# DEVELOPMENT OF MAGNETOPHORETIC ACTUATION COMPOSITE MEMBRANES FOR REMOVAL OF HUMIC ACID

NG QI HWA

UNIVERSITI SAINS MALAYSIA 2016

# DEVELOPMENT OF MAGNETOPHORETIC ACTUATION COMPOSITE MEMBRANES FOR REMOVAL OF HUMIC ACID

by

NG QI HWA

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

June 2016

# DEVELOPMENT OF MAGNETOPHORETIC ACTUATION COMPOSITE MEMBRANES FOR REMOVAL OF HUMIC ACID

by

## NG QI HWA

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

**June 2016** 

#### ACKNOWLEDGEMENT

With earnest gratitude and appreciation, I would like to express my deepest and most heart-felt gratitude to my beloved parents and siblings for their unequivocal support throughout all the difficult situations during the period of my entire study.

It is my great pleasure to express my deepest appreciation and gratitude to my dedicated supervisor Dr. Low Siew Chun and co-supervisors Prof. Abdul Latif Bin Ahmad and Assoc. Prof. Lim Jit Kang for their excellent supervision, enormous effort spent in guiding, invaluable advice, practical view, and helping me throughout my PhD studies. My achievement of this research project is a reflection of prominent supervision works from my supervisors.

In particular, I would like to show my gratitude to all the laboratory technicians and administrative staff of the School of Chemical Engineering, Universiti Sains Malaysia for the assistance rendered to me.

On top of that, I would like to convey heartfelt gratitude and thanks to all my beloved friends and colleagues: Siew Hoong, Peck Loo, Man Kee, Wei Ming, Zhi Hua, Choon Ming, Hui Yen, Swee Pin, Sim Siong, Susan, Jing Yao, Huey Ping, Zeinab, Chuan Chun, Arthur, Qian Yee, Peng Chee, Atiah, and Wani for their encouragement, kindness and support towards me. Last but not least, the financial support given by Ministry of Higher Education (MOHE) and Universiti Malaysia Perlis (UniMAP) is gratefully acknowledged.

#### NG QI HWA,

June 2016

## **TABLE OF CONTENTS**

# Page

Acknowledgement	.ii
Table of Contents	iii
List of Tables	viii
List of Figures	х
List of Plates	xvi
List of Abbreviations	.xviii
List of Symbols	xxi
Abstrak	xxiv
Abstract	xxvi

#### **CHAPTER 1 - INTRODUCTION**

1.1	Potential of Membrane in Water Treatment	1
1.2	Nano-composite Membrane	3
1.3	Problem Statement	5
1.4	Objectives	8
1.5	Scope of Study	9
1.6	Organization of the Thesis	11

#### CHAPTER 2 - LITERATURE REVIEW

2.1	Develop	pment of Membrane in Water Treatment	
	2.1.1	History	14
	2.1.2	Classification of Membrane	
2.2	Humic S	Substances	
	2.2.1	Properties of Humic Substances (HS)	22
	2.2.2	Humic Acid (HA)	23
	2.2.3	Humic Acid in Water and Wastewater	25
2.3	Humic A	Acid Removal Technology	
	2.3.1	Traditional Methods on Removal of Humic Acid and Its Prob	lems 27
		2.3.1(a) Flocculation	
		2.3.1(b) Oxidation Methods	

