuring the MilliQ water flux versus TMP before and after the experiments, and after membrane cleaning.

6.3 Results and discussion

6.3.1 Characterization of Singapore NOM

The general characteristics of samples of Singapore water obtained from the reservoirs have been described in details in Chapter 4 (section 4.3.3). These characteristics include the NOM concentration indicated as total organic concentration (TOC), aromatic fractions defined as SUVA (UV_{254}/DOC), pH and ion concentrations present in the reservoirs. There were several ions in the raw water, particularly calcium, which would influence the status of the NOM.

The molecular weight and molecular weight distributions of the NOM in Singapore reservoirs can be found in Figure 6.1. The molecular weights of NOM range from

Figure 6.1 Molecular weight distribution of NOM after MIEX treatment

6. Hybrid process with MIEX and low-pressure membranes...

1 to 100kDa and the main fraction is around 1- 40kDa, representing about 50% of the raw natural organics.

6.3.2 NOM removal by MIEX & membrane filtration

(i) MIEX jar testing

The MIEX jar tests were carried out by mixing MIEX resins into 1L Singapore raw water at different MIEX concentrations, following the protocol recommended by Orica. The mixture of MIEX resins and raw water was stirred at 150rpm for about 30 minutes and then settled for about 30 minutes before removing the supernatant. The concentrations of NOM indicated as TOC change with time during the jar testing are shown in Figure 6.2. It can be seen that raw water with an initial TOC concentration of about 6.7mg/l could be dropped to 1.4mg/l after the MIEX treatment, i.e., approximately 78.5% of NOM was removed.

Figure 6.2 MIEX Jar tests

The TOC removal efficiency at different MIEX concentrations was also compared. It was found from Figure 6.4 that higher loadings of MIEX resulted in faster initial NOM removal. However the TOC in the solution had an increasing trend after the settling of MIEX residues. This phenomenon was more evident at lower MIEX

6. Hybrid process with MIEX and low-pressure membranes...

loading than at higher MIEX loading. For example, the TOC of the solution increased from 2.3mg/l to 4.1mg/l after 30min settling during 2g/L of MIEX treatment, while the TOC of the solution increased from 1.2mg/l to 1.4mg/l after 30min settling during 10g/L of MIEX treatment. The reversal in TOC concentration may have been caused by the relatively high ion concentrations in the Singapore raw water, which could break the balance between the MIEX resins and NOM and release the organic compounds into the solution. This means that contact time and settling need to be carefully controlled for this type of feed.

The molecular weight fractions of the feed water and MIEX treated water are shown in Figure 6.1. Note that this figure shows the relative amounts of species within a given sample. From this figure, the effect of MIEX treatment on the NOM molecular fraction can be seen, and thus provides important information for the subsequent membrane treatment. It was found that the fractions of NOM larger than 40kDa and smaller than 1kDa were effectively removed by the MIEX treatment; and the main portions remaining in the treated solution were in the molecular range of 1k-40kDa.

(ii) Membrane filtration performance without MIEX

Several low-pressure membranes were used during the NOM fouling study. The measured retentions of these membranes are shown in Table 6.1 and it can be seen that the retentions of NOM were very low, even for UF membranes. Without MIEX treatment, the highest retention of these membranes was obtained using the YM100 membrane and it only reached 16% removal efficiency. However, the UV retentions were much higher (up to 38%) indicating that the aromatic groups have relatively larger molecular weight.

The pure water fluxes and the membrane resistances are also listed in Table 6.1. The HVLP membrane had a much higher pure water flux, at 7738L/m² h, than the other MF membranes, the pure water fluxes of GVVP and GVHP membrane were 3869L/m² h and 3024L/m² h, respectively. The UF membranes exhibited much

6. Hybrid process with MIEX and low-pressure membranes...

lower pure water fluxes than the MF membranes, and were only around a few hundreds of L/m².h.

Figures 6.3 to 6.7 show the fouling behavior of these membranes without MIEX pretreatment running under different operating conditions; constant pressure of 50kPa at dead end mode and at 200rpm stirring speed, constant flux at 60, 100 and 150 L/m².h.

Figure 6.3 Fouling performance during NOM filtration- constant pressure (50kPa),no MIEX

Figure 6.4 Fouling performance during NOM filtration- constant pressure (50kPa, 200rpm),no MIEX

6. Hybrid process with MIEX and low-pressure membranes...

Figures 6.3 and 6.4 showed filtration resistance development at a constant pressure of 50kPa in dead-end mode and with stirring at 200rpm. The MF membranes (HVLV, GVVP, and GVHP) showed very little increase in resistance, whereas the two UF membranes (PBHK and YM100) showed a steady rise in resistance. It is interesting to note that stirring (Figure 6.4) produced an apparent increase in resistance particularly in the UF membranes. It is more usual for stirring to decrease resistance. There are a number of possible reasons for these observations. Firstly, if the feed contains fine colloids ($< 1\mu\text{m}$) they could selectively deposit the smallest due to shear-induced separation; this could cause a more rapid fouling due to higher resistance solids. Secondly, NOM has a broad range of MWts and can exert some osmotic pressure. If stirring increases retention of some species it could increase surface concentration and raise osmotic pressure to reduce the overall driving force. Fortunately the current trend in water treatment is to operate MF and UF membranes without imposed fluid shear in the boundary layer.

Figure 6.5 Fouling performance during NOM filtration- constant flux (60/m².h), no MIEX

The data for constant flux, without MIEX, are shown in Figures 6.5 to 6.7. At all fluxes the hydrophobic GVHP showed a more significant resistance than the hydrophilic GVVP. Since the major property difference was membrane

6. Hybrid process with MIEX and low-pressure membranes...

hydrophobicity this result points to the potential importance of this type of interaction with the raw NOM.

The UF membranes showed an initially low resistance that built up over time. This was presumably a slow accumulation of foulant on the membranes, or the aforementioned slow rise in osmotic pressure diminishing the driving force.

Figure 6.6 Fouling performance during NOM filtration- constant flux (100l/m².h),no MIEX

Figure 6. 7 Fouling performance during NOM filtration- constant flux (150l/m².h),no MIEX

6. Hybrid process with MIEX and low-pressure membranes...

Our interim conclusions are that for Singapore NOM alone, without MIEX, there is better fouling control with hydrophilic MF membranes at controlled modest flux and probably in the absence of stirring. Of course, the low retentions of NOM do not make this a viable separation process until an NOM removal agent, such as MIEX, is added.

6.3.3 Impact of MIEX on the membrane filtration performance

Comparison of membrane fouling between the hybrid MIEX system and the no-MIEX membrane system was made using the two filtration protocols: constant pressure and constant flux. During MIEX pretreatment, the raw water was treated by 10g/l of MIEX for 30 minutes followed by MIEX settling for 30 minutes, and then the top solution removed from the MIEX residue was used for membrane filtration studies.

There was about 1-2ppm NOM left in the solution after MIEX pretreatment. Thus the hybrid systems could remove about 85% NOM from the raw water. Compared to the hybrid system, the retention of the sole membrane filtration treatment was much lower at about 10-15 %.

