ULTRAFILTRATION AND NANOFILTRATION HYBRID SYSTEMS IN WASTEATER TREATMENT AND REUSE

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CERTIFICATE

I certify that this thesis has not already been submitted for any degree and is not being submitted as part of candidature for any other degree.

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TABLE OF CONTENTS

Title	e page		i
Cert	tificate		ii
Tab	le of con	tents	iii
Non	nenclatu	re	xiii
List	of the ta	ables	XV
List	of the fi	gures	xix
Abs	tract		xxix
CH	[APTE]	R 1	
INT	ΓRODU	UCTION	1-1
1.1	Introduc	etion	1-2
1.2	Structu	are of the Study	1-2
1.3	Object	ives	1-5
Ch	apter 2		
LI	ΓERAT	TURE REVIEW	2-1
2.1	Introduc	etion	2-2
2.2	Wastev	water Reclamation/Reuse in Australia	2-2
2.3	Wastev	water Characteristics	2-4
2.4	Typica	ll Processes Used in Wastewater Treatment	2-6
2.5	Effluer	nt Organic Matter (EfOM) in Wastewater	2-7
	2.5.1	Overview	2-7
	2.5.2	Constituents of EfOM in BTSE	2-8

	2.5.3	Characteristics of EfOM from BTSE	2-11
	2.5.4	Specific EfOM Components Present in BTSE	2-13
	2.	5.4.1 Extracellular Polymeric Substances (EPSs) and Soluble	
		Microbial Products (SMPs)	2-15
	2.	5.4.2 Protein	2-16
	2.	5.4.3 Carbohydrate	2-17
	2.	5.4.4 Fat, Oil and Grease	2-19
	2.	5.4.5 Surfactant	2-20
	2.	5.4.6 Priority Pollutant	2-22
	2.	5.4.7 Endocrine disrupting chemicals (EDCs) and pharmaceutical	
		and personal care products (PPCPs)	2-22
2.6	Advers	e and Benign Effects of EfOM	2-26
2.7	Typical	treatment processes of EfOM	2-27
	2.7.1	Introduction	2-27
	2.7.2	Removal of EfOM by Flocculation	2-29
	2.	7.2.1 General	2-29
	2.	7.2.2 Flocculation for EfOM removal	2-30
	2.7.3	Removal of EfOM by Adsorption	2-33
	2.	7.3.1 General	2-33
	2.	7.3.2 Adsoprtion for EfOM removal	2-34
	2.7.4	Removal of EfOM by Biofiltration	2-36
	2.	7.4.1 General	2-36
	2.	7.4.2 Biofiltration for EfOM removal	2-38
	2.7.5	Removal of EfOM by Ion Exchange	2-39
	2.	7.5.1 General	2-39
	2.	7.5.2 Removal of EfOM by MIEX® Process	2-42
	2.7.6	Removal of EfOM by Advanced Oxidation Process (AOP)	2-44
	2.	7.6.1 General	2-44
	2.	7.6.2 AOPs for EfOM removal	2-46
	2.7.7	Removal of EfOM by Membrane Technology	2-50
	2.	7.7.1 General	2-50
	2.	7.7.2 Membrane technology for EfOM removal	2-52
2.8	Compa	rison of Different Treatment Methods used in EfOM Removal	2-57
29	Conclu	ding Remarks	2-61

CHAPTER 3

EX	PER	IMENTAL INVESTIGATION	3-1
3.1	Introdu	ction	3-2
3.2	Experi	mental Materials	3-2
	3.2.1	Wastewater	3-2
	3.	2.1.1 Synthetic Wastewater	3-2
	3.	2.1.2 Real Wastewater	3-3
	3.2.2	Membranes	3-5
	3.2.3	Activated Carbon	3-7
	3.2.4	Photocatalytic powder	3-8
3.3	Experi	mental Methods	3-9
	3.3.1	Flocculation	3-9
	3.3.2	PAC Adsorption	3-9
	3.3.3	GAC Biofilter	3-10
	3.3.1	Photocatalytic Set-up	3-11
	3.3.5	Crossflow Filtration Set-up	3-12
3.4	Experi	mental Analyses	3-13
	3.4.1	EfOM Characterization	3-13
	3.	4.1.1 Dissolved Organic Carbon (DOC) and Specific UV	
		Absorbance (SUVA)	3-13
	3.	4.1.2 Colloidal Organic Fraction	3-14
	3.	4.1.3 Fractionation of EfOM	3-15
	3.	4.1.4 Molecular Weight (MW) Distribution	3-17
	3.	4.1.5 MW Distribution of BTSE-W/S	3-18
	3.	4.1.6 MW Distribution of Fractions in BTSE-S	3-19
	3.	4.1.7 Fluorescence Excitation-Emission Matrix (EEM)	3-20
	3.	4.1.8 Fluorescence Chromatograms of BTSE-W/S	3-20
	3.	4.1.9 Fluorescence Chromatograms of Fractions in BTSE-S	3-21
	3.	4.1.10 Diffusion Coefficient	3-22
	3.4.2	Membrane Characterization	3-23
	3.	4.2.1 Zeta potential	3-23

	3.4	4.2.2 Contact Angle	3-24
	3.	4.2.3 ATR-FTIR for Functional Groups	3-25
	3.	4.2.4 Scanning Electron Microscopy (SEM) and Atomic	
		Force Microscope (AFM)	3-26
CH	APTEF	R 4	
INF	LUEN	CE OF FLOCCULATION AND ADSORPTION	
AS]	PRETR	REATMENT TO MEMBRANE FILTRATION	4-1
4.1	Introduc	etion	4-2
4.2	DOC R	emoval and SUVA with Pretreatment	4-5
4.3	Remova	l of Colloidal Organics	4-5
4.4	Remova	d of Fractions with Pretreatment	4-6
4.5	MW Di	stribution	4-7
4.6	Fluores	cence Chromatograms	4-10
4.7	Experin	nents with Ultrafiltration (UF) Membrane	4-11
	4.7.1	DOC Removal	4-11
	4.7.2	MW Distribution	4-13
4.8	Experin	nents with NF Membrane	4-14
	4.8.1	DOC Removal	4-14
	4.8.2	MW Distribution Analysis of NF Effluent	4-15
4.9	Compar	ison of UF and NF Performances	4-16
4.10	Membra	ane Characterization with/without Pretreatment	4-18
	4.10.1	Effect of Contact Angle	4-18
	4.10.2	Zeta Potential	4-20
	4.10.3	ATR-FTIR Spectroscopy Results for Different Pretreatments	4-20
	4.10.4	SEM Analysis of Clean and Fouled Membranes	4-23
4.11	Charact	erization of Foulants on Membrane Surfaces	4-25
	4.11.1	DOC Concentration of the Foulant	4-25
	4.11.1	Foulant Interpretation	4-26
4 12	Conclud	ling Remarks	4-27