		2.3.1(c)	Electrochemical Methods	29
	2.3.2	Membrar	ne Technology on Removal of Humic Acid	30
2.4	Membr	ane Foulin	g	32
	2.4.1	Membrar	ne Fouling Analysis (Blocking Filtration Law)	37
	2.4.2	Conventi	onal Cleaning Methods to Mitigate Membrane Fouling.	42
		2.4.2(a)	Physical Cleaning Methods	43
		2.4.2(b)	Chemical Cleaning Methods	45
		2.4.2(c)	Drawbacks of Physical and Chemical Cleaning Method	ds47
2.5	Alterna	tive Metho	ods to Mitigate Membrane Fouling	47
	2.5.1	Membrar	ne Surface Modification	48
	2.5.2	Nano-coi	nposite Membrane	50
		2.5.2(a)	Titanium Dioxide (TiO <sub>2</sub> ) based Nano-composite	
			Membrane	51
		2.5.2(b)	Zeolite based Nano-composite Membrane	52
		2.4.2(c)	Magnetite Nanoparticles based nano-composite	
			Membrane	53
2.6	Stimuli	Responsiv	e Membrane	54
	2.6.1	Membrar	ne Indirect Stimulated by Thermodynamic Environment	55
	2.6.2	Membrar	ne Direct Stimulated by Chemical Cues	56
	2.6.3	Membrar	ne Stimulated by a Specific External Electromagnetic Fi	eld
		Signal		57
2.7	Quartz	Crystal Mi	crobalance with Dissipation Monitoring (QCM-D)	58
	2.7.1	QCM Tee	chnique	59
	2.7.2	Dissipati	on Factor	62
	2.7.3	Some Co	mmon QCM-D Applications	63
2.8	Future	Direction of	of Study	65
CHAP	ΓER 3 - Ι	MATERIA	LS AND METHODOLOGY	
3.1	Raw M	aterials and	d Chemicals	69

	3.1.1	Raw Materials	.69
	3.1.2	Chemicals	69
3.2	Surface	Modification of Magnetite Nanoparticles	71
3.3	Develop	oment of Magnetophoretic Actuation Composite Membranes	72

	3.3.1	Quantitative Measurement of the Adsorbed F-MNPs and HA	
		Foulants on Modified or Neat PES Membranes via Quartz Crystal	
		Microbalance with Dissipation (QCM-D)	72
		3.2.1(a) Adsorption Kinetics of F-MNPs	73
		3.2.1(b) Monitoring of HA Adsorption and Cleaning of HA from	
		the Membrane Surfaces	73
	3.3.2	Preparation of Magnetophoretic Actuation Composite Membrane	.74
3.4	Charac	cterization of Magnetite Nanoparticle	75
	3.4.1	Dynamic Light Scattering (DLS) and Electrophoretic Light	
		Scattering	.75
	3.4.2	Thermogravimetric Analysis (TGA)	75
	3.4.3	Transmission Electron Microscope (TEM)	76
	3.4.4	X-ray Diffraction (XRD)	76
3.5	Charac	cterization of Magnetophoretic Actuation Composite Membranes	77
	3.5.1	Attenuated Total Reflectance Fourier Transform Infrared	
		Spectroscopy (ATR-FTIR)	77
	3.5.2	Field Emission Scanning Electron Microscopy (FESEM) and	
		Energy Dispersive Spectroscopy (EDS) Analysis	.77
	3.5.3	X-ray Photoelectron Spectroscopy (XPS) Analysis	78
	3.5.4	Atomic Force Microscopy (AFM) Analysis	.78
	3.5.5	Contact Angle Measurement	80
	3.5.6	Pore Size Distribution	80
	3.5.7	Vibrating Sample Magnetometer (VSM)	81
3.6	Perfor	mance Evaluation of the Neat PES and Magnetophoretic Actuation	
	Comp	osite Membranes	82
	3.6.1	Membrane Filtration Test	83
3.7	Stabili	ty of the Membrane Coated Magnetic-responsive Functional Layer (F-	
	MNPs	) toward pH-dependent Aqueous Medium	86
	3.7.1	Quantitative Measurement of the Detachment of the Magnetic-	
		responsive Functional Layer from the Modified PES Membranes	
		via QCM-D Technique	86
	3.7.2	Performance Evaluation of Magnetophoretic Actuation Composite	
		Membranes toward pH-dependent Humic Acid Solution	87

3.8	Long Term Membrane Performance Evaluation		
	3.8.1	Longevity Study on the Magnetophoretic Actuation Composite	
		Membrane in Treating Synthetic Organic Foulant (Humic Acid)	88
	3.8.2	Longevity Study on the Magnetophoretic Actuation Composite	
		Membrane in Treating River Water	91
3.9	Experi	ment Flow Diagram	91