(i) Impact of MIEX on the membrane filtration performance under constant pressure mode

Figures 6.8, 6.9 and 6.10 show the fouling behavior of GVVP, GVHP and PBHK membranes respectively when the MIEX pretreated feed was filtered under conditions of dead end and 200 rpm stirring (i.e. without/with shear force) along with the results of un-pretreated raw water. The constant pressure mode was used. There was negligible difference between the hybrid systems with MIEX pretreatment and the sole membrane filtration process for the dead end filtration protocol. The membrane fouling resistance of either protocol was slightly increased with permeate throughput increase. However, different fouling performances were found with 200 rpm stirring. For the filtration of MF membranes (GVVP and

6. Hybrid process with MIEX and low-pressure membranes...

Figure 6.8 Effect of MIEX pretreatment on the fouling of GVVP membrane –Constant Pressure 50kPa

Figure 6.9 Effect of MIEX pretreatment on the fouling of GVHP membrane –Constant Pressure 50kPa

GVHP), the fouling resistance after MIEX pretreatment with stirring was much higher than that of untreated raw water. This detrimental effect of stirring may be due to the shear induced ‘classification’ effect mentioned earlier, that preferentially allows the smallest particles to deposit. MIEX resin can produce fines and the stirring appears to have exacerbated fouling of the MF membranes by fines, possibly providing internal fouling. It should be noted that the resistance for the hydrophobic GVHP (Figure 6.9) was much higher than for the hydrophilic GVVP, signifying hydrophobic interactions with the NOM coated fines.

6. Hybrid process with MIEX and low-pressure membranes...

Figure 6.10 Effect of MIEX pretreatment on the fouling of PBHK membrane –Constant Pressure 50kPa

For the PBHK UF membrane MIEX provided benefit, particularly evident under stirred conditions. This difference from the MF membranes would be due to the different mechanisms of permeability loss. UF would be more prone to pore closure by smaller solutes or alternatively exhibit loss of driving force due to osmotic pressure effects. As note earlier stirring could increase retention of NOM species and increase osmotic effects. MIEX would sequester these species leading to higher permeability. Therefore, it can be concluded that the MIEX pretreatment is favorable to reduce membrane fouling when it is followed by UF membrane filtration with some surface shear (stirring) under constant pressure mode of operation.

(ii) Impact of MIEX on the membrane filtration performance under constant flux mode

For constant flux operation, the effect of the MIEX pretreatment on the membrane fouling performance varied with imposed flux values. It should be noted that the final fouling resistances observed were generally much larger than would be applied in the field. The usual practice with constant flux operation is to have periodic backwash cycles to avoid severe fouling. The level of suction applied in these tests might have influenced the final fouling resistance.

6. Hybrid process with MIEX and low-pressure membranes...

To evaluate the effects of MIEX pretreatment for four kinds of membranes under dead-end operation at different fluxes of 60, 100 and 150 L/m² h, the filtration fouling resistances of membranes with and without MIEX pretreatment are shown in Figures 6.11-6.13. As shown in Figure 6.11, for a flux of 60 L/m² h, MIEX provided a benefit (less resistance) for the large pore HVLP and the hydrophobic GVHP (0.2 µm) but there was negligible benefit (or detriment) for the hydrophilic GVVP (0.2 µm). However the GVVP had a significantly lower resistance than its hydrophobic version (GVHP). Overall the GVVP at this moderate flux performed very well giving a high TPC removal in the hybrid process. The UF membrane (PBHK) also did not show any ‘fouling’ difference with or without MIEX.

Figure 6.11 Effect of MIEX pretreatment on the fouling of membranes
 –Constant flux 60 L/m² h: (a) HVLP, (b) GVVP, (c) GVHP, (d) PBHK

At higher fluxes of 100 L/m² h (Figure 6.14) and 150 L/m² h (Figure 6.13) the benefits of MIEX tended to be lost or became detriments in terms of fouling control. One exception to these trends was the hydrophilic GVVP MF membrane at 100 L/m² h (again showing no difference with or without MIEX). The other

6. Hybrid process with MIEX and low-pressure membranes...

Figure 6.12 Effect of MIEX pretreatment on the fouling of membranes –Constant flux, 100l/m².h: (a) HVLP, (b) GVVP, (c) GVHP, (d) PBHK

Figure 6.13 Effect of MIEX pretreatment on the fouling of membranes –Constant flux, 150l/m².h: (a) HVLP, (b) GVVP, (c) GVHP, (d) PBHK

6. Hybrid process with MIEX and low-pressure membranes...

exception was the PBHK (UF) membrane which started to show a MIEX benefit as the experiments progressed, presumably due to reduced amounts of smaller solutes restricting pores. However the general trends seen at higher fluxes were presumably due to the presence of MIEX fines that tend to foul membranes as flux is raised. Thus to ensure the benefits of MIEX it is necessary to use moderate flux or perform some post treatment fines removal.

The effect of stirring (200rpm) was also examined at constant flux. It should be recalled that at constant pressure stirring was either detrimental (MF) or relatively in effective (UF). Figures 6.14, 6.15 and 6.16 show results for the (0.2 μ m) hydrophilic and (0.2 μ m) hydrophobic MF membranes and the UF (PBHK) membrane at a flux of 100L/m²h. It is apparent that with MIEX pretreatment this level of stirring is beneficial, suggesting that the back transport of MIEX fines has been sufficiently augmented to reduce fouling; the benefit is more clearly seen for the more fouling prone hydrophobic GVHP and UF membranes. The relative merits of stirred cross flow or some form of post treatment to scavenge fines need to be further examined.

**Figure 6.14 Effect of MIEX pretreatment on the fouling of HVLP membrane
–Constant flux 100L/m².h**

6. Hybrid process with MIEX and low-pressure membranes...

Figure 6.15 Effect of MIEX pretreatment on the fouling of GVHP membrane
–Constant flux 100L/m².h

Figure 6.16 Effect of MIEX pretreatment on the fouling of PBHK membrane
–Constant flux 100L/m².h

6.3.4 Fouling morphology studies

To assist understanding the results obtained from the filtration studies, the morphology of the fouling layers obtained during NOM filtration was examined by FE-SEM.

6. Hybrid process with MIEX and low-pressure membranes...

Figure 6.17 shows the cake layer formed on the HVLP membranes during constant pressure dead end filtration, without MIEX pretreatment, and Figure 6.18 shows the layer formed during filtration at the same conditions, but for MIEX pretreated feed. It can be observed that the cake layer in Figure 6.17 was much denser than that shown in Figure 6.18. This illustrates qualitatively why the MIEX pretreatment reduced the NOM fouling when operated under this condition.

Figure 6.17 NOM fouling without MIEX pretreatment – HVLP CP

Figure 6.18 NOM fouling after MIEX pretreatment – HVLP CP

Another example is shown in Figures 6.19 and 6.20. The morphologies of the cake layers which formed onto the GVVP membranes under the constant pressure with stirring were studied. From these figures, it can be seen that the cake layers after MIEX pretreatment were denser and thicker than the layers without MIEX pretreatment, and this coincides with the greater fouling resistance.

6. Hybrid process with MIEX and low-pressure membranes...

Figure 6.19 NOM fouling without MIEX pretreatment – GVVP CP

Figure 6.20 NOM fouling after MIEX pretreatment – GVVP CP

6.4 Conclusions

For the low pressure membranes tested, MIEX raised the removals of NOM from about 15% to about 85% for Singapore-sourced tropical waters. Under some conditions the MIEX pretreatment also reduced the fouling tendency of the membranes.

At a constant pressure (50kPa) and dead-end (unstirred) MIEX did not have detrimental fouling effects on the MF membranes tested. However under stirring (200rpm) the MIEX produced a higher fouling resistance, which is attributed to shear-induced selection of fines that preferentially deposit during the high initial flux period with these high permeability membranes. For the UF membrane the

6. Hybrid process with MIEX and low-pressure membranes...

MIEX proved beneficial for fouling control, particularly when stirred. For UF it is probable that MIEX has removed species that either close UF pores or contribute to an osmotic pressure effect.