СН	APTE]	R 5	
EFI	FECT (OF SEMI FLOCCULATION AND SEMI ADSORPTION	[
AS	PRETI	REATMENT TO ULTRAFILTRATION	5-1
5.1	Introdu	ection	5-2
5.2	Remov	al of DOC from Synthetic Wastewater by Different Treatments	5-4
5.3	Effect	of Semi Flocculation	5-5
	5.3.1	Removal of DOC by Semi FeCl ₃ Flocculation	5-5
	5.3.2	Flux Decline of UF with Pretreated Wastewater	5-6
	5.3.3	Molecular Weight (MW) Distribution	5-7
	5.3.4	Effect of Semi Flocculation Followed by Semi Adsorption (SFSA)	5-11
	5	.3.4.1 Removal of DOC by SFSA	5-11
	5	3.4.2 Flux Decline of UF with Pretreated Wastewater	5-13
	5	3.4.3 Molecular Weight (MW) Distribution of Organic Matter	5-15
5.4	Conclu	ding Remarks	5-20
СН	APTE:	R 6	
RO	LE OF	DIFFERENT FRACTIONS IN WASTEWATER	
ON	MEM	BRANE FOULING	6-1
011	1,111,1		0 1
5.1	Introdu	action	6-2
5.2	Theore	tical consideration	6-3
	6.2.1	Isotherm Equilibrium	6-3
	6	2.1.1 Freundlich Model	6-3
	6	.2.1.2 Sips Model	6-4
	6	2.1.3 Talu Model	6-4
	6	.2.1.4 Adsorption Batch Kinetics	6-5
5.3		rane Filtration	6-6
	6.3.1	Performance of UF with Different Fractions of BTSE-S	6-6
	6.3.2	Fouling of Different Fractions during UF Membrane at Constant	

6-7

Transmembrane Pressure

	6.3.3	Membrane Characterization of the Fouled Membrane Surface	
		with Different Fractions	6-8
	6	.3.3.1 Foulant Concentration	6-8
	6	.3.3.2 Contact Angle	6-9
	6	.3.3.3 Zeta Potential	6-10
	6	.3.3.4 ATR-FTIR Spectroscopy Results for Different Pretreatments	3
			6-11
6.4	Effect of	of Pretreatment for Different Fractions of BTSE-S	6-12
	6.4.1	Flocculation as Pretreatment for BTSE-S	6-12
	6.4.2	Adsorption as Pretreatment for BTSE-S	6-13
	6.4.3	Adsorption Kinetics of BTSE-S	6-15
	6.4.4	Adsorption as Pretreatment for Different Fractions of BTSE-S	6-16
6.5	MW D	istribution	6-19
	6.5.1	MW Distribution of Different Fractions	6-19
	6.5.2	After Flocculation of Different Fractions of BTSE-S	6-20
	6.5.3	After Adsorption of Different Fractions of BTSE-S	6-21
	6.5.4	MW Distribution with HP	6-22
	6.5.5	MW Distribution with TP	6-22
	6.5.6	MW Distribution with HL	6-23
6.5	Conclu	ding Remarks	6-23
CH	APTE	R 7	
PR	ODUC'	TIVITY ENHANCEMENT IN A CROSS-FLOW	
UL	TRAFI	ILTRATION MEMBRANE SYSTEM THROUGH	
ΑU	TOMA	ATED DE-CLOGGING OPERATIONS	7-1
7.1	Introdu	action	7-2
7.2	Theore	tical	7-3
	7.2.1	Net Productivity	7-3
	7.2.2	Membrane Resistance	7-4
	7.2.3	Automated Operation	7-5
7.3	Experi	mental	7-6

7.4	Results	and Discussion	7-10
	7.4.1	Effect of Different Pressures	7-10
	7.4.2	Effect of Relaxation, Cross-flow and Relaxation and Cross-flow	
		Cleanings	7-12
	7.4.3	Effect of Different Cleaning Intervals	7-15
	7.4.4	Modeling of Effective Flux Loss	7-17
	7.4.5	Effect of Cleaning Time Ratio	7-21
	7.4.6	Effect of Different Pressures with Optimum Cleaning Conditions	7-23
	7.4.7	Effect of Different Cleaning Intervals	7-15
	7.4.8	Effect of Adsorption with Optimum Cleaning Conditions	7-25
7.5	Conclud	ding Remarks	7-27
CH	IAPTEF	R 8	
MA	ATHMA	ATICAL MODELING OF ULTRAFILTRATION	
AS	SOCIA	TED WITH PRETREATMENT	8-1
8.1	Introduc	ction	8-2
8.2	Theoret	ical	8-4
	8.2.1	Empirical Flux Decline (EFD) Model	8-4
	8.2.2	Series Resistance Flux Decline (SRFD) Model	8-7
	8.2.3	Modified Series Resistance Flux Decline (MSRFD) Model	8-8
	8.2.4	Model Application	8-9
8.3	Results	and Discussion	8-9
	8.3.1	EFD Model Prediction of Experimental Results with Different	
		Pressures	8-9
	8.3.2	EFD Model Prediction of UF Experimental Results with Different	
		Pretreatments	8-10
	8.3.3	Pretreatments SRFD Model Prediction of Experimental Results	8-10 8-12
	8.3.3 8.3.4		
		SRFD Model Prediction of Experimental Results	

7.3.1

Automation Set-up

7-6

		Different Pressures	8-15
8.4	Conclu	ding Remarks	8-16
CH	APTE	R 9	
PH	OTOC.	ATALYSIS HYBRID SYSTEM IN THE REMOVAL	
OF	ORGA	NIC MATTER FOR WASTEWATER REUSE	9-1
9.1	Introdu	action	9-2
	9.1.1	Photo-Fenton reaction	9-3
	9.1.2	Chloride-based flocculant	9-3
	9.1.3	pH Effect	9-4
	9.1.4	PAC addition	9-4
9.2	Comparison of Nanofiltration with		
	Floccul	ation-Microfiltration-Photocatalysis Hybrid system	9-5
	9.2.1	Flocculation-Microfiltration-Photocatalysis Hybrid System	9-5
	9	.2.1.1 DOC Removal	9-5
	9	.2.1.2 Molecular Weight Distribution	9-6
	9	.2.1.3 Nanofiltration for SOM Removal	9-8
	9.2.2	Chemical Coupling of Photocatalysis with Flocculation and	
		Adsorption in the Removal of Organic Matter	9-10
	9.2.2	2.1 Effect of the Surface Area of UV Lamp on Photocatalytic	
		Reaction	9-10
	9	2.2.2 Effect of TiO ₂ Concentration on Photocatalytic Reaction	9-11
	9.2.2	2.2 Effect of PAC Adsorption as a Pretreatment to TiO ₂	
		Photocatalysis	9-13
	9	2.2.4 Performance of Simultaneous Addition of PAC and TiO ₂ in the	
		Photocatalytic System	9-14
	9	2.2.5 Effect of FeCl ₃ Flocculation as a Pretreatment to TiO ₂	
		Photocatalysis	9-15
	9	.2.2.6 Molecular Weight Distribution	9-15
	9	.2.2.7 Synergistic Effect of FeCl ₃ Flocculation to Photocatalysis	9-17
	9.2.3	Application of Photocatalysis Hybrid System to Biologically	