## CHAPTER 4 - RESULTS AND DISCUSSION

Prepara	ation of Sta	ble Fe <sub>3</sub> O <sub>4</sub> Colloid Suspension	94
4.1.1	Stability	of Bare Magnetite Nanoparticles (MNPs)	94
4.1.2	Polymer	Stabilized Magnetite Nanoparticles (F-MNPs)	97
Develo	pment of N	Aagnetophoretic Actuation Composite Membrane	104
4.2.1	Quantitat	tive Measurement of the Adsorbed F-MNPs Film on	
	Modified	PES Membrane via QCM-D technique	105
4.2.2	Quantitat	tive Measurement of the Adsorbed/Desorbed of HA	
	Foulants	on the Modified PES Membrane/Neat PES membrane via	ı
	QCM-D	Technique	117
4.2.3	Modifica	tion of Neat MF PES Membrane to UF Magnetophoretic	
	Actuation	n Composite Membrane	119
Membrane Performance Test		133	
4.3.1	Study the	e Extent of Magnetophoretic Actuation due to Different	
	Concentr	ations of F-MNPs (100, 1000, 2500 ppm) Coated on the	
	Membrar	ne Surface	133
	4.3.1(a)	Morphological and Chemical Composition for Different	
		Concentrations of F-MNPs (100, 1000, 2500 ppm)	
		Coated on the Membrane Surface	134
	4.3.1(b)	Deposition Kinetics and Adsorbed Mass of F-MNPs on	
		PSS-PDDA-Modified PES Polymer	141
	4.3.1(c)	Magnetophoretic Actuation and the Membrane Anti-	
		fouling Behavior	143
4.3.2	Stability	of the Magnetic-responsive Functional Layer in pH-	
	depender	nt Aqueous Mediums	153
	Prepara 4.1.1 4.1.2 Develo 4.2.1 4.2.2 4.2.3 Membr 4.3.1	Preparation of Sta 4.1.1 Stability 4.1.2 Polymer Development of M 4.2.1 Quantitat Modified 4.2.2 Quantitat Foulants QCM-D 4.2.3 Modifica Actuation Membrane Perfor 4.3.1 Study the Concentr Membran 4.3.1(a) 4.3.1(b) 4.3.1(c) 4.3.2 Stability depender	<ul> <li>Preparation of Stable Fe<sub>3</sub>O<sub>4</sub> Colloid Suspension</li></ul>

		4.3.2(a)	Quantitative Measurement of the Detachment of F-MNP	'S
			from Modified PES Membranes via QCM-D Technique.	154
		4.3.2(b)	Membrane Filtration Performance in Different pH of HA	L
			Solutions	. 159
4.4	Analys	is of Fouli	ng Mechanisms	164
	4.4.1	Characte	ristic Curves	165
	4.4.2	Classical	Filtration Models	168
	4.4.3	The Con	bined Models	174
4.5	Long T	erm Memb	prane Performance Evaluation	. 178
	4.5.1	Membra	ne Longevity Analysis	178
	4.5.2	Interval	Cleaning to Improve Membrane Sustainability	185
	4.5.3	Performa	ance Evaluation of Magnetophoretic Actuation Composite	
		Membra	ne in Treating River Water	189
4.6	Design	Protocol o	of the Magnetophoretic Actuation Composite Membrane	
	use in l	Practice		. 192

#### CHAPTER 5 - CONCLUSIONS AND RECOMMENDATIONS

5.1	Conclusions	197
5.2	Recommendations	199

References
------------

Appendices HA Calibration Curve Magnetic Field Strength Sample of Calculation for Membrane Performance Sample of Calculation for the Shear Rate on the Membrane Surface River Water Collection Point