At constant flux and deadend, the MIEX was beneficial for fouling control at a modest flux of $60\text{ L/m}^2\text{h}$ for the fouling prone MF membranes. The hydrophilic $0.2\text{ }\mu\text{m}$ MF had low fouling tendency with or without MIEX. Similarly the UF membrane showed neither benefit nor detriment in terms of fouling due to MIEX. At higher fluxes ($100, 150\text{ L/m}^2\text{h}$) the MIEX pretreatment tended to increase fouling tendency, except for the hydrophilic $0.2\text{ }\mu\text{m}$ MF membrane. In general to see the benefit of MIEX it is necessary to use moderate flux and/or post treat the supernatant to scavenge fines.

However at higher flux ($100\text{ L/m}^2\text{h}$) the MIEX pretreatment can be made beneficial by use of stirring that appears to provide sufficient back transport to overcome serious deposition. The relative merits of stirred cross flow or some form of post treatment need to be evaluated.

Overall, the MIEX-membrane hybrid can achieve upto 85 % removal of Singapore-sourced NOM. Judicious choice of membranes and operating conditions show that a benefit (or no detriment) in terms of fouling can be an added spin off of MIEX usage. Constant moderate flux under deadend conditions with MIEX pretreatment is favoured by the MF and UF membranes tested. Although higher flux operation loses this benefit it can be restored by the application of stirring (cross flow).

7.

DEVELOPMENT OF A NOVEL ELECTROPHORESIS-UV GRAFTING TECHNIQUE TO MODIFY PES UF MEMBRANES USED FOR NOM REMOVAL *

7.1 Introduction

Technical advances in the lower pressure membrane processes such as ultrafiltration (UF), coupled with more stringent water quality standards, has lead to wide use of UF membranes in water treatment processes. However, UF membranes have a limitation in their retention of natural organic matters (NOM) from surface water because of their generally larger molecular weight cut-off (MWCO) compared to the relative molecular weight of NOM. In addition, serious fouling by NOM has been reported (Maartens *et al.*, 1999; Cho *et al.*, 2000; Taniguchi *et al.*, 2003). This is due to the complex mixture of organic compounds found in NOM with a broad spectrum of functional groups, sub-structures and molecular weight distributions. NOM contains several classes such as hydrophilic neutrals, hydrophobic acids, transphilic acids, and hydrophilic charged components. The hydrophobic acids have been found to play an important role to induce NOM fouling during UF membrane filtration process (Seidel and Elimelech, 2002; Makdissy *et al.*, 2004).

Preventing or reducing of NOM fouling could significantly cut the cost of raw water treatment, extend membrane life and reduce energy demand. Much effort has been made regarding this aspect, and modification of the membrane surface is recognized as an attractive approach to reducing membrane fouling caused by NOM. A large amount of research regarding the interactions between NOM and membrane surfaces has indicated that hydrophilic membranes, with hydroxyl,

7. Development of a novel electrophoresis-UV grafting technique ...

amine or carboxylic acid groups are less prone to fouling than hydrophobic membranes (Li *et al.*, 1996; Pieracci *et al.*, 1999; Marchese *et al.*, 2003; Zhang *et al.*, 2003). Unfortunately, most commercially available UF membranes are made from relatively hydrophobic materials with low surface energies such as polypropylene, polysulfone and polyethersulfone as they offer better chemical, thermal and biological stability. These membranes are often close to neutral charge on the surface. It should be possible to combine the lower fouling potential of hydrophilic negative charged surfaces with the stability of hydrophobic membranes by surface modification treatment.

Surface modification was discussed in section 2.2.8 (iii) of Chapter 2 and is briefly summarized here. The modification is frequently implemented by the adsorption of surfactants and soluble polymers onto the membrane surface to change its wettability and surface charge and thereby to enhance the membrane performance. Several surface modification techniques for commercially available UF membranes have been developed, which included: 1) physically coating a thin layer of suitable material onto the surface of the membrane (Hester *et al.*, 1999), 2) initiating polymerization by radiation and grafting reactions onto a support membrane to impart hydrophilic properties (Hosch and Staude, 1996), 3) deposition of a layer from a glow discharge plasma onto the membrane (Kull *et al.*, 2005), 4) chemical attachment of selected polymers and/or monomers etc (Belfer *et al.*, 1998). The choice of a specific surface modification technique depends on the chemical structure of the given support membrane and the desired characteristics of the surface modification required.

Among these modification methods, UV assisted grafting has distinct advantages in simplicity, cost and breadth of application. This simple method increases membrane surface wettability and shifts the membrane pore size distribution to smaller sizes. The results of previous studies suggested that the selective UV excitation of a photo-initiator adsorbed onto the polymer surface causes a heterogeneous hydrogen abstraction and subsequent initiation by polymer mechanisms for polymer surface modification. In this way, the surface modification is achieved by applying a very

7. Development of a novel electrophoresis-UV grafting technique ...

simple, inexpensive graft polymerization technique to graft hydrophilic monomers onto hydrophobic membranes such as poly(ether sulfone) (PES), polysulfone, etc (Kilduff *et al.*, 2000; Taniguchi *et al.*, 2003; Liu *et al.*, 2004). It should be possible to take the UV-grafting technique a step further by depositing polyelectrolyte monomers onto the membrane surface during the grafting process to induce negative charge to the membrane surface. The potential of such an approach was to reduce NOM fouling via not only hydrophobicity/hydrophilicity interaction but also by control of electrostatic interactions at the membrane surface (Carroll *et al.*, 2002).

In this chapter, a novel surface modification technique is described which combines controlled deposition of charged moieties by electrophoresis, with UV grafting of monomers on the membrane surface to treat PES UF membranes with five different monomers. The monomers included three strong polyelectrolytes which exhibited as polar molecules [Methacrylic acid (MA), Acrylic acid (AA) 2- Acryamido glycolic acid (AAG)] and two weak polyelectrolytes which had neutral property [(2-Hydroxyethyl)-methacrylate (HEMA) N-Vinylformamide (NVF)]. The advantage of introducing the electrophoresis step into the UV grafting process is to generate a homogeneous deposition of the monomers used on the membrane surface before the grafting reaction, which may lead to the formation of a uniform layer on the membrane surface after the polymerization. However, there are no reports of the use of the electrophoresis for membrane surface modification of microporous membranes, and the electrical properties of polyelectrolytes have rarely been utilized in the modification process. Our study involved the following steps: 1) to modify commercial and in-house made PES membranes with different polyelectrolytes in a hybrid reactor containing an electrophoresis system and a UV chamber; 2) to compare the properties of modified/unmodified membranes in terms of MWCO, pure water flux, wettability and surface charge; 3) to evaluate the filtration performances of modified/unmodified membranes in terms of NOM retention and hydrodynamic resistance and fouling by a tropical NOM solution; 4) to examine the surface morphology of modified/unmodified membrane by FE-SEM in order to understand the modification mechanisms. This study was an attempt to

7. Development of a novel electrophoresis-UV grafting technique ...

develop an effective method to modify UF membranes to meet the NOM removal requirement and to control the fouling caused by NOM in the filtration process.