		Treated Sewage Effluent (BTSE)	9-19
	9.	2.3.1 Effect of UV Light Intensity on Photodegradation	9-19
	9.	2.3.2 Effect of Fractions in Photodegradation	9-21
	9.	2.3.3 Effect of Simultaneous FeCl ₃ and TiO ₂ Addition in	
		Photocatalysis	9-22
	9.	2.3.4 Effect of FeCl ₃ Flocculation Followed by Photocatalysis	9-23
	9.	2.3.5 Effect of PAC Adsorption as a Pretreatment to TiO ₂	
		Photocatalysis	9-24
9.3	Conclud	ding Remarks	9-26
CH	APTEF	R 10	
CO	NCLUS	SIONS AND RECOMMENDATIONS	10-1
10.1	Conclus	sions	10-2
	10.1.1	Characteristics of Wastewater and Membrane	10-2
	10.1.2	Flocculation as Pretreatment	10-3
	10.1.3	Adsorption as Pretreatment	10-4
	10.1.4	Flocculation Followed by Adsorption as Pretreatment	10-5
	10.1.5	Biofiltration as Pretreatment	10-7
	10.1.6	Photocatalysis Membrane Hybrid System	10-8
	10.1.7	Automated Declogging Hybrid System	10-9
	10.1.8	Pretreatment of Different Fractions in BTSE	10-10
	10.1.9	Flux Decline Model with Pretreatment	10-11
10.2	Recom	mendations	10-11
	10.2.1	Near-Zero Fouling System I	10-12
	10.2.2	Near-Zero Fouling System II	10-13
	10.2.3	Near-Zero Fouling System III	10-14

References	R-1
Appendix A	
Normalized molecular weight distribution	A-1
Appendix B	
Simple calculations of series resistances	A-5
Appendix C	
Synergistic effect of flocculation and photocatalysis	A-6
Appendix D	
Publications made from the study	A-14

NOMENCLATURE

a'' modified series resistance flux decline (MSRFD) constant with Langmuir h'' MSRFD constant with Langmuir C bulk organic concentration (ML⁻³) = bulk concentration (ML⁻³) C_{b} equilibrium organic concentration (ML⁻³) C_{e} = interfacial membrane concentration (ML⁻³) C_{m} permeate concentration (ML⁻³) $C_{\mathfrak{p}}$ saturation organic concentration (ML⁻³) C_{s} flux decline kinetic constant (T⁻¹) d = organic diffusion coefficient (L²T⁻¹) D = equivalent hydraulic diameter (L) d_h surface diffusion coefficient of organic (L²T⁻¹) D_{c} adsorption constant, function of temperature Н = Jpermeate flux at a given time of operation (MT⁻¹) pure water permeate flux (MT⁻¹) J_0 apparent photodegradation rate constant (T⁻¹) k K Talu reaction constant flux decline potential which is dimensionless k_0 = rate constant (T⁻¹) \mathbf{k}_1 =external film mass transfer coefficient of organic (LT⁻¹) $k_{\rm f}$ $K_{\rm F}$ Freundlich constant K_F' series resistance flux decline (SRFD) constant with Freundlich constant K_F " MSRFD constant with Freundlich isotherm constant K_{s} = energy of adsorption K_s,, MSRFD constants with Sips Boltzmann constant (ML²T⁻² K⁻¹) k_{SE} channel length (L) L pure water permeability (MT⁻¹kPa⁻¹) L_{p} M weight of the adsorbent (M) i is an incrementing index over all MW present (Da) M_i =

number-average molecular weight (Da)

 M_n

 M_w = weight-average molecular weight (Da)

 M_z = z-average molecular weight (Da)

 N_i = number of molecules having a MW

1/n = Freundlich constant

1/n' = SRFD constant with Freundlich constant

1/n'' = MSRFD constants with Freundlich isotherm constant

P = polydispersivity

q = measured amount organic adsorbed (MM⁻¹)

 $q_m = sorption capacity (MM^{-1})$

 q_m '' = sorption capacity with Sips

 R_{as} = resistance due to strong adsorption (L^{-1})

 R_{aw} = resistance due to weak adsorption (L⁻¹)

 R_{cp} = resistance due to concentration polarization (L⁻¹)

 R_g = resistance due to the gel layer (L^{-1})

 r_p = radius of adsorbent particle (L)

t = illumination (operation) time (T)

T = absolute temperature (K)

U = average velocity of the feed fluid (ML^{-1})

V = volume of the solution in batch reactor (L^3)

 \overline{q} = average adsorbed phase organic concentration (MM⁻¹)

 T_P = duration of permeate production cycle (T)

 T_C = duration of cleaning cycle (T)

 $C_{coefficient}^{baseline}$ = experimental value of the flux decline

 $Flux_{net}$ = productivity of the cross-flow membrane system operating with periodic cleaning

 $C_{coefficient}^{simulated}$ = simulated flux values for different model coefficients

 μ = dynamic viscosity (kPaT⁻¹)

 η = viscosity of the organic phase (L²N⁻¹T⁻¹)

 ξ = zeta potential (mV)

 ρ_p = particle density of adsorbent (ML⁻¹)

