Development of high-performance polydimethylsiloxane-based nanofibrous composite membranes for phenol removal from wastewater

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**DEVELOPMENT OF HIGH-PERFORMANCE
POLYDIMETHYLSILOXANE-BASED
NANOFIBROUS COMPOSITE MEMBRANES FOR
PHENOL REMOVAL FROM WASTEWATER**

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
TABLE OF CONTENTS	v
LIST OF PUBLICATIONS	ix
LIST OF FIGURES	xi
LIST OF TABLES	xvi
LIST OF SYMBOLS	xvii
ABSTRACT	xxi
CHAPTER 1. Introduction	1
1.1. Background	1
1.2. Research objectives	5
1.3. Thesis outline	7
CHAPTER 2. Literature review	10
2.1. Aqueous-aqueous extractive process	10
2.1.1. Introduction	10
2.1.2. Extractive Membrane Bioreactor (EMBR)	12
2.1.2.1. Concept and advantages of EMBR	12
2.1.2.2. EMBR applications and challenges	14
2.1.2.3. Current status of EMBR membranes	15
2.2. Polydimethylsiloxane (PDMS) membranes	19
2.2.1. Preparation of PDMS membranes	19
2.2.2. Development of filled PDMS mixed-matrix membranes (MMMs)	22
2.2.3. Development of PDMS-based composite membranes	24
2.3. Electrospun nanofibrous membranes (ENMs)	28
2.3.1. Advantages of ENMs	28
2.3.2. Fabrication of ENMs	29
2.3.3. Design and development of ENMs	32
2.3.3.1. Manipulation of fabrication parameters	32
2.3.3.2. Exploitation of electrospinning techniques	41
CHAPTER 3. Fabrication of nanofibrous composite membranes for phenol removal in an extractive membrane bioreactor	43

3.1. Introduction	43
3.2. Experimental	46
3.2.1. Materials and chemicals	46
3.2.2. Preparation of polyvinylidene fluoride (PVDF) ENMs	47
3.2.3. Preparation of PDMS-coated PVDF nanofibrous composite membranes with tiered structures	49
3.2.4. Membrane characterizations	50
3.2.5. Leakage test	51
3.2.6. Aqueous-aqueous extractive tests	51
3.2.7. Extractive membrane bioreactor tests	52
3.3. Results and discussion	54
3.3.1. Characterization of PVDF ENMs	54
3.3.2. Optimization of the composite membranes with tiered structure ...	56
3.3.2.1. Effect of substrate pore size on composite membrane preparation	56
3.3.2.2. Effect of PDMS preparation method on composite membrane preparation	58
3.3.2.3. Effect of pre-wetting agent on composite membrane preparation	60
3.3.3. Long term performance in an aqueous-aqueous extractive test	66
3.3.4. EMBR process	67
3.3.5. Comparison of phenol extractive performance of various membranes	69
3.4. Conclusions	71
CHAPTER 4. Development of high-performance nanofibrous composite membranes by optimizing polydimethylsiloxane architectures for phenol removal	73
4.1. Introduction	73
4.2. Experimental	77
4.2.1. Materials and chemicals	77
4.2.2. Preparation of dense PDMS membranes	77
4.2.3. Preparation of a tiered PVDF electrospun nanofibrous substrate ...	78

4.2.4. Preparation of nanofibrous composite membranes via spray coating	79
4.2.5. Membrane characterizations	79
4.2.6. Partition coefficient measurements	80
4.2.7. Aqueous-aqueous extractive tests	80
4.3. Results and discussion	81
4.3.1. Characterization of different dense PDMS membranes	81
4.3.2. Phenol partition coefficients of dense PDMS membranes	85
4.3.3. Optimization of phenol partition coefficients of dense PDMS membranes	89
4.3.4. Mechanical properties of dense PDMS membranes	93
4.3.5. Overall mass transfer efficiency of dense PDMS membranes	95
4.3.6. Aqueous-aqueous extractive performance of nanofibrous composite membranes	97
4.4. Conclusions	103
CHAPTER 5. Development of highly efficient nanofibrous composite membranes via confinement-assisted in situ self-assembly strategy for phenol removal	105
5.1. Introduction	105
5.2. Experimental	109
5.2.1. Materials and chemicals	109
5.2.2. Synthesis of zeolitic imidazolate framework-8 (ZIF-8) nanoparticles	110
5.2.3. Preparation of ZIF-8@PDMS MMMs	110
5.2.4. Preparation of ZIF-8@PDMS/PVDF nanofibrous composite membranes	111
5.2.5. Membrane characterizations	112
5.2.6. Aqueous-aqueous extractive experiments	113
5.3. Results and discussion	113
5.3.1. Confinement effect on dispersion of ZIF-8 nanoparticles	113
5.3.2. Chemico-physical characterization of ZIF-8@PDMS MMMs	115
5.3.3. Aqueous-aqueous extractive performance of ZIF-8@PDMS MMMs	118