7.2 Materials and methods

7.2.1 Materials

Figure 7.1 Chemical structure of different monomers used for electrophoresis-UV grafted polymerization of PES membranes. (2-Hydroxyethyl)-methacrylate (HEMA), N-Vinylformamide (NVF), Methacrylic acid (MA), Acrylic acid (AA) and 2-Acrylamidoglycolic acid (AAG)

Three types of PES membranes were used in this study. Two were the commercial membranes (PW and PT), which were obtained from GE Osmonics, USA. The PW/PT membranes were asymmetric poly(ether sulfone) membranes with 58 and 27kDa molecular weight cut-offs (MWCO), as determined in-house using a Gel Permeation Chromatography and dextrans of various molecular weights. The other was an in-house prepared PES UF membrane with MWCO of 60kDa, which was denoted as the ZS membrane. For the in-house made PES UF membranes, PES (Ultrason E6020, CAS#: 25667-42-9) supplied by BASF was used as the membrane material. N-methyl-2-pyrrolidone (NMP, >99.5%, CAS#: 872-50-4) supplied by Merck was used as a solvent. Water as a non-solvent additive was produced by a Milli-Q ultrapure water system. A dope solution of PES/NMP/H₂O/LiNO₃/Tween 80 (18/74.41/7.08/0.50/0.01wt%) was cast onto a glass plate, and immediately

7. Development of a novel electrophoresis-UV grafting technique ...

immersed into a water bath without an evaporation step at room temperature. The gap between the knife and the glass plate was 200 μ m. The resulting membranes were kept in the water bath for several days to remove residual solvents.

Methacrylic acid (MA), (2-Hydroxyethyl)-methacrylat (HEMA), Acrylic acid (AA) and N-vinylformamide (NVF) were purchased from Merck Pte. Ltd. The 2-Acrylamidoglycolic acid (AAG) was purchased from Standard General Superintendence & Test Laboratory Pte. Ltd. All the chemicals were used as received. The chemical structures of the monomers are shown in Figure 7.1. The HEMA and NVF were chosen because of their hydrophilic character and neutral property; the AAG, AA and MA were chosen as they are weak acids which exhibit a strong polyelectrolyte character in aqueous solutions. High quality Milli-Q water (Millipore USA) was used for the preparations of NOM solutions and for membrane fouling performance experiments.

Table 7.1 Characteristics of tropical NOM in MilliQ water

	TOC (mgL ⁻¹)	SUVA (cm ⁻¹ mg ⁻¹ L)	pH	Na (mgL ⁻¹)	Ca (mgL ⁻¹)	Mg (mgL ⁻¹)	K (mgL ⁻¹)	Al (mgL ⁻¹)	Fe (mgL ⁻¹)	Mn (mgL ⁻¹)	Ni (mgL ⁻¹)
Natural water 1	8.04	0.025	7.8	14.9	27.6	2.49	5.44	0.68	0.49	0.011	0.001
Natural water 2	10.20	0.043	7.7	18.4	22.1	3.10	7.30	0.61	0.44	0.026	0.001
Natural water 3	8.06	0.034	7.1	14.3	27.1	5.9	2.69	0.001	0.011	0.01	0.001

The raw water and NOM isolates were collected from Kranji reservoir. The characteristics of the water samples in this study were listed in Table 7.1. The NOM was isolated from raw water and reconstructed at the same DOC level with the raw water for large amount filtration studies. The reconstituted NOM simulated the raw water well, and the details of the NOM isolation process and characterization can be found in Chapter 4. During the NOM isolation process, the raw water was pumped through a high-volume filter cartridge with 1 μ m pore size to eliminate particulate matter such as bacteria and inorganic particles. The pretreated water was sent

7. Development of a novel electrophoresis-UV grafting technique ...

directly to a RO system. The concentrates were collected in a sealed bottle and stored in a cooler for filtration and fouling studies.

7.2.2 Methods

(i) Membrane modification

The PES membranes were modified by a combined electrophoresis-UV grafting system which is schematically presented in Figure 7.2. There were UV lamps of 254nm wavelength assembled onward the reactor and an electrophoresis quartz chamber was placed in the centre of the UV reactor. The fresh membrane was mounted on the anode side of the electrophoresis and immersed in monomer aqueous solutions with different concentrations (ranging from 0.5wt% to 5wt%). The system was sealed and degassed by sparging with pure nitrogen gas for approximately 15 minutes. The electrophoresis process was carried out for a total 2 hours under a maximum voltage of 100V and a maximum current of 30mA. For the last 30 minutes, the UV irradiation was carried out at room temperature under a nitrogen atmosphere. The depth of the solution in the reactor was 6mm. After

Figure 7.2 Schematic diagram of the combined electrophoresis-UV grafting

7. Development of a novel electrophoresis-UV grafting technique ...

modification, the membrane was washed with MilliQ water by shaking for 2h, and then dipped in an ethanol solution to remove homopolymers and unreacted monomers from the membrane surface. All the membranes were dried by a solvent exchange process, which submerged the membranes into 25%, 50%, 75% and 100% EtOH/water solutions in a sequence and exposed under room temperature. Some pieces were dried at 45°C overnight and weighed for calculating the degree of grafting (Dg). Dg was defined as:

$$D_g (\%) = \frac{W_g - W_o}{W_o} \times 100 \quad (7.1)$$

Where W_g was the dried membrane weight after grafting with different monomers, W_o was the original membrane weight before modification.

(ii) Membrane property analyses

The filtration performance of each membrane was tested by a stir-cell filtration system as described in Chapter 3, section 3.2.3. The MWCOs of the membranes were tested by the HPSEC method, which was described in details in Appendix I (section A. 1).

The membrane surface properties include contact angle and zeta potential, the procedures of these tests were shown in Appendix I (section A. 2 and A. 3) and the surface morphology was measured by field emission scanning electron microscopy (FE-SEM) which was also described in Appendix I (section A. 4).

The Total organic carbon (TOC) content of feed and permeate solutions was analyzed as described in Chapter 3, section 3.2.4.

(iii) NOM fouling parameters

The fouling effect was described by Darcy's law which has been described in details in Chapter 4 (section 4.2.6). The hydraulic resistance R_m , the total additional

7. Development of a novel electrophoresis-UV grafting technique ...

resistance R_c and the flux of the permeate were used to describe the membrane fouling performances.

7.3 Results and discussion

7.3.1 Grafting yield and surface properties of modified membranes

The degree of grafting achieved during the modification process of PW PES membrane as a function of the monomer concentration is shown in Figure 7.3. In general, grafting yield increased with the increase of monomer concentration except at lower concentrations (0.5~1wt%). To evaluate the influence of electrophoresis during the modification process, PES membranes were treated under two conditions of UV irradiation only and UV - electrophoresis treatment. It was found that the Dg of PES membrane treated by AAG and MA increased significantly under the UV irradiation after the electrophoresis deposition. However, the Dg of the PES membrane modified by HEMA showed not much difference between the UV grafting and the UV-electrophoresis treatments. These results suggested that the electrophoresis treatment facilitate charged monomers deposit onto the membrane surface and increase the modification efficiency of UV irradiation. As strong

Figure 7.3 The effects of monomer concentration and electrophoresis on the degree of grafting during the modification of PES membranes

7. Development of a novel electrophoresis-UV grafting technique ...

polyelectrolytes, the AAG and MA grafting were influenced by the electrophoresis deposition much more than the HEMA, which exhibited as a very weak polyelectrolyte.