List of Publications

#### LIST OF TABLES

# Page

Table 2.1	Summary of the membrane separation processes (Cesar de, 2015, Wagner, 2001, Mortazavi, 2008).	17
Table 2.2	Chronological development of membrane technology in removal of HA.	32
Table 2.3	Factors that may affect membrane fouling (Laboy-Nieves et al., 2008).	35
Table 24	Summary of the classical filtration models at constant pressure (Bolton et al., 2006).	41
Table 2.5	Summary of the combined fouling models at constant pressure (Bolton et al., 2006).	42
Table 2.6	Cleaning solutions according to the type of foulant (Fritzmann et al., 2007).	46
Table 3.1	Lists of chemical reagents used in this study.	69
Table 3.2	Membrane samples description.	83
Table 4.1	Average hydrodynamic diameter of F-MNPs at various PSS/MNPs molar ratios (fixed MNPs concentration at 0.0025 g mL <sup>-1</sup> ). The samples standard deviations were obtained from at least three replicate measurements.	98
Table 4.2	Amount of PSS polymer that bound onto the functionalized MNPs.	102
Table 4.3	Zeta potential measurement for the polyanion (PSS) and polycation (PDDA) polyelectrolytes and the magnetite nanoparticles (F-MNPs).	110
Table 4.4	Surface roughness parameters of neat and modified membranes.	125
Table 4.5	Membrane top surface chemical composition obtained from Energy Dispersive Spectroscopy (EDS).	127
Table 4.6	Membrane top surface chemical composition obtained from X-ray Photoelectron Spectroscopy (XPS).	129
Table 4.7	Membrane cross section chemical composition obtained via energy dispersive spectroscopy (EDS).	130

Table 4.8	Membrane top surface chemical composition obtained from X-ray Photoelectron Spectroscopy (XPS).	136
Table 4.9	Surface roughness parameters of modified membranes.	138
Table 4.10	Contact angles measurements of neat and modified membranes.	147
Table 4.11	HA rejections in the presence of an oscillating magnetic field (WM) or without the presence of a magnetic field (WOM) for membrane filtration. HA feed concentration: $50 \text{ mg L}^{-1}$ at pH 8.	153
Table 4.12	HA rejections in the presence of an oscillating magnetic field (WM) or without the presence of a magnetic field (WOM) for the filtration of 50 mg $L^{-1}$ solution of HA with different pH in the membrane fouling process.	
Table 4.13	Model fit error for the classical models.	173
Table 4.14	Fit model parameter for the cake classical model.	173
Table 4.15	Model fit error for the combined models.	177
Table 4.16	Fit model parameters for the cake-standard combined model.	177
Table 4.17	Comparison of water qualities of raw river water, permeate, and the rejection performance.	191

#### LIST OF FIGURES

Figure 2.1	Classification scheme of synthetic polymeric membranes (Pinnau and Freeman, 1999).	18
Figure 2.2	Physical and chemical properties of humic substances (Stevenson, 1994).	23
Figure 2.3	Structure of humic acid (Wu et al., 2003).	24
Figure 2.4	Schematic diagram external and internal membrane fouling (Nath, 2008).	33
Figure 2.5	Schematic draw of the fouling mechanisms considered by blocking filtration laws: (A) Cake filtration, (B) Intermediate blocking, (C) Standard blocking, and (D) Complete blocking.	38
Figure 2.6	Cleaning flow direction of forward and reverse flushing (Arnal et al., 2011).	45
Figure 2.7	Schematic diagram of a typical piezoelectric crystal.	59
Figure 2.8	AT-cut quartz crystal.	60
Figure 3.1	Schematic of the different combinations. Deposition of F-MNPs (a) without precursor, (b) coated with the precursor of polycation PDDA, and (c) coated with the precursors of polyanion PSS and polycation PDDA.	73
Figure 3.2	Schematic diagram showing the positioning of the magnetic field source controlled by a PLC rotor controller, demonstrating that the magnetic bar setup can be arranged by pointing the north poles either to or away from each other with respect to the dead-end filtration cell.	84
Figure 3.3	Schematic diagram presenting the orientation of the solenoid generates alternating magnetic field with respect to the cross-flow filtration cell.	89
Figure 3.4	Schematic diagram for overall research methodology.	92
Figure 4.1	(a) Flocculation kinetic profile presenting the hydrodynamic size (d.nm) of bare MNPs vs. time (minutes), and (b) Effect of pH on the zeta potential of bare MNPs and PSS polyelectrolytes.	95