5.3.4. Aqueous-aqueous extractive performance of ZIF-8@PDMS/PVDF nanofibrous composite membranes	122
5.3.5. Comparison of aqueous-aqueous phenol extractive performance of various membranes	127
5.4. Conclusions	130
CHAPTER 6. Conclusions and recommendations.....	132
6.1. Overall conclusions	132
6.2. Recommendations for future research	137
6.2.1. Development of new nanofibrous composite membranes	137
6.2.2. Exploitation of new application for nanofibrous composite membranes	139
References	141

LIST OF PUBLICATIONS

- *Journals*

- **M.-Y. Jin**, Y. Liao, C. H. Loh, C.-H. Tan, R. Wang, Preparation of polydimethylsiloxane–polyvinylidene fluoride composite membranes for phenol removal in extractive membrane bioreactor, *Ind. Eng. Chem. Res.*, 56 (2017) 3436-3445.
- **M.-Y. Jin**, Y. Liao, C.-H. Tan, R. Wang, Development of high performance nanofibrous composite membranes by optimizing polydimethylsiloxane architectures for phenol transport, *J. Membr. Sci.*, 549 (2018) 638-648.
- **M.-Y. Jin**, Y. Lin, Y. Liao, C.-H. Tan, R. Wang, Development of highly efficient nanofibrous composite membranes via confinement-assisted in situ self-assembly strategy for phenol removal, *J. Membr. Sci.*, (2018), manuscript in preparation.

- *Conference presentations*

- **M.-Y. Jin**, C. H. Loh, Y. Liao, R. Wang, S. Goh, B. J. L. Yeo, A.G. Fane, High flux aqueous-aqueous extractive membranes based on electrospun nanofibrous PVDF scaffolds and PDMS coating for removal of phenol, The North American Membrane Society (NAMS) 25th Annual Meeting, Boston, Massachusetts USA, 30 May - 3 June 2015 (Poster presentation).
- **M.-Y. Jin**, Y. Liao, R. Wang, Fabrication of polydimethylsiloxane (PDMS) thin film composite membranes

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July 2016 (Poster presentation).

LIST OF FIGURES

Figure 1-1. Growth of research activities on organic removal from wastewater streams presented by the number of publications recorded in referred database (Science Direct) per year.....	3
Figure 2-1. Schematic of an aqueous-aqueous extractive process.....	11
Figure 2-2. Reaction pathways for PDMS membrane preparation from (A) condensation reaction and (B) hydrosilylation reaction.....	21
Figure 2-3. Comparison of permeate transport process in a (A) solid-particle filled and (B) a porous-particle filled PDMS MMM.	23
Figure 2-4. Schematic diagram of an electrospinning setup.	31
Figure 3-1. The coating protocol for preparing the PDMS-coated PVDF composite membranes with tiered structures.....	50
Figure 3-2. FE-SEM images of PVDF electrospun nanofibrous membranes (ENMs): SL (A1: surface; A2: cross section; A3: enlarged cross section) and DL (B1: surface; B2: cross section; B3: enlarged cross section).....	55
Figure 3-3. Surface morphologies of PDMS-coated PVDF composite membranes made from different substrates: SL-A-DI (A1; A2: enlarged surface displaying the defects) and DL-A-DI (B: smooth surface completely covered by PDMS).....	58

Figure 3-4. FE-SEM images of PDMS-coated PVDF composite membranes fabricated by different PDMS preparation methods or pre-wetting agents, with varied PDMS intrusion levels. A1-A3: membrane DL-A-DI; B1-B3: membrane DL-B-DI; C1-C3: membrane DL-B-AA; D1-D3: membrane DL-B-DG21; E1-E3: membrane DL-B-DG11. A1-E1: cross sections, yellow arrows indicate location of PDMS (top distinct layers and intermediate layers); A2-E2: enlarged cross sections at the boundaries between top distinct PDMS layers and the intermediate layers; A3-E3: bottom surfaces.	60
Figure 3-5. Comparisons of (A) thickness, (B) OMTC, or k_0 , and (C) tensile modulus of various PDMS-coated PVDF composite membranes prepared using different pre-wetting agents.....	63
Figure 3-6. (A) Correlation of PDMS intrusion thickness and k_0 for composite membranes prepared with different pre-wetting agents; (B) schematic diagram showing the membrane resistance contributed by different layers of a tiered composite membrane; and (C) the electrical circuit analog for the resistance model.....	65
Figure 3-7. (A) Long term performance of aqueous-aqueous phenol extractive test, (B) EMBR performance, and (C) biofilm growth profile during EMBR test for membrane DL-B-DG11.	67
Figure 4-1. Reaction pathways and schematic diagrams of the as-synthesized dense PDMS membranes PA (A and B) and PB (C and D).....	82
Figure 4-2. ATR-FTIR spectrum of the dense PDMS membranes.....	83

Figure 4-3. (A) Chemical structures of the siloxy units present in polysiloxanes; Si 2p XPS spectra for the dense PDMS membranes: (B) PA, (C) PB and (D) PK.