 Ψ = concentration spreading parameter

LIST OF TABLES

- Table 2.1 Annual wastewater reuse from WWTPs in Australia, 2001 (adapted from Radcliffe, 2003)
- Table 2.2 Wastewater reuse in State capital cities expressed as a percentage of sewage effluent treated, 2001 (adapted from Radcliffe, 2003)
- Table 2.3 Physical, chemical and biological characteristics of wastewater and their sources (adapted from Tchobanoglous and Burton, 1991)
- Table 2.4 Percentage composition of EfOM in BTSE (adapted from Painter, 1973)
- Table 2.5 Physical, chemical and biological characteristics of wastewater and their sources (adapted from Tchobanoglous and Burton, 1991)
- Table 2.6 Composition of organic materials in wastewater (adapted from Balmat, 1957; Levine et al., 1985)
- Table 2.7 Global characteristics of EfOM in wastewater and BTSE (adapted from Dignac et al., 2000)
- Table 2.8 Concentrations of specific organic compounds in the influent and BTSE (adapted from Dignac et al., 2000)
- Table 2.9 Comparison of the distributions of amino acids in the influent wastewater and their efficiencies (adapted from Dignac et al., 2000)
- Table 2.10 Comparison of the distributions of monosaccharide in the influent wastewater and their efficiencies (adapted from Dignac et al., 2000)
- Table 2.11 Comparison of the distributions of fatty acids in the influent wastewater and their removal efficiencies (adapted from Dignac et al., 2000)
- Table 2.12 Composition of a soapless washing powder (adapted from Tchobanoglous and Burton, 1991)
- Table 2.13 Concentration and removal of EDC and PPCP in WWTP (adapted from Snyder et al., 2003)
- Table 2.14 Classes of emerging compounds (adapted from Barceló, 2003)
- Table 2.15 EfOM removal by flocculation
- Table 2.16 Removal efficiency (%) of EDC and PPCP with different flocculants (adapted from Snyder and Westerhoff, 2005)
- Table 2.17 Classes of organics adsorbed onto activated carbon (adapted from Montgomery, 1985)

- Table 2.18 EfOM removal from BTSE by adsorption
- Table 2.19 Removal of EDC and PPCP from BTSE by PAC adsorption (adapted from Snyder et al., 2003)
- Table 2.20 Typical biofilter design parameters used in tertiary wastewater and surface water treatment (adopted from Rachwal et al., 1996)
- Table 2.21 Lists of the DOC removal by filtration with BTSE
- Table 2.22 Removal of EDC and PPCP with full scale GAC biofilter in ppt unit (adapted from Snyder and Westerhoff, 2005)
- Table 2.23 Characteristics of resins used in the treatment of BTSE
- Table 2.24 Removal of EDC and PPCP by different concentrations of MIEX® (adapted from Snyder and Westerhoff, 2005)
- Table 2.25 Advanced oxidation processes used in water treatment
- Table 2.26 Comparison of DOC removal with different AOP in BTSE
- Table 2.27 Easily oxidized organic compounds by photocatalytic processes (adapted from Pirkanniemi and Sillanpaa, 2002)
- Table 2.28 Removal of EDC and PPCP with chlorination at pH 5.5 (adapted from Snyder and Westerhoff, 2005)
- Table 2.29 Removal of EDC and PPCP with ozone/H₂O₂ (adapted from Snyder and Westerhoff, 2005)
- Table 2.30 Size range of membrane separation process (adapted from Cho, 2005)
- Table 2.31 DOC removal by different membrane processes
- Table 2.32 Removal of EDC and PPCP by UF (adapted from Snyder and Westerhoff, 2005)
- Table 2.33 Removal of EDC and PPCP by NF (adapted from Snyder and Westerhoff, 2005)
- Table 2.34 DOC removal by membrane technology with pretreatment
- Table 2.35 Efficiency of different treatment processes in the removal of different fractions from BTSE
- Table 2.36 Unit processes and operations used for EDC and PPCP removal in WWTP (adapted from Barceló, 2003)
- Table 2.37 Unit processes and operations used for EDC and PPCP removal (adapted from Snyder et al., 2003)
- Table 3.1 Constituents and characteristics of the synthetic wastewater

- Table 3.2 Characteristics of biologically treated sewage effluent during one year (adapted from GCHERI, 2005)
- Table 3.3 Skin-layer functional groups of membranes (adapted from Thanuttamavong, 2002)
- Table 3.4 Specification of membranes obtained by the manufacturer (Nitto Denko Corp., Japan)
- Table 3.5 Values of pure water permeability with membranes used in this study
- Table 3.6 Characteristics of powdered activated carbon (PAC) used (James Cumming & Sons Pty Ltd., Australia)
- Table 3.7 Physical properties of GAC used (Calgon Carbon Corp., USA)
- Table 3.8 Characteristics of P25 Degussa photocatalytic powdered used
- Table 3.9 Comparison of SUVA values by different water sources (adapted from Cho, 1998; Her, 2002)
- Table 3.10 Organic colloidal portion (in DOC) in the BTSE
- Table 3.11 Characteristics of UF and NF membranes used
- Table 3.12 FTIR functional group on the clean membrane
- Table 4.1 DOC removal and SUVA values with different pretreatments.
- Table 4.2 Organic colloidal portion (in DOC) in the secondary effluent with and without a treatment of flocculation and adsorption
- Table 4.3 HP, TP, and HL fractions in BTSE-W (FeCl₃: 41 mg-Fe/L and PAC: 1 g/L)
- Table 4.4 Removal of HP, TP, and HL fractions in BTSE-S (FeCl₃: 28 mg-Fe/L and PAC: 1 g/L)
- Table 4.5 The contact angle of the clean and fouled UF membrane surfaces
- Table 4.6 The effect of the contact angle on different membrane surfaces
- Table 4.7 Functional groups obtained by IR spectra (on the fouled membrane surfaces)
- Table 4.8 MW values of foulants on the UF membranes (initial BTSE-S number-averaged (median value) MW (M_n^*) : 759 daltons, weight-averaged MW (M_w^{**}) : 1158 daltons and polydispersivity $(P^{***} = M_w/M_n)$: 1.53)
- Table 4.9 MW values of foulants on the NF membrane (initial number-averaged (median) MW (M_n^*) : 759 daltons, weight-averaged MW (M_w^{**}) : 1158 daltons and polydispersivity $(P^{***} = M_w/M_n)$: 1.53)
- Table 5.1 Relationship between the size in nm and MW in daltons