- Figure 4.2 Schematic diagram presenting the charge of bare MNPs in 96 acidic and alkaline mediums.
- Figure 4.3 Schematic diagram showing the functionalization of MNPs 99 with different PSS concentration.
- Figure 4.4 Flocculation kinetic profile presenting the hydrodynamic 100 size (d.nm) of functionalized magnetite nanoparticles (F-MNPs) vs. time (minutes).
- Figure 4.5 TGA analyses of (a) bare MNPs and PSS polymer; (b) F- 101 MNPs with various PSS concentrations.
- Figure 4.6 XRD patterns of (a) bare MNPs and (b) F-MNPs. 104
- Figure 4.7 ATR-FTIR spectra for commercial MF PES membrane and 106 PES coated on crystal.
- Figure 4.8 The frequency (grey line) and dissipation (black line) 108 changes for the  $3^{rd}$  overtone as a function of time during adsorption of composite film F-MNPs dispersed in PSS solution on different PES-coated crystal cells: (a) PES-coated quartz cell without polyelectrolyte precursor, (b) PES-coated quartz cell coated with polycation PDDA precursor, and (c) PES-coated quartz cell coated with polycation PSS and then polycation PDDA precursors. The overall deposition mass was represented by the frequency changes ( $|\Delta f|$ ).
- Figure 4.9 The frequency (grey line) and dissipation (black line) 109 changes for the  $3^{rd}$  overtone as a function of time during adsorption of composite film F-MNPs dispersed in DI water on different PES-coated crystal cells: (a) PES-coated quartz cell without polyelectrolyte precursor, (b) PES-coated quartz cell coated with polycation PDDA precursor, and (c) PES-coated quartz cell coated quartz cell coated with polyanion PSS and then polycation PDDA precursors. The overall deposition mass was represented by the frequency changes ( $|\Delta f|$ ).
- Figure 4.10 The  $3^{rd}$  overtone dissipation change ( $\Delta D_3$ ) versus frequency 111 shift ( $\Delta f_3$ ) profile for the adsorption of F-MNPs dispersed in PSS solution (black line) and blank PSS solution without F-MNPs (grey line) on the surface of the modified PES quartz cell. (a1) refer to the first coated layer of PSS followed by a DI water rinsing step. (a2) refer to the second coated layer of PDDA followed by a DI water rinsing step. (a3) refer to the F-MNPs dispersed in PSS solution (grey line) and the blank PSS solution without F-MNPs (black line) followed by a DI water rinsing step.

- Figure 4.11 The  $3^{rd}$  overtone dissipation change ( $\Delta D_3$ ) versus frequency 112 shift ( $\Delta f_3$ ) profile for the adsorption of F-MNPs dispersed in DI water on the surface of the modified PES quartz cell. (a1) refer to the first coated layer of PSS followed by a DI water rinsing step. (a2) refer to the second coated layer of PDDA followed by a DI water rinsing step. (a3) refer to the third/top functional layer of the magnetic responsive F-MNPs in DI water followed by a DI water rinsing step.
- Figure 4.12 Amount of F-MNPs (dispersed in DI water) adsorbed on a 115 PES spin-coated quartz crystal sensor as a function of time at conditions (a) without precursor, (b) with a single layer coating of polycation PDDA precursor, and (c) with a bilayer coating of polyanion PSS and polycation PDDA precursors.
- Figure 4.13 Adsorption and desorption of HA on a modified PES 118 membrane and an unmodified neat PES membranes as a function of time.
- Figure 4.14 Effect of coating of polyelectrolytes and F-MNPs on 122 membrane surface pore size distributions.
- Figure 4.15 Representative EDS spectra of membrane surface samples A 126 (Neat MF PES membrane, P1), B (PDDA-PSS-PES membrane, P2), and C, (2500 ppm F-MNPs-PDDA-PSS-PES membrane, P5).
- Figure 4.16 XPS spectra of membrane surface samples A (Neat MF PES 128 membrane, P1), B (PDDA-PSS-PES membrane, P2), and C (2500 ppm F-MNPs-PDDA-PSS-PES membrane, P5).
- Figure 4.17 Specific magnetization vs. applied field for the bare MNPs, 132 neat MF PES membrane (P1) and 2500 ppm F-MNPs-PDDA-PSS-PES membrane (P5).
- Figure 4.18 Amount of F-MNPs adsorbed on a polyelectrolyte modified 141 bilayer (PSS and PDDA) PES coated quartz crystal surface as a function of time.
- Figure 4.19 Deposition rate of F-MNPs onto a polyelectrolyte modified 142 bilayer (PSS and PDDA) PES coated quartz crystal surface as a function of F-MNPs concentration. Error bars representing the sample standard deviations were obtained from at least three replicate measurements.
- Figure 4.20 Normalized flux for the filtration of 50 mg L<sup>-1</sup> solutions of 143 HA on the membrane fouling process with different concentration of F-MNPs suspensions coated on the membrane surface: (a) 0 ppm (neat MF PES membrane, P1), (b) 0 ppm (PDDA-PSS-PES membrane, P2), (c) 100 ppm F-MNPs (P3), (d) 1000 ppm F-MNPs (P4), and (e) 2500 ppm

F-MNPs (P5).