..... 84

Figure 4-4. Phenol partition coefficients (K , gradients of the linear lines) of dense PDMS membranes prepared with condensation reaction (PA), hydrosilylation reaction (PB) and commercial S184 kit method (PK). 86

Figure 4-5. Schematic diagrams showing phenol transport through PDMS unit volume and the primary interactions between phenol molecules and PDMS: (A) PA with network architecture, (B) PB with a linear architecture and (C) PK with a combination of linear and branch architectures. 89

Figure 4-6. Phenol partition coefficients (K , gradients of the linear lines) of dense PDMS membranes PA prepared with low-mass PDMS precursor (PA-L), middle-mass PDMS precursor (PA-M) and high-mass PDMS precursor (PA-H).

..... 90

Figure 4-7. Phenol partition coefficients (K , gradients of the linear lines) of dense PDMS membranes PA-H prepared with 3 wt% TEOS (PA-H-3), 5 wt% TEOS (PA-H-5), 10 wt% TEOS (PA-H-10) and 20 wt% TEOS (PA-H-20).... 91

Figure 4-8. C 1s, O 1s and Si 2p XPS spectra of dense PDMS membranes PA-H-5 (A, C and E) and PA-H-20 (B, D and F). 93

Figure 4-9. Stress-strain curves and tensile moduli of the dense PDMS membranes PA prepared with different PDMS precursor molecular weights (A and B), and TEOS amounts (C and D). 94

Figure 4-10. (A) The cross-sectional images of PVDF nanofibrous support with a tiered structure; the surface morphologies of (B) a top ultrafine PVDF nanofibrous layer and (C) a bottom coarse PVDF nanofibrous layer.....	97
Figure 4-11. Surface and cross-section FESEM images of PDMS-coated nanofibrous composite membranes M1 (A1 and A2) and M2 (B1 and B2); EDX images of PDMS-coated nanofibrous composite membranes M1 (A3 and A4) and M2 (B3 and B4) showing levels of PDMS intrusion into PVDF substrate pores, blue color denotes the presence of Si element, and green color denotes the presence of F element.....	99
Figure 4-12. Long term performance of the nanofibrous composite membrane M1.	100
Figure 5-1. Schematic illustration of confinement-assisted in situ self-assembly strategy for preparation of ZIF-8@PDMS/PVDF nanofibrous composite membranes.....	109
Figure 5-2. Schematic diagram of fabrication protocol for ZIF-8@PDMS MMMs.....	111
Figure 5-3. DLS and FESEM analyses of ZIF-8 colloidal suspensions prepared by (A1) and (A2) confinement-assisted in situ self-assembly strategy and (B1) and (B2) conventional drying and redispersion process.	114
Figure 5-4. Surface FESEM images of the ZIF-8@PDMS MMMs: (A) ZIF-8@PDMS-0 (pristine PDMS membrane); (B) ZIF-8@PDMS-1 (1 wt% ZIF-8);	

(C) ZIF-8@PDMS-4 (4 wt% ZIF-8) and (D) ZIF-8@PDMS-8 (8 wt% ZIF-8).	117
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Figure 5-5. (A) XRD and (B) FTIR patterns of pristine PDMS membrane, ZIF-8@PDMS-4 and pure ZIF-8 nanocrystals.	118
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Figure 5-6. Schematic diagram of an aqueous-aqueous phenol extractive process based on a pseudo “tri-mode” transport mechanism for a ZIF-8@PDMS MMM.	120
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Figure 5-7. The effect of ZIF-8 loadings (0, 1, 2, 4 and 8 wt%) on the aqueous-aqueous phenol extractive performance of ZIF-8@PDMS MMMs.	121
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Figure 5-8. Surface FESEM images of (A) a tiered PVDF electrospun nanofibrous support; (B) ZIF-8@PDMS-4/PVDF nanofibrous composite membrane M1; and (C) cross-sectional FESEM image of M1.	124
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Figure 5-9. (A) surface and (B) cross-sectional EDX analyses of ZIF-8@PDMS-4/PVDF nanofibrous composite membrane M1.	125
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Figure 5-10. Long-term performance of the nanofibrous composite membranes M1 and M2.	127
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Figure 6-1. Chemical structures of polymeric materials.	139
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LIST OF TABLES

Table 2-1. Effects of fabrication parameters on nanofiber formation [115, 116].	33
Table 3-1. Dope compositions and characteristics of PVDF nanofibrous substrates.	48
Table 3-2. Effects of substrate pore size, PDMS preparation method and pre- wetting agent.....	57
Table 3-3. Phenol extractive performance of various membranes.....	70
Table 4-1. Overall mass transfer coefficients, k_0 , of selected dense PDMS membranes from aqueous-aqueous phenol extractive tests.....	96
Table 4-2. Aqueous-aqueous phenol extractive performances of PDMS-coated nanofibrous composite membranes.....	100
Table 4-3. Comparison of aqueous-aqueous phenol extractive performance of various membranes.	102
Table 5-1. Aqueous-aqueous phenol extractive performance of nanofibrous composite membranes.	126
Table 5-2. Comparison of aqueous-aqueous phenol extractive performance of various membranes.	129

LIST OF SYMBOLS

ATR-FTIR	Attenuated total reflectance Fourier transform infrared
b	Block
c	Total solid concentration of coating solution
CA	Cellulose acetate
CNT	Carbon nanotube
DBTDL	Dibutyltin dilaurate
DI	Deionized
DL	