Table 7.2 shows the contact angle and zeta potential of unmodified (original) and modified PW-PES membranes for different types of monomers under different treating conditions with and without electrophoresis. The electrophoresis device was controlled to operate at a maximum voltage of 100V and a maximum current of 30mA. During the electrophoresis deposition process, the strong polyelectrolytes including AAG, MA and AA presented a maximum current of 29mA while the operating voltages were quite low. On the other hand, the weak polyelectrolytes of HEMA and NVF exhibited very low currents of less than 10mA while the maximum operation voltage to 100V was reached during the electrophoresis deposition. These results indicated that different monomers possessed different

Table 7.2 Properties of modified PW-PES membrane

Monomer	Monomer concentration (wt %)	Electrophoresis conditions		Contact angle (°)*		Zeta potential (mV)**	
		Voltage (V) max=100	Current (mA) max=30	UV	UV - electrophoresis	UV	UV - electrophoresis
unmodified				70.5		-1.2	
MA	0.5	55	29	45.4	36.8	-7.2	-12.8
	1.0	47	29	37.0	31.6	-8.3	-17.9
	2.0	36	29	40	33.2	-6.9	-15.4
AAG	0.5	35	29	50.4	39.8	-6.1	-17.3
	1.0	23	29	43.1	31.8	-6.8	-22.2
	2.0	13	29	43.8	37.3	-7.9	-24.9
AA	0.5	54	29	47.4	32.1	-8.5	-13.0
	1.0	43	29	38.7	27.8	-8.8	-17.2
	2.0	33	29	36.1	16.9	-9.2	-18.5
HEMA	0.5	100	3	45.8	48.4	-4.4	-8.6
	1.0	100	5	37.8	34.7	-4.6	-10.5
	2.0	100	8	30.4	26.4	-6.2	-11.4
NVF	0.5	100	1	48.4	43.0	-2.0	-1.3
	1.0	100	2	41.6	45.3	-1.8	-2.2
	2.0	100	2	41.3	46.8	-1.5	-2.1

* Average value ** at pH=7

The unmodified PW-PES membrane was considered to be relatively hydrophobic as its contact angle was 70 degrees. However the modified membranes exhibited

7. Development of a novel electrophoresis-UV grafting technique ...

hydrophilic surface characteristics after either UV grafting or the electrophoresis-UV grafting treatment with either monomer. The contact angles of modified surfaces were in the range 30 ~ 50 degree. However, the effect of the monomer concentration on the contact angle of the modified membrane was not significant and was negligible. Comparing the contact angles of modified membranes—using strong electrolytes of AAG, MA and AA by UV grafting with those by the UV-electrophoresis deposition, it was found that with electrophoresis assistance, the UV grafting made the membranes present lower contact angles than without the assistance from electrophoresis. However, there was not much difference for the contact angle between UV modified and UV-electrophoresis modified membranes using HEMA and NVF monomers.

Among the strong electrolytes of AAG, MA and AA, the influence of each monomer on the modification was also different. The different modification effects were probably caused by different monomer sizes and chemical groups, degree of polymerization and surface coverage. These effects could be controlled by choosing different monomers, the concentration of the monomers, the strength of the electric field produced by the electrophoresis and the strength of UV irradiation.

Table 7.3 Contact angle (degree) of membranes modified by UV grafting and electrophoresis-UV grafting

ZS Membrane		1	2	3	4	5	6	7	8	9	10	SD*
NVF	UV-grafting	43	24.3	65	67	55.3	45.3	54.8	37.2	33.5	44.9	13.6
	Electrophoresis-UV grafting	47.1	60.4	35.3	51.5	41.6	66.1	60.7	34.8	38.1	29.4	12.7
HEMA	UV-grafting	24.4	33.3	49.0	46.7	39.4	22.5	50.1	51.4	27.3	34.3	11.05
	Electrophoresis-UV grafting	30.9	31.7	31.6	34.9	37.4	37.9	34.9	36.6	34.8	36.2	2.51
AAG	UV grafting	27.5	33.2	42.8	43.8	50.4	56.3	35.2	36.8	60	44.9	10.33
	Electrophoresis-UV grafting	28.8	30.8	27.5	32.4	34.4	32.1	32.1	34.8	33.9	31.7	2.33

*SD: standard deviation

7. Development of a novel electrophoresis-UV grafting technique ...

Similar results were found in surface charge analysis by zeta potential measurement at pH 7. It can be seen that all the modified membranes by the strong polyelectrolytes such as AAG, MA, AA exhibited much greater negative charges than the unmodified membrane, especially for those under UV-electrophoresis treatment. But for the NVF treated membranes, there was not much difference for the surface charge as the NVF monomer was a nearly neutral molecule. This suggests that the membranes modified with strong polyelectrolytes by UV-electrophoresis system would lead to better modification results.

The function of electrophoresis in the UV grafting process was further studied by examine the homogeneity of the grafting layer of the membranes modified by either UV grafting or the electrophoresis -UV grafting in terms of membrane contact angle. The PES-ZS membranes modified by the NVF, HEMA and AAG were cut into 10 pieces of the same size for the test. As shown in Table 7.3, the contact angle of the NVF modified membranes varied from 24.3 to 67 degree with a standard deviation of 13.6 for the UV grafting, and it ranged from 29.4 to 66.1 degree with a standard deviation of 12.7 after the UV-electrophoresis treatment. This result indicates that electrophoresis did not work for the neutral monomer.

In contrast, the contact angle of the HEMA modified membranes varied from 22.5 to 51.4 degree with a standard deviation of 11.05 and from 27.5 to 60 degree with a standard deviation of 10.33 for the AAG modified membranes after the UV grafting. However, the electrophoresis-UV grafting modification made the contact angles of different pieces of the HEMA and AAG modified membranes much closer with a standard deviation of 2.51 and 2.33 respectively. This indicates that the electrophoresis induced monomer deposition before the UV grafting made the surface properties of the modified membranes much more homogeneous for the polyelectrolyte such as the HEMA, AAG.

7.3.2 MWCO and pure water flux (PWF)

The MWCOs of unmodified/modified membranes are shown in Figure 7.4. It was found that different PES membranes possess different MWCOs with respect to the

7. Development of a novel electrophoresis-UV grafting technique ...

same monomer modification and the same original PES membranes vary their MWCOs after the modification using different monomers. Specifically, the MWCOs of the PW and PT membranes were reduced from 56.3 to 26.4kDa and from 24.4 to 21.5kDa, respectively, after the surface modification by the MA monomer; while the MWCO of the PT membrane was increased from 24.4 to 79 kDa after the HEMA treatment and reduced from 24.4 to 9.9kDa after the surface treatment by the AAG monomer. Furthermore, It was noticed that the HEMA modification increased the MWCOs of both the PW and PT membranes. In contrast, the influence of grafting on the MWCO of in-house made ZS membranes was less than for the PW and PT membranes. The MWCO was slightly reduced from 60kDa to 50kDa by each monomer. This may be due to the fact that although all the membranes were made from the same PES materials, the different preparation processes may impart the membranes with different surface chemistry apart from different pore structures, which may respond differently to the same surface modification. The following discussions are mainly focused on PW/PT membranes.

Figure 7.4 Molecular weight cut-off (MWCO) of membranes modified with different monomers at 1wt%

The pure water flux (PWF) of PES membranes were changed after surface treatment. The PWF of unmodified and modified PW/PT membranes are shown in Figure 7.5. From the figure, it can be seen that the PWF of the PW membranes

7. Development of a novel electrophoresis-UV grafting technique ...

decreased about 37% and 90% after the MA and AAG treatment respectively, and increased slightly after the HEMA modification. The same trend was found for the PT membranes except that the PWF decreased about 42% after the AAG treatment.

Figure 7.5 Pure water flux of the PW/PT membranes modified with different monomers at 1wt%

There are two possible mechanisms responsible for the above results, i.e. the monomers grafted onto the membrane surface can produce competitive effects of pore plugging from graft polymerization and pore size enlargement from monomer dissolution. A permeable thin-layer could be formed on the surface of the PES membrane with the monomer deposition and grafting. This top layer can extend towards the interior of the porous active layer and thus plug the pores of the PES membranes. On the other hand, the monomer may dissolve the PES membranes to make the pore size larger. This opposite effect had been reported in the previous literature (Taniguchi and Belfort 2004).