- Figure 4.21 Schematic diagram representing the magnetophoretic 149 actuation effect with different concentration of coated F-MNPs on membrane surface.
- Figure 4.22 Specific magnetization vs. applied field for different 151 concentration of F-MNPs suspensions coated on membrane surfaces.
- Figure 4.23 The  $3^{rd}$  overtone frequency ( $\Delta f$ , black line) and dissipation 155 ( $\Delta D$ , grey line) change as a function of time during the adsorption/desorption processes for stability tests on the magnetite functional layer (zone D) in various pH aqueous mediums (a) non-pH-adjusted DI water, DI water in (b) pH 2, (c) pH 3, (d) pH 6, (e) pH 8, (f) pH 10, (g) pH 11, and (h) pH 12.
- Figure 4.24 Mass changes (adsorption-positive value or desorptionnegative value) of the thin composite magnetic-responsive functional layer on quartz crystal surface during the stability tests in various pH aqueous mediums (**zone D** in Figure 1).
- Figure 4.25 The normalized flux for the filtration of a 50 mg L<sup>-1</sup> solution 161 of HA at (a) pH 8, (b) pH 10, and (c) pH 12.
- Figure 4.26  $\text{Log}(d^2t/dV^2)$  versus  $\log(dt/dV)$  characteristic curves for the 166 filtration of 50 mg L<sup>-1</sup> HA solution at (a) pH 8, (b) pH 10, and (c) pH 12 using a magnetophoretic actuation composite membrane (P5) in the presence of the magnetic field (WM) or without the presence of the magnetic field (WOM).
- Figure 4.27 Membrane filtration profile fitted to the classical models for 170 the HA solution fed at (a) pH 8, (b) pH 10, and (c) pH 12, in the present of an oscillating magnetic field (WM) or without the present of a magnetic field (WOM) throughout filtration.
- Figure 4.28 Membrane filtration profile fitted to the classical models for 171 the HA solution fed at (a) pH 8, (b) pH 10, and (c) pH 12, in the present of an oscillating magnetic field (WM) or without the present of a magnetic field (WOM). Note: Filtration profile was plotted between 10-12 hrs for the filtration process.
- Figure 4.29 Membrane filtration profile fitted to the combined models 175 for the HA solution fed at (a) pH 8, (b) pH 10, and (c) pH 12, in the present of an oscillating magnetic field (WM) or without the present of a magnetic field (WOM) throughout filtration.

- Figure 4.30 Membrane filtration profile fitted to the combined models 176 for the HA solution fed at (a) pH 8, (b) pH 10, and (c) pH 12; in the present of an oscillating magnetic field (WM) or without the present of a magnetic field (WOM). Note: Filtration profile was plotted between 10-12 hrs for the filtration process.
- Figure 4.31 Flux decline behaviour of neat MF PES membrane (P1) and 179 2500 ppm F-MNPs-PDDA-PSS-PES membrane (P5) for the filtration of HA feed solution (50 mg L<sup>-1</sup>) in cross-flow filtration mode.
- Figure 4.32 Flux decline behaviour of neat UF PES membrane and 181 magnetophoretic actuation composite membrane (P5) for the filtration of HA feed solution (50 mg  $L^{-1}$ ) in cross-flow filtration mode.
- Figure 4.33 QCM-D measurements of the stability of F-MNPs on the 185 PDDA-PSS-PES substrate as a function of time.
- Figure 4.34 Flux decline behaviour of seven cycles of the filtration of 186 HA feed solution (50 mg  $L^{-1}$ ) through magnetophoretic actuation composite membrane (P5) in cross-flow filtration mode.  $J_0=9.48\times10^{-6} \text{ m}^3/\text{m}^2\text{s}$
- Figure 4.35 Flux decline behaviour representing the 8<sup>th</sup> cycle of the 188 filtration of HA feed solution (50 mg L<sup>-1</sup>) through magnetophoretic actuation composite membrane (P5) in cross-flow filtration mode after chemical cleaning.
- Figure 4.36 Flux decline behaviour of neat UF PES membrane and 190 magnetophoretic actuation composite membrane (P5) for the filtration of river water in cross-flow filtration mode.
- Figure 4.37 Schematic diagram showing the spiral wound membrane 193 module (Anonymous, 2016).
- Figure 4.38 Schematic diagram presenting the orientation of the solenoid 194 generates alternating magnetic field inside the core that embedded with the spiral wound membrane module.
- Figure 4.39 Schematic illustration of the concept: (a) Rotational motion 194 of the F-MNPs on the membrane surface due to the presence of oscillating magnetic field; (b) Lateral motion of the F-MNPs on the membrane surface due to the presence of the magnetic force acting on it; and (c) Actuation motion of the F-MNPs on the membrane surface due to the presence of both magnetic force and oscillating magnetic field.