- Table 5.2 Weight-averaged MW values of the effluent samples after pretreatment (weight-averaged MW of initial = 29760 daltons)
- Table 5.3 Weight-averaged MW values of organic matter after pretreatment of flocculation and adsorption after post treatment of UF (all units: daltons)
- Table 6.1 FTIR functional group with different fractions
- Table 6.2 FTIR functional group with the HL fraction
- Table 6.3 Isotherm parameter values (PAC with BTSE-S at initial concentration of 6.5 mg/L)
- Table 6.4 Film mass transfer coefficient (k_f) and diffusion coefficient (D_s) of batch experiments at initial PAC concentration of 1 g/L
- Table 6.5 Isotherm parameter values for different fractions
- Table 6.6 Film mass transfer coefficient (k_f) and diffusion coefficient (D_s) of fractions at initial PAC concentration of 1 g/L
- Table 7.1 Status of solenoid valves during varied modes of operation.
- Table 7.2 Membrane cross-flow rate and transmembrane pressure for each operating mode
- Table 7.3 Flux recovered for each varied production interval
- Table 8.1 Effect of the k_0 value for EFD model ($k_1 = 0.201$ and d = 0.002)
- Table 8.2 Effect of the k_1 value for EFD model ($k_0 = 0.060$ and d = 0.002)
- Table 8.3 Effect of the d value for EFD model ($k_0 = 0.060$ and $k_1 = 0.201$)
- Table 8.4 Sensitivity of K_F ' (1/n' = 0.773)
- Table 8.5 Sensitivity of $1/n'(K_F' = 1.0E+11)$
- Table 8.6 EFD model coefficients obtained from experimental data with different pressures ($k_1 = 2.15E-02$)
- Table 8.7 Flux decline coefficients by EFD model with pretreatment ($k_1 = 2.15E-02$)
- Table 8.8 Flux decline coefficients by SRFD model (Freundlich) with automation $(1/n^2 = 7.75E-01)$
- Table 8.9 Flux decline coefficients by SRFD model (Freundlich) with pretreatment $(1/n^2 = 7.75E-01)$
- Table 8.10 Concentration of organic matter and adsorption resistance
- Table 8.11 Flux decline coefficients by MSRFD model (Freundlich) with different pressures

LIST OF FIGURES

- Figure 1.1 Schematic of research scope conducted in this study
- Figure 2.1 Future recycling commitments (adapted from Kahn, 2004)
- Figure 2.2 Typical organic constituents in BTSE and their size ranges (adapted from Levine et al., 1985)
- Figure 2.3 Different fractions of DOC and their constituents (adapted from Thurman, 1985; Cho, 1998)
- Figure 2.4 Components of a closed water cycle with indirect potable reuse (adapted from Petrović et al., 2003)
- Figure 2.5 Size ranges of the applied treatments in treating EfOM
- Figure 2.6 DOC removal mechanisms by MIEX® resin (adapted from Bourke et al., 1999)
- Figure 2.7 DOC removal by different processes (FeCl₃ flocculation, PAC adsorption, IX with MIEX[®], AOP (photocatalysis) with TiO₂, GAC biofiltration, UF (with 17500 daltons MWCO membrane), NF1 (with 700 daltons MWCO membrane) and NF2 (with 200 daltons MWCO membrane)) in biologically treated sewage effluent from a wastewater treatment plant (adapted from Shon et al., 2004 and 2005)
- Figure 2.8 MW distribution of the influent BTSE and effluents from different treatments (flocculation, adsorption, GAC biofiltration, photocatalysis, MIEX®, UF and NF)
- Figure 3.1 Schematic of treatment processes in Gwangju wastewater treatment plant
- Figure 3.2 Pure water permeability (L_p) of membranes used at 30°C of temperature
- Figure 3.3 Schematic of the batch experimental set-up (speed controller 0-150 rpm, beaker 1 L)
- Figure 3.4 Schematic drawing of the fixed bed GAC biofilter
- Figure 3.5 Comparison of (a) TiO₂ (non-porous media) and (b) PAC (porous media)
- Figure 3.6 Schematic of the photocatalytic reactor
- Figure 3.7 Schematic drawing of cross-flow unit studied
- Figure 3.8 Schematic drawing of colloidal and non-colloidal fractions with Spectra/Por-3 regenerated cellulose dialysis membrane bag (MWCO, 3500 daltons)

- Figure 3.9 Schematic drawing of fractionation for hydrophobic, transphilic and hydrophilic components with XAD-8 and XAD-4 resins
- Figure 3.10 High pressure size exclusion chromatography (HPSEC) to measure MW distirubtion
- Figure 3.11 MW distribution of (a) BTSE-W and (b) BTSE-S
- Figure 3.12 MW distribution of HP, TP, and HL fractionations
- Figure 3.13 Schematic drawing of HPLC-UVA-fluorescence
- Figure 3.14 Comparison of (a) fluorescence chromatogram and (b) MW distribution of EfOM with BTSE-S (initial DOC concentration = 6.5 mg/L)
- Figure 3.15 Comparison of (a) fluorescence chromatogram and (b) MW distribution of HP, TP and HL fractions with BTSE-S
- Figure 3.16 Schematic drawing of diffusion cell
- Figure 3.17 Zeta potential of clean membrane surfaces as a function of solution pH (background electrolyte concentration = 10 mM NaCl)
- Figure 3.18 FTIR spectra on clean membranes (NTR 7410, NTR 729HF, LES 90 and LF 10)
- Figure 3.19 Top and side views of beam energies on filed FE-SEM images of each membrane (working distance of 12 mm and magnification of 50000 and 5000)
- Figure 3.20 AFM images of each membrane (adapted from Thanuttamavong, 2002)
- Figure 4.1 MW distributions of the BTSE-W with and without pretreatments (a) flocculation, b) PAC adsorption and c) Floc-Ads)
- Figure 4.2 MW distribution of BTSE-S after different treatments (flocculation, adsorption and Floc-Ads)
- Figure 4.3 Fluorescence chromatograms after different treatments with BTSE-S
- Figure 4.4 Effect of different pretreatment methods in terms of DOC removal with BTSE-S (UF membrane used = NTR 7410; MWCO of 17500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number: 735.5, shear stress: 5.33 Pa)
- Figure 4.5 MW distribution of the soluble EfOM after different pretreatments in BTSE-S and in UF; a) UF alone, GAC biofilter, and Floc-Ads and b) after flocculation and PAC adsorption (membrane used = NTR 7410 UF with a MWCO of 17500, crossflow velocity = 0.5 m/s and transmembrane pressure = 300 kPa)