The MA and AAG are weak acids, which are strong polyelectrolytes in aqueous solutions. These monomers deposited onto the membrane surface more homogeneously under the electrophoresis compared with the HEMA, which is a more neutral compound. With the UV-grafting treatment, they formed a thin layer on the membrane surface and reduced the porosity and pore size of the PES UF membranes. The AAG was more sensitive than the MA because it moved faster

7. Development of a novel electrophoresis-UV grafting technique ...

under the same voltage during the electrophoresis deposition, thus leading to a more compacted grafted-layer on the membrane surface, resulting in a lower permeability. However, the HEMA is a weak polyelectrolyte, and deposited less rapidly and tightly onto the membrane surface. In this case, the polymer dissolution was the dominating mechanism, leading to increased MWCO and PWF of the treated membranes. These results were further confirmed by the membrane morphology studies with FE-SEM analysis.

Figure 7.6 shows the pure water flux of the PW membranes modified with the MA at different concentrations. The PWF of unmodified PW membrane was $80 \text{ l/m}^2 \cdot \text{h}$, and it reduced to $50 \text{ l/m}^2 \cdot \text{h}$ after modification by a 2wt% MA solution and reduced to $16 \text{ l/m}^2 \cdot \text{h}$ after being modified at a concentration of 5wt%. At the higher MA concentration solution, the amount of the monomer deposited onto the membrane surface by the electrophoresis was higher and the grafted-matter surface coverage was greater. This resulted in a significant flux decrease and demonstrates that the monomer concentration is one of the main factors to control the modified membrane surface properties.

Figure 7.6 Pure water flux of the PW membranes modified with MA at different concentrations

7. Development of a novel electrophoresis-UV grafting technique ...

7.3.3 NOM filtration performance

The DOC concentration of the NOM solutions was around 10ppm as shown in Table 7.1. The NOM retentions of modified and unmodified membranes measured as DOC removal are depicted in Figure 7.7. For the in-house made ZS membranes, the NOM retention varied from 60% to 66%, 54% and 51% after the MA, AAG and HEMA modifications, respectively; so only MA gave an improved retention. For the PW membranes, the NOM retention increased from 53.2% to 60.9% or 62.4% after the MA or AAG treatments, but decreased to 39.7% with the HEMA modification. Regarding the PT membranes, the NOM retention increased from 77.7% to 83.2% after the MA treatment and to 84.4% after the AAG treatment, but reduced to 36.5% after the HEMA modification. In summary, the NOM removal of the modified membranes was moderately increased after the MA and AAG modifications, but was significantly decreased after the HEMA modification.

Figure 7.7 Retentions of NOM solutions through the modified membranes

It is known that NOM retention depends on the NOM molecular sizes as well as charge interaction. The molecular weight distribution of Singapore NOM shows that about 80% NOM was larger than 10kDa (referring to section 4.3.3 in Chapter 4) [9]. From Figure 7.3 it can be seen that the PT membrane modified by the AAG had the smallest MWCO value of 9.9kDa and this corresponds to the fact that the

7. Development of a novel electrophoresis-UV grafting technique ...

NOM retention of this modified membrane was the highest. In the surface modification process, the MA or AAG monomer deposited onto the membrane surface under the function of the electrophoresis and reacted with the membrane. The grafted layer acts as a permeable interface between the NOM solution and the membrane pores. The grafted species appear to have reduced the pore size providing better exclusion of the larger NOM species. The increase surface charge may also have increased retention of charged NOM components. In contrast the negative effect on the NOM retention caused by HEMA modification is consistent with the objective. Increased MWCO and PWF of the modified membrane, due to the surface pore enlargement by the HEMA monomers during the UV-assisted modification.

7.3.4 NOM fouling study

A fouling comparison between the unmodified PES and modified PES membranes was made under the constant pressure protocol. It is recognized that differences in initial flux may play a role in fouling but in these tests the initial fluxes were within $50 \pm 10 \text{ l/m}^2 \cdot \text{h}$ (PT) and $80 \pm 10 \text{ l/m}^2 \cdot \text{h}$ (PW). The filtration resistances R_c versus time for the Singapore NOM filtered through the MA and HEMA modified PT membranes as well as the original PT membranes are shown in Figure 7.8.

Figure 7.8 Fouling performances during NOM filtration using the PT membranes

7. Development of a novel electrophoresis-UV grafting technique ...

It can be seen that the filtration resistance of modified PT membranes was more than 10 times lower than the unmodified membranes. A similar trend was found for the MA and HEMA modified PW membranes, as shown in Figure 7.9. It can also be noticed from Table 7.4 and Figure 7.4 that although the MA modified PW membrane had a similar pure water flux and MWCO as an unmodified PT membrane, the former possessed much lower NOM fouling tendency than the latter. The differences in final fouling resistance were 0.5 and 8.5×10^{13} respectively.

Figure 7.9 Fouling performances during NOM filtration using the PW membranes

In general, the main mechanisms responsible for NOM fouling in UF membranes are the interactions between the NOM species and the membrane surfaces. As mentioned before, the Singapore NOM contains hydrophobic acids which are negatively charged in their natural ionic environment (referring to Chapter 4) [9]. These characteristics of Singapore NOM required a tight UF membrane which is hydrophilic and negatively charged to reach the required removal.

As indicated in section 7.3.2, the modified membranes were hydrophilic and negatively charged, while the unmodified membranes were relatively hydrophobic and effectively neutral in nature. This explains why the modified membranes had a much lower fouling tendency with NOM.

7. Development of a novel electrophoresis-UV grafting technique ...

7.3.5 Membrane morphologies

Figure 7.10 presents the surface morphology of an untreated PW membrane sample. A smooth surface without any particles attached can be seen in this figure. The surface morphologies of the AAG modified PW membrane is shown in Figure 7.11. A thin layer appeared on the modified membrane surface as the result of the interaction between the monomer and the PES membrane. The morphology of the HEMA modified PW membrane is shown in Figure 7.12. It can be seen that the membrane surface was not only coated with a thin layer but also appears to be damaged by the HEMA dissolution. Some large pores appeared on the membrane surface, which explains the increased MWCO and PWF of the membranes and the lowered NOM retention.

Figure 7.10 Surface of the PW membrane with MWCO of 56kDa (magnification: 40k)

The surface morphology of a fouled unmodified PW membrane is shown in Figure 7.13. A dense cake layer was observed on the top of the membrane surface compared with an unfouled unmodified membrane as shown in Figure 7.9. This cake layer evidently played a major role in the NOM fouling. The surfaces of the MA modified PW membranes were partially covered with the NOM species after

7. Development of a novel electrophoresis-UV grafting technique ...

filtration as shown in Figures 7.14. This demonstrates that the MA modified membranes had much less fouling tendency compared with the unmodified counterpart.

Figure 7.11 Surface of the AAG modified PW membrane (magnification: 40k)

Figure 7.12 Surface of the HEMA modified PW membrane (magnification: 40k)

7. Development of a novel electrophoresis-UV grafting technique ...

Figure 7.13 Surface of the fouled unmodified PW membrane after NOM filtration (magnification: 3k)

Figure 7.14 Surface of the fouled PES-PW membrane modified by 2% MA after NOM filtration (magnification: 3k)

7. Development of a novel electrophoresis-UV grafting technique ...

7.4 Conclusions

This is the first reported attempt to control the surface properties of UF membranes by the combined application of electrophoresis and UV grafting. Three types of PES UF membranes were modified by weak acids of Methacrylic acid (MA) and 2-Acrylamidoglycolic acid (AAG), as well as a neutral compound of (2-Hydroxyethyl)-methacrylat (HEMA). The MWCO, PWF, wettability, surface charge and surface morphology of modified and unmodified membranes were measured. The filtration and fouling performance with Singapore NOM was also studied.