Figure 4.40 Schematic diagram presenting the orientation of the solenoid 196 generates alternating magnetic field either at section X and section Y with respect to the spiral wound membrane module.

#### LIST OF PLATES

Plate 3.1 The photograph of the dead-end filtration test rig. 84 Plate 3.2 The photograph of the cross-flow filtration test rig. 89 Plate 4.1 TEM images showing (a) bare MNPs, and (b) RuO<sub>4</sub> vapor 103 stain F-MNPs. Plate 4.2 FESEM micrographs (Accelerating Voltage: 5 kV and 121 Magnification: 20,000) for top surface of samples A (Neat MF PES membrane, P1), B (PDDA-PSS-PES membrane, P2), and C (2500ppm F-MNPs-PDDA-PSS-PES membranes, P5). Plate 4.3 Three-dimensional surface AFM images of samples A (Neat 124 MF PES membrane, P1), B (PDDA-PSS-PES membrane, P2), and C (2500 ppm FMNPs-PDDA-PSS-PES membrane, P5). Plate 4.4 FESEM micrographs (Accelerating Voltage: 5 kV and 131 Magnification: 10,000) for cross section of samples A (Neat MF PES membrane, P1), B (PDDA-PSS-PES membrane, P2), and C (2500 ppm F-MNPs-PDDA-PSS-PES membrane, P5). Plate 4.5 FESEM micrographs (Accelerating Voltage: 5 kV and 135 Magnification: 20,000) for top surface of samples A (P3), B (P4), and C (P5). Plate 4.6 Three-dimensional surface AFM images of samples A (P3), 137 B (P4), and C (P5). Plate 4.7 SEM-EDS line-scan profile (Accelerating Voltage: 20 kV 139 and Magnification: 5,000) across the membrane surface at two different regions illustrating the Fe<sub>3</sub>O<sub>4</sub> distribution pattern on 2500 ppm F-MNPs-PDDA-PSS-PES membrane (P5). Plate 4.8 Membrane top surface area mapping under magnification of 1401,000, illustrating the  $Fe_3O_4$  distribution pattern on (a) 100 ppm F-MNPs (P3), (b) 1000 ppm F-MNPs (P4), and (c) 2,500 ppm F-MNPs (P5) coated membranes. Plate 4.9 FESEM micrographs (Accelerating Voltage: 5 kV and 180 Magnification: 20,000) for top surface of neat MF PES membrane (P1) used to filter 50 mg  $L^{-1}$  HA solution for 48

Page

hours (a) clear membrane and (b) fouled membrane.

- Plate 4.10 FESEM micrographs (Accelerating Voltage: 5 kV and 182 Magnification: 20,000) for top surface of neat UF PES membrane used to filter 50 mg  $L^{-1}$  HA solution for 48 hours (a) clear membrane and (b) fouled membrane.
- Plate 4.11 FESEM micrographs (Accelerating Voltage: 5 kV and 183 Magnification: 20,000) for top surface of magnetophoretic actuation composite membrane (P5) used to filter 50 mg L<sup>-1</sup> HA solution for 48 hours (a) clear membrane and fouled membrane operated (b) without and (c) with the oscillating magnetic field.

## LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
BSA	Bovine serum albumin
CAB	Cellulose acetate butyrate
CIP	Clean-in-place
DBPs	Disinfection by-products
DI	Deionized
DLS	Dynamic light scattering
EC	Electrocoagulation
EDS	Energy dispersive spectroscopy
EO	Electro-oxidation
FA	Fulvic acid
FESEM	Field emission scanning electron microscopy
F-MNPs	Functionalized-magnetite nanoparticles
НА	Humic acid
HAAs	Haloacetic acids
HCI	Hydrochloride acid
HS	Humic substance
IR	Infrared
LCST	Lower critical solution temperature
MF	Microfiltration
MNPs	Magnetite nanoparticles
MWCO	Molecular weight cut-off
NaOH	Sodium hydroxide

NF	Nanofiltration
NMP	N-methyl-pyrrolidone
NOM	Natural organic matter
P(St-AA-NVP)	Poly(styrene-acrylic acid-N-vinylpyrrolidone)
PA	Polyamide
PAI	Polyamideimide
PDDA	Poly(diallyldimethylammonium chloride)
PEM	Polyelectrolyte multilayer
PES	Polyethersulfone
PLC	Programmable logic controller
РМАА	Poly(methacrylic acid)
PNIPAAm	Poly(N-isopropylacrylamide)
PSS	Poly(sodium-4-stryene sulfonate)
PVDF	Polyvinylidene fluoride
PVP	Poly(N-ethyl-4-vinylpyridinium bromide)
QCM-D	Quartz crystal microbalance with dissipation
RO	Reverse osmosis
SDI	Slit density index
SSR	Sum of squared residuals
TEM	Transmission electron microscopy
TFC	Thin film composite
TGA	Thermogravimetric analysis
THMs	Trihalomethanes
TOC	Total organic carbon
TSP	Trisodium phosphate

UF	Ultrafiltration
UV	Ultraviolet
VSM	Vibrating sample magnetometer
WHO	World health organization
WM	With external oscillating magnetic field
WOM	Without external oscillating magnetic field
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

### LIST OF SYMBOLS

А	Effective membrane area
Å	Amplitude
В	Magnetic field strength
С	Mass sensitivity constant of the QCM-D
C <sub>p</sub>	Permeate concentration
C <sub>F</sub>	Feed concentration
C <sub>cr</sub>	Specific critical salt concentration
D	Dissipation factor
ΔD	Change in the dissipation factor
Edissipated	Dissipated energy
E <sub>stored</sub>	Energy stored in the oscillating quartz crystal
f	Resonant frequency
$\Delta f$	Change in frequency
$\mathbf{h}_{0}$	Thickness of the crystal
h <sub>1</sub>	Film thickness
На	Hartmann number
J	Membrane flux at time t
Jo	Membrane initial flux
k	Fouling coefficient
K <sub>b</sub>	Complete pore blocking coefficient
K <sub>c</sub>	Cake filtration constant
K <sub>i</sub>	Intermediate pore blocking coefficient
K <sub>s</sub>	Standard pore blocking coefficient

- L Characteristic length scale
- M<sub>s</sub> Saturation magnetizations
- $\Delta m$  Change in mass adsorbed per unit surface of the quartz crystal surface
- n Dimensionless filtration constant
- η Overtone number
- $\eta_1$  Film viscosity
- $\eta_3$  Viscosity of the bulk liquid
- ρ<sub>o</sub> Density of the crystal
- $\rho_1$  Film density
- $\rho_3$  Density of the bulk liquid
- R Rejection percentage
- R<sub>a</sub> Mean roughness parameter
- Re Reynold number
- R<sub>q</sub> Root mean square roughness parameter
- R<sub>z</sub> Mean difference between five highest peaks and lowest valleys
- t Time
- τ Decay time
- U<sub>E</sub> Electrophoretic mobility
- μ Dynamic viscosity
- μ<sub>1</sub> Film elasticity
- V Cumulative volume of filtrate
- V<sub>max</sub> Maximum volumetric capacity
- Y Filtrate volume collected through an available membrane area
- α Angular frequency of the oscillation
- $\dot{\gamma}$  Shear rate