- Figure 4.6 Organic removal by NF with and without pretreatment in BTSE-S (membrane used = LES 90, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa)
- Figure 4.7 MW distribution of the NF effluent with different pretreatments (BTSE-S; LES 90 with a MWCO of 250 daltons; crossflow velocity = 0.5 m/s and transmembrane pressure = 300 kPa)
- Figure 4.8 Temporal variation of filtration flux and DOC ratio with and without pretreatment in BTSE-S (UF NTR 7410, $J_0 = 3.01$ m/d at 300 kPa; crossflow velocity = 0.5 m/s; NF LES 90, $J_0 = 0.77$ m/d at 300 kPa; crossflow velocity = 0.5 m/s; C and C_0 = the effluent and influent DOC values; J_0 = pure water permeate flux)
- Figure 4.9 The effect of pretreatments on the zeta potential of UF membrane
- Figure 4.10 FTIR spectra (a) for clean membrane and for fouled membranes without any pretreatment and after a pretreatment of Floc-Ads (b) for membranes after pretreatments of flocculation, PAC adsorption and GAC biofilter (NTR 7410 membrane with BTSE-S)
- Figure 4.11 FTIR spectra with clean membrane, without any pretreatment, and after Floc-Ads (a) NTR 729HF membrane, (b) LES 90 membrane, and (c) LF 10 membrane with BTSE-S
- Figure 4.12 Cross section of beam energies on filed FE-SEM images of NTR 7410 membrane after 18-hour filtration (working distance of 12 mm and magnification of 20,000)
- Figure 4.13 DOC concentration of adsorbed EfOM on the fouled membrane surfaces after different pretreatments (a) EfOM concentration adsorbed on the UF membrane and b) on the NF membrane)
- Figure 5.1 DOC removal of different membranes with and without pretreatment
- Figure 5.2 DOC removal by semi flocculation followed by UF
- Figure 5.3 Temporal variation of filtration flux of UF after a pretreatment of flocculation at different FeCl₃ doses (NTR 7410 UF membranes, $J_0 = 1.84$ m/d at 300 kPa; crossflow velocity = 0.5 m/s; MWCO of 17,500 daltons; Reynold's number: 735.5; shear stress: 5.33 Pa)
- Figure 5.4 MW distribution of SOM in the synthetic wastewater (a), b): individual components in the wastewater; c) wastewater (with all compounds mixed together)

- Figure 5.5 MW distribution in the flocculated effluent ($J_0 = 1.84$ m/d at 300 kPa; crossflow velocity = 0.5 m/s; MWCO = 17,500 daltons; Reynold's number.: 735.5; shear stress: 5.33 Pa; a) MW distribution of SOM with higher doses of FeCl₃ (17 23 mg-Fe/L); b) with FeCl₃ of lower doses (7 14 mg-Fe/L flocculation); c) flocculation followed by UF
- Figure 5.6 Correlation between the FeCl₃ concentrations and the corresponding weight-averaged MW values in the flocculated effluent.
- Figure 5.7 DOC removal by PAC adsorption at different doses of PAC
- Figure 5.8 DOC removal of SFSA and UF (UF membrane used = NTR 7410; MWCO of 17500 daltons; crossflow velocity = 0.5 m/s; transmembrane pressure = 300 kPa; Reynold's number: 735.5; shear stress: 5.33 Pa; DOC removal with UF alone: 75.3%)
- Figure 5.9 Temporal variation of filtration flux with UF NTR 7410 after adsorption pretreatment ($J_0 = 1.84 \text{ m.d/L}$ at 300 kPa; crossflow velocity = 0.5 m.s/L; MWCO of 17500 daltons; Reynold's number: 735.5; shear stress: 5.33 Pa)
- Figure 5.10 Temporal variation of filtration flux and DOC ratio with semi flocculation followed by semi adsorption (SFSA) with UF NTR 7410 ($J_0 = 1.84 \text{ m/d}$ at 300 kPa; crossflow velocity = 0.5 m/s; MWCO of 17,500 daltons; Reynold's number: 735.5; shear stress: 5.33 Pa; (a) after 23 mg-Fe/L flocculation; (b) after 17 mg-Fe/L; (c) after 10 mg-Fe/L; (d) after 3 mg-Fe/L)
- Figure 5.11 MW distribution after (a) adsorption with the large doses of PAC, and (b) adsorption with the small doses of PAC
- Figure 5.12 MW distribution of organic matter after semi flocculation followed by semi adsorption
- Figure 5.13 MW distribution after flocculation and adsorption as pretreatment and UF as post treatment ($J_0 = 1.84$ m/d at 300 kPa; crossflow velocity = 0.5 m/s; MWCO of 17500 daltons; Reynold's number: 735.5; shear stress: 5.33 Pa)
- Figure 5.14 Correlation of flocculant and adsorbent concentration vs DOC concentration and averaged-weight MW (J₀ = 1.84 m/d at 300 kPa; crossflow velocity = 0.5 m/s; MWCO = 17500 daltons; Reynold's number.: 735.5; shear stress: 5.33 Pa; (a) FeCl₃ concentration vs DOC concentration of semi flocculation followed by semi adsorption; (b) FeCl₃ concentration versus MW of semi flocculation followed by semi adsorption)

- Figure 6.1 DOC removal of different fractions with UF performance (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number.: 735.5, shear stress: 5.33 Pa)
- Figure 6.2 Temporal variation of filtration flux with different fractions ($J_0 = 3.01 \text{ m/d}$) (125.4 L/m²· h) at 300 kPa; crossflow velocity = 0.5 m/s)
- Figure 6.3 DOC concentration of adsorbed fractions on the fouled UF membrane surfaces
- Figure 6.4 Contact angle on the fouled UF membrane surfaces
- Figure 6.5 Zeta potential on the fouled UF membrane surfaces
- Figure 6.6 DOC removal efficiency of different fractions by FeCl₃ flocculation
- Figure 6.7 Effect of PAC dose in the DOC removal from BTSE-S (initial DOC = 6.5 mg/L; conductivity = 15 mS/cm)
- Figure 6.8 Adsorption isotherm results (BTSE-S with 15 mS/cm: 6.5 mg/L; Temp.: 25 °C)
- Figure 6.9 Adsorption kinetics of BTSE-S with 1 g/L PAC at 25 °C
- Figure 6.10 DOC removal of different BTSE-S fractions by PAC adsorption (PAC dose: 1 g/L; initial DOC concentration: 6.5 mg/L; mixing speed: 100 rpm; operation: 1 h; pH: 7)
- Figure 6.11 Adsorption isotherm plots (initial DOC concentration: 6.5 mg/L; Temp.: 25 °C)
- Figure 6.12 Adsorption kinetics result by PAC adsorption
- Figure 6.13 MW distribution of HP, TP, and HL fractions in terms of UV response and
- Figure 6.14 MW distribution of (a) BTSE-S and (b) different fractions after flocculation
- Figure 6.15 MW distribution of BTSE-S before and after PAC adsorption (PAC dose: 1 g/L)
- Figure 6.16 MW distribution of a) different PAC concentrations and b) batch kinetics
- Figure 6.17 MW distribution of a) different PAC concentrations and b) batch kinetics
- Figure 6.18 MW distribution of a) different PAC concentrations and b) batch kinetic
- Figure 7.1 Schematic representations of resistances in series