Experimental results revealed that after the electrophoresis-UV grafting treatment, most membrane surfaces were grafted with selected monomers which exhibited more hydrophilic and negative charged properties. The MA and AAG grafting reduced the MWCO of the PES membranes, decreased the permeability to less than half of the original flux, but they also increased the NOM retention because of the formation of a thin layer onto the membrane surface which reduced the porosity and pore size of treated membranes. In contrast, the HEMA grafted membrane increased the MWCO and the permeability as a result of the monomer dissolution which enlarged the membrane pore sizes. FE-SEM observation confirmed these two mechanisms.

The modified PES membranes also presented lower fouling tendency than the unmodified membranes due to their hydrophilic and negative charged feature after modification. Comparing the MA modified PW membrane with unmodified PT membrane, the former exhibited the same MWCO and flux as the latter, but the modified PW membranes possessed much lower NOM fouling tendency than the PT membranes.

8.

CONCLUSIONS AND RECOMMENDATIONS

8.1 Overall conclusions

This thesis focuses on the natural organic matters (NOM) removal potential from a tropical water source by UF membranes. The source of NOM and solution conditions such as ionic composition, ionic strength are confirmed to be important in determining the conformation of NOM species and subsequent filtration performance. Two types of tropical NOM from a Singapore reservoir were isolated using a RO system and characterized by a series of analyses. This assessment was believed to be the first report of a tropical NOM. In addition, the filtration performance of UF membranes under different operation conditions and modes was evaluated and compared. The optimal operating strategies to improve NOM removal performance have been identified based on the comparison. In addition, a hybrid membrane system, which integrates MIEX pretreatment and UF membrane filtration, and a novel surface modification technique, which combines controlled deposition of charged moieties by electrophoresis with UV grafting of monomers on the membrane surface, have been proved to be effective ways to improve NOM removal by UF membranes. It is the first reported attempt to control the surface properties of UF membranes by the combined application of electrophoresis and UV grafting.

8.1.1 Influence of ionic strength on NOM size and removal by ultrafiltration

8. Conclusions and recommendations

The effects of Na^+ and Ca^{2+} interaction with the NOM on the apparent molecular size distribution of the species and the NOM removal efficiency were investigated over a wide range of ionic strengths. Three types of NOM, namely, Singapore NOM (a reservoir-based sample), IHSS NOM (a river-based standard) and Biohumic NOM (a soil-based sample) were used to prepare model solutions at different ion concentrations. The effective particle sizes and molecular size distributions of the NOM before and after the addition of ions were analyzed. The filtration performance was evaluated in a dead-end filtration cell fitted with a UF membrane.

- The effective size of the NOM was found to be significantly reduced by increasing the concentration of Na^+ in the NOM solution due to coil-to-globule conversion and polyelectrolyte interaction, which changed the conformation of the NOM from linear to spherical.
- Increasing the concentration of Ca^{2+} showed competing effects on the size of the NOM. At relatively low concentrations of Ca^{2+} , the size of the NOM was reduced, presumably by the same mechanism observed in the case of Na^+ . As the concentration of Ca^{2+} in the solution was further increased, there was an increase in NOM size, presumably due to aggregation or chelation between humic acid in NOM and Ca^{2+} becoming the dominant factor.
- Ion interactions with NOM had a significant impact on the NOM removal in the ultrafiltration process. With the addition of Na^+ to the solution, the Singapore NOM retention decreased from 52% to 29%. In contrast, the retention of Biohumic NOM increased from 45% to around 70% with an increase in Ca^{2+} concentration.

8.1.2 Characteristics of tropical NOM and its influence on UF membrane fouling

Two types of tropical NOM, the S-NOM I and S-NOM II, were isolated and characterized. Membrane filtration of the natural water sample, reconstituted

8. Conclusions and recommendations

tropical NOMs and IHSS NOM through the PBGC and YM10 UF membranes were conducted in order to understand the impact of the characteristics of tropical NOM on UF membrane fouling.

- Compared with the IHSS NOM, the tropical NOM contained similar fractions of humic substances but had more fractions of smaller molecular weights (less than 0.1 kDa) and its molecular weight distribution was more dispersed than that of the IHSS NOM.
- The tropical NOM species in the range of 0.1 to 10kDa were found to have a strong tendency to coagulate or chelate with the multivalent ions in the source water.
- The S-NOM II, which was derived from a mixture of the dissolved NOM and the calcium coagulum generated in the isolation, contained a greater fraction of aromatic elements than the S-NOM I derived from the dissolved NOM, as the higher concentration of multivalent ions in the tropical water tended to react with the aromatic elements to form calcium coagulum.
- The aromatic elements in the S-NOM II were retained the most by either the PBGC or the YM10 UF membranes, which demonstrated that the chelating of the aromatic elements with multivalent ions could result in a high retention.
- The presence of calcium coagulum in the feed water tended to generate more severe reversible fouling due to cake formation on the membrane surface. At the same time, it reduced the irreversible fouling caused by pore closure and pore plugging, as the formation of calcium coagulum reduced the amounts of smaller molecules available in the NOM.
- The cake layer was able to prevent the small molecules of NOM from penetrating into the membrane pores and being adsorbed. Cake layer

8. Conclusions and recommendations

formation on the membrane surface was the main fouling mechanism of tropical NOMs during the UF filtration.

8.1.3 Impact of operating conditions on NOM removal and membrane fouling in ultrafiltration processes

To improve UF membrane performance for NOM removal from surface water, a systematic study was carried out by using different UF membranes with MWCO around 10-30 kDa. A full spectrum of operating strategies, which included the constant pressure and constant flux modes with non-stirring and stirring at different speeds in dead-end cells, was examined in terms of NOM removal efficiency and their fouling performance.

- The UF membrane exhibited a higher NOM retention under the stirring for either the constant pressure or constant flux modes. The removal efficiency further increased when the stirring speed was increased.
- The membrane fouling also decreased with the provision of stirring, especially for the hydrophobic membrane. This result was due to the fact that the stirring facilitated back-transport, which could help to prevent the foulant from depositing onto the membrane surface and into the membrane pores. Membrane morphology studies provided further evidence for this.
- By comparing the constant flux mode with the constant pressure mode, it was found the small pore size membranes operated at constant flux exhibited much less fouling resistance than when operated at the constant pressure mode. The optimal operating conditions recommended for the NOM removal was the constant flux mode with 300-400rpm stirring speed.

8.1.4 Hybrid process with MIEX and low-pressure membranes: effects of MIEX pretreatment on NOM removal and membrane fouling

8. Conclusions and recommendations

The hybrid membrane process with MIEX and low pressure membranes has been evaluated for a NOM-laden water from a tropical source. Experiments were performed at the bench-scale with both MF and UF membranes, operated deadend (unstirred) and stirred, at constant pressure and constant flux.

- It was found that MIEX pretreatment allowed about 85 % removal of NOM, compared with only 10 to 15 % removal by the membranes alone.
- In terms of fouling control, the MIEX pretreatment could be beneficial or detrimental.
- Conditions where MIEX reduced (or did not increase) fouling for all membranes were deadend and constant moderate flux (in this case 60 L/m²h). Higher constant fluxes (100 L/m²h) also showed a MIEX benefit provided stirring (cross flow) was applied.

8.1.5 Development of a novel electrophoresis-UV grafting technique to modify PES UF membranes used for NOM removal

Membrane surface modification is an attractive approach to reduce membrane fouling by foulants such as natural organic matters (NOM). A novel technique which combines controlled deposition by electrophoresis of charged moieties, with UV grafting on the membrane surface has been applied to modify Poly(ether sulfone) membranes with several different monomers. The monomers included three strong polyelectrolytes [Methacrylic acid (MA), Acrylic acid (AA) and 2-Acrylamido glycolic acid (AAG)] and two weak polyelectrolytes [(2-Hydroxyethyl)-methacrylate (HEMA), *N*-Vinylformamide (NVF)]. The molecular weight cut-off, pure water flux, wettability, surface charge and surface morphology were measured for modified and unmodified membranes. The filtration and fouling performance was tested and compared using surface water from a Singapore reservoir.

8. Conclusions and recommendations

- The modified membrane surfaces exhibited more hydrophilic and negative charged features after the electrophoresis-UV grafting treatment.
- The MA and AAG grafting reduced the MWCO of the PES membranes to improve NOM retention, and decreased the permeability to less than half of the original. The reason for this was the formation of a thin layer on the membrane surface which reduced the porosity and pore size of the treated membranes.
- The HEMA grafted membrane showed increased MWCO and permeability as a result of the monomer dissolution which enlarged the membrane pore sizes. Membrane characterization by FE-SEM observation confirmed these two mechanisms.
- With electrophoresis assistance, the modified membranes exhibited more homogeneous surface properties than without electrophoresis.
- The modified PES membranes also exhibited lower fouling tendency than the unmodified membranes when filtering NOM due to their hydrophilic and negative charge character after modification.
- Although the MA modified commercial PW membrane had the same MWCO and pure water flux as the unmodified commercial PT membrane, it had a much lower NOM fouling tendency.

8.2 Recommendations and Future Work

Increasingly stringent regulations related to the treated water quality drive a worldwide interest in surface water treatment. The research on NOM and NOM removal for drinking water production becomes more complex and needs to be considered for long-term studies. More new questions have been opened as the research goes into depth. Below is a list of areas where further research is needed.

8. Conclusions and recommendations

The NOM studies, membrane properties, operating processes and economical effects are included in this list.

1. NOM has been found to vary in different water sources. The variation and complexity of the NOM causes it to be very hard to build a standard method to characterize and remove NOM from drinking water systems. On a fundamental level, some of the current researches are limited by analytical techniques. The molecular size and the structures of the NOM are still being discussed. The shape of different NOM under different environmental leads to a problem for the membrane technology application. Similar limitations apply to the structural analysis of natural organics and their aggregates. Combining several analytical methods such as FTIR, NMR, GC-MS may provide more information about the NOM structure.
2. Membrane technology has been developing rapidly with the time, however, some issues are still not clear. The formation mechanisms of the membranes are being explored, the heterogeneous nature of the membrane surfaces and the interaction between the membrane and the foulants are not well understood. The overall results and the average parameters such as zeta potential, contact angle and surface roughness can be measured; but the nature and the dynamic distribution are unknown. A better understanding of the membrane properties could lead to a wider membrane application while avoiding serious membrane fouling.
3. The operating parameters during membrane treatment for NOM removal have a strong effect on performance. However there is a lack of consensus concerning the protocols for testing membranes at the laboratory or small scale. Many studies apply a constant pressure mode whereas the industry tends to apply constant flux. There is clearly a need to define a standard protocol. Similarly some studies apply crossflow (stirring) and others apply deadend operation; again same standard protocol is required. From this thesis it would be recommended to compare both stirred and unstirred. It

8. Conclusions and recommendations

may be appropriate to apply some crossflow at the large scale to improve retention and reduce fouling, and also to limit the use of chemicals. To assist in this comparison of crossflow versus deadend, it may be necessary to develop more effective simulation models.

4. An overall consideration of the health risks, energy input, the treatment costs, and the environmental impact of membranes for water treatment is required. How much energy is reasonable to use for water treatment, how much chemical addition can be justified? Do we really need to treat all the water we use? These issues go beyond the concerns of membrane technology and include life Cycle Assessment of the options for water production and techniques such as Least Cost Planning to identify the optimal strategies. However it is likely that membrane will play a vital role in the technologies required.

Appendix I

MEMBRANE PROPERTY ANALYSES

A1.1 Molecular weight cut-off (MWCO)

Membrane pore size in UF is characterized by the molecular weight cut-off (MWCO) value, which is the molecular weight above which rejections are expected to be higher than 90%. In this thesis, Dextran was used to determine the MWCOs of the membranes in a stirred cell filtration system. A wide distribution was achieved by mixing four fractions of dextran (1500, 6000, 10000 and 40000g/mol mean molecular weight) at equal concentrations of 1g/L (i.e. total of 4g/L). After the surface of the membrane disk was prepared, the membrane was put into the stirred cell and use to filter dextran solution under 100kPa pressure at a stirring speed 400 rpm. 20 ml permeate and retentate were each taken for analysis by High Pressure Size Exclusion Chromatography (HPSEC) after 45 minutes filtration. The HPSEC had a RI detector/ UV detector and was manufactured by Waters. Ultrahydrogel column types 120, 250 and 500 from Waters were used for HPSEC analysis. Prior to HPSEC measurement, water samples were filtered by a 0.45µm microfiltration membrane to remove large particles and colloids. The examples of HPSEC results could be found in Figure A.1.

The retention R of a membrane can be calculated from the concentration of solute in the concentrate and permeate. The ratio of these two concentrations was represented by the ratio of corresponding differential areas in the HPSEC spectra as follows

$$R_i = 1 - \frac{c_{p,i}}{c_{c,i}} = 1 - \frac{A_{p,i}}{A_{c,i}} \quad (\text{A.1})$$

where the index i means that these definitions should be applied to all the fractions from the HPSEC analysis. The MWCO of a UF membrane as shown in Figure A.2

Appendix I

can be found at the resulting retention curve according to its definition of 90% retention.

Figure A. 1: The HPSEC results of the permeate and retentate of PES membrane filtration (dextran filtration)

Figure A.2 Retention curve of PES membrane: MWCO 36kDa

A.2 Contact angle

Appendix I

Contact angle is an important index of the wettability of a membrane surface. The angle between a water droplet, the membrane surface and air was measured by the sessile drop method using a goniometer (Contact Angle Analysis OCA 20) supplied by LMS Technologies PTE. LTD. The medium used was Milli-Q water.

A.3 Zeta potential

Streaming potential resulting from the motion of ions quantitatively relates to the zeta potential of the membrane channel. Using an Electro Kinetic Analyzer from Anton Paar, the zeta potential of the membrane was determined by measuring both the streaming potential and specific electrical conductivity of the electrolyte solution.

A.4 Field emission scanning electron microscopy (FE-SEM)

Field emission scanning electron microscopy (FE-SEM) was used to evaluate the difference between unmodified and modified membranes. A JSM-6340F (Zeiss instrument, Leo, Germany) was used to observe membrane specimens at ultrahigh resolution in this study. Samples for FE-SEM measurement were prepared according to the standard procedure and covered with a thin (10–20nm) Pt layer. Cross-sections were prepared using the technique of cryo-fracturing using liquid nitrogen. The FE-SEM was operated at 5keV accelerating voltage to determine the morphology of modified/unmodified membranes.

A.5 Total organic carbon (TOC)

The Total organic carbon (TOC) content of feed and permeate solutions was analyzed using a Shimadzu TOC-V_{CSH} Total Organic Carbon analyzer and the analysis was conducted within one day of sample collection to avoid any changes to the NOM.

A. 6 UV/Vis analysis

Appendix I

UV/Visible absorbance spectra of NOM were collected on a Hitachi U2000 Spectrophotometer using a double beam and 1cm quartz cells with MilliQ UV water as the reference. UV absorbance at 254nm (UVA₂₅₄) has been used to determine the humic content or aromaticity of the NOM, which is the most important material in the formation of chlorination disinfection by-products.

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