- Figure 7.2 Block diagram for the control system used for periodic cleaning of the cross-flow membrane system
- Figure 7.3 Experimental set-up of the cross-flow membrane system with the inclusion of 4 automated solenoid valves for control of the operating modes
- Figure 7.4 Operating mode popup screen in the SCADA system with Windows application
- Figure 7.5 Results of the flux decline versus time for the three different values of transmembrane pressure (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 100, 300 and 500 kPa, Reynold's number: 735.5, shear stress: 5.33 Pa)
- Figure 7.6 Different membrane resistances by fouling and flux decline at different pressures
- Figure 7.7 Results of the flux decline versus time for different cleaning techniques (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number: 735.5, shear stress: 5.33 Pa)
- Figure 7.8 Different membrane resistances by fouling and flux decline at different cleaning techniques
- Figure 7.9 Results of the flux decline versus time for different production periods (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number: 735.5, shear stress: 5.33 Pa)
- Figure 7.10 Different membrane resistances by fouling at different production periods
- Figure 7.11 Results of the flux recovery versus cleaning time used with the relaxation and the high rate cross flow
- Figure 7.12 Results of the flux decline versus the production time used at a transmembrane pressure of 300 kPa
- Figure 7.13 Results of the net flux loss versus the production time used
- Figure 7.14 Results of the flux decline versus time for the 3 different cleaning ratios (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number: 735.5, shear stress: 5.33 Pa)

- Figure 7.15 Different membrane resistances by fouling and flux decline at the 3 different cleaning ratios
- Figure 7.16 Results of the flux decline versus time for the optimal cleaning conditions (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 100 and 500 kPa, Reynold's number: 735.5, shear stress: 5.33 Pa)
- Figure 7.17 Results of the flux decline versus time after FeCl₃ flocculation for the optimal cleaning conditions (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number: 735.5, shear stress: 5.33 Pa)
- Figure 7.18 Different membrane resistances by fouling and flux decline at different FeCl₃ concentrations
- Figure 7.19 Results of the flux decline versus time after adsorption for the optimal cleaning conditions (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number: 735.5, shear stress: 5.33 Pa)
- Figure 7.20 Different membrane resistances by fouling and flux decline at different PAC concentrations
- Figure 8.1 Effect of k_0 , k_1 and d values on flux decline (UF membrane used = NTR 7410; MWCO of 17,500 daltons; crossflow velocity = 0.5 m/s; transmembrane pressure = 300 kPa (J_0 = 1.84 m/d); Reynold's number: 735.5; shear stress: 5.33 Pa)
- Figure 8.2 Effect of K_F' and 1/n' on flux decline
- Figure 8.3 Experimental and predicted flux decline profiles with different pressures
- Figure 8.4 Experimental and predicted flux decline in UF after a pretreatment (UF membrane of MWCO 17,500 daltons; pressure = 300 kPa)
- Figure 8.5 Comparison of flux-decline coefficients by EFD model
- Figure 8.6 Experimental and predicted flux decline in UF after a) different pressures, b) flocculation and c) PAC adsorption (UF membrane of MWCO 17,500 daltons; pressure = 300 kPa)
- Figure 8.7 Comparison of experimental and predicted adsorption resistance values calculated from MSRFD model
- Figure 8.8 Comparison of flux-decline coefficients by MSRFD model

- Figure 9.1 DOC removal by photocatalysis with and without pretreatment (T = 25 °C; Air = 1.5 VVM; $TiO_2 = 1$ g/L without pretreatment; UV lamp intensity = 8 W; C_0 and C = influent and effluent DOC concentration)
- Figure 9.2 MW size distributions of synthetic wastewater with photocatalysis at different times (T = 25 °C; air = 1.5 VVM; $TiO_2 = 1$ g/L without pretreatment; UV lamp intensity = 8 W)
- Figure 9.3 Molecular size distributions of SOM (after the treatment of flocculation and microfiltration (T = 25 °C; Air = 1.5 VVM; $TiO_2 = 0.5$ g/L with pretreatment, UV lamp intensity = 8 W)
- Figure 9.4 Schematic of Photo-Fenton degradation of SOM (modified from Sarria et al., 2003)
- Figure 9.5 DOC removal and permeate flux with NF unit (NTR 729HF nanofiltration membrane, Nitto Denko Corp., operating pressure 300 kPa, flow rate = 0.5 m/s, T = 30 °C)
- Figure 9.6 MW size distribution of nanofiltation effluent with synthetic wastewater (NTR 729HF nanofiltration membrane, Nitto Denko Corp., operating pressure 300 kPa, flow rate = 0.5 m/s, T = 30 °C, Reynold's no. = 735.5 (laminar flow) and shear stress = 5.33 Pa)
- Figure 9.7 Effect of surface area of UV lamp on photocatalysis ($TiO_2 = 1$ g/L; initial DOC of the wastewater = 11.46 mg/L; T = 25 °C; Air = 3.3 VVM; intensity = 8 W UV-C)
- Figure 9.8 Effect of TiO_2 concentration on photocatalysis (initial concentration (C_0) = 11. 46 mg/L (in terms of DOC); T = 25 °C; Air = 3.3 VVM; intensity = 8 W with the 3 lamps)
- Figure 9.9 Effect of PAC adsorption followed by photocatalysis (wastewater concentration (DOC) = 11. 46 mg/L; $TiO_2 = 2$ g/L; T = 25 °C; Air = 3.3 VVM; intensity = 8 W with the 3 lamps)
- Figure 9.10 Performance of coupling of PAC adsorption with TiO_2 photocatalysis system (wastewater concentration (DOC) = 11.46 mg/L; TiO_2 = 2 g/L; T = 25 °C; Air = 3.3 VVM; intensity = 8 W with the 3 lamps)
- Figure 9.11 Effect of FeCl₃ flocculation followed by photocatalysis (wastewater concentration (DOC) = 11.46 mg/L; $\text{TiO}_2 = 2 \text{ g/L}$; T = 25 °C; Air = 3.3 VVM; intensity = 8 W with the 3 UV lamps)

- Figure 9.12 MW distribution after FeCl₃ flocculation (mixing speed: 1 min at 100 rpm and 20 min at 30 rpm) and PAC adsorption (mixing speed: 100 rpm; contact time: 1 h)
- Figure 9.13 MW distribution of PAC adsorption followed by photocatalysis (wastewater concentration (DOC) = 11.46 mg/L; T = 25 °C; Air = 3.3 VVM; each 3 UV lamps intensity = 8 W; TiO_2 concentration = 2 g/L)
- Figure 9.14 MW distribution after FeCl₃ flocculation followed by TiO_2 photocatalysis (wastewater concentration (DOC) = 11. 46 mg/L; FeCl₃ dose = 23 mg-Fe/L; T = 25 °C; Air = 3.3 VVM; three lamps with an intensity of each lamp = 8 W; TiO_2 concentration = 2 g/L)
- Figure 9.15 DOC removal by i) TiO₂ adsorption alone, ii) flocculation alone, iii) flocculation followed by TiO₂ adsorption, iv) photocatalysis at pH 4 alone and flocculation followed by photocatalysis at pH 4
- Figure 9.16 (a) DOC variations and (b) reaction rates of different initial concentrations in photocatalysis ($T = 30 \,^{\circ}\text{C}$; Air = 0.1 VVM; intensity = 8 W with the 3 lamps)
- Figure 9.17 C/C₀ variation at different UV intensities (initial DOC concentration = 6.5 mg/L; TiO₂ concentration = 2 g/L; air = 25 L/min)
- Figure 9.18 MW distribution of EfOM at different UV intensities (initial DOC concentration = 6.5 mg/L; TiO₂ concentration = 2 g/L; air = 25 L/min)
- Figure 9.19 (a) C/C_0 profile and MW distribution of different fractions of EfOM by photocatalysis with (b) HP, (c) TP, and (d) HL fractions (initial concentration = 6.5 mg/L; TiO_2 concentration = 2 g/L; air = 5 VVM; UV intensity = UV-C 15W)
- Figure 9.20 (a) C/C_0 profile and (b) MW distribution after simultaneous FeCl₃ and TiO_2 additions in photocatalysis (initial concentration = 6.5 mg/L; TiO_2 concentration = 2 g/L; air = 5 VVM; UV intensity = UV-C 15W; Figure (b) corresponds to 56 mg-Fe/L addition)
- Figure 9.21 (a) C/C₀ variation and (b) MW distribution with FeCl₃ flocculation (69 mg-Fe/L) followed by photocatalysis (initial DOC concentration = 6.5 mg/L; TiO₂ concentration = 2 g/L; air = 5 VVM)
- Figure 9.22 C/C₀ variation of (a) simultaneous PAC addition and (b) PAC adsorption followed by photocatalysis (initial concentration = 6.5 mg/L; TiO₂ concentration = 2 g/L; air = 5 VVM)

- Figure 9.23 MW distribution of EfOM with PAC adsorption followed by photocatalysis (initial concentration = 6.5 mg/L; TiO_2 concentration = 2 g/L; 5 VVM)
- Figure 10.1 Schematic of near-zero fouling system I
- Figure 10.2 Schematic of near-zero fouling system II
- Figure 10.3 Schematic of near-zero fouling system III

ABSTRACT

Wastewater reuse is increasingly seen as an essential strategy for making better use of limited freshwater resources, and as a means of preventing deterioration of the aquatic environment from wastewater disposal. Membrane processes are now being successfully used to obtain water of recyclable quality. However, membrane fouling is a critical limitation on the application of membranes to wastewater reuse. Pretreatment of biologically treated sewage effluent (BTSE) prior to membrane processes will reduce organic deposition and subsequent biogrowth on membranes due to dissolved organic matter. Pretreatment also reduces the need for frequent chemical cleaning, which is a major factor that impacts on membrane life. From these perspectives, pretreatment offers significant potential for improving the efficiency of membrane processes.

The main objectives in this study are i) to evaluate different pretreatment methods of removing effluent organic matter (EfOM) from BTSE and in reducing membrane fouling, ii) to investigate the variation in the ultrafiltration (UF) and nanofiltration (NF) membrane foulant characteristics in terms of molecular weight (MW) distribution of foulants and the characteristics of fouled membrane, iii) to examine the effect of semi flocculation and semi adsorption (with partial doses of flocculants and adsorbents, respectively) on the membrane filtration, iv) to study the phenomena of membrane filtration and pretreatment using different fractions (hydrophobic (HP), transphilic (TP) and hydrophilic (HL)) of BTSE, v) to assess the effect of hybrid hydrodynamic cleaning with high rate crossflow and relaxation modes in comparison with pretreatment to membrane, vi) to evaluate the merits/demerits photocatalysis hybrid system in comparison with NF and UF with pretreatment and vii) to develop different flux decline models to quantitatively compare different pretreatments.

The highest removal of organic matter was observed when flocculation followed by adsorption was used as pretreatment. The flocculation and adsorption removed 68.5% and 71.4% of hydrophobic organic matter. After the flocculation pretreatment, the majority of large MW EfOM was removed. The pretreatment of the flocculation followed by adsorption led to very high removal of both small and large organic matter. Further, this pretreatment led to practically no filtration flux decline. The weight averaged MW (M_w) of the organics in the foulant on the membrane surface was 510

daltons (UF) and 190 (NF) without pretreatment and 350 (UF) and 180 (NF) after pretreatment with flocculation followed by adsorption, respectively. The flux decline with the HP fraction was high compared with the TP and HL fractions. It was observed that a particular amount of flocculant and adsorbent to UF was necessary below which the UF membrane became heavily fouled. The detailed analysis of M_w indicated that the M_w values of organic matter in the synthetic wastewater and in the flocculated effluent were 29800 daltons (initial), > 25000 (after flocculation with 40 mg/L FeCl₃ or less) and < 1000 (after flocculation with 50 mg/L FeCl₃ or more). The M_w values suggested the reason why the permeate flux was decreased with 40 mg/L FeCl₃ semi flocculation followed by semi adsorption due to the remaining large M_w.

A detailed investigation of the utilisation of two automated cleaning techniques to reduce fouling problems was explored. The two cleaning techniques studied were periodic membrane relaxation and a periodic high rate cross-flow. The study found that an optimised usage of these two de-clogging techniques, with a 1 hour production period followed by a 1 minute relaxation period and then a 1 minute high cross-flow rate period resulted in a net productivity increase of 14.8%. Three different semiempirical mathematical models were investigated to partially quantify the effects of different pressures and pretreatments. The three different models used were i) empirical flux decline (EFD) model, ii) series resistance flux decline (SRFD) model and iii) modified series resistance flux decline (MSRFD) model. The flux decline coefficient values determined from the EFD and SRFD models can be used as an index to assess flux decline and compare different operating conditions and pretreatments. With the MSRFD model, when flocculation of 21 mg-Fe/L was used as a pretreatment at a pressure of 300 kPa, the values of the bulk concentration (C_b), the concentration on the membrane surface (C_m) and adsorption resistance (R_a) significantly decreased by 4.4, 3.1 and 12.9 times, respectively. After 0.1 g/L adsorption as a pretreatment, the values decreased by 2.2, 2.0 and 1.8 times, respectively. Thus, pretreatment can significantly decrease membrane fouling.

Although pretreatment reduces flux decline caused by membrane fouling, it cannot completely prevent membrane fouling. Further, as time proceeds, membrane fouling by organic matter is converted into biofouling and the concentration from the retentate

constantly increases. To resolve these problems, this study recommends three near-zero fouling systems with an integrated photocatalysis membrane hybrid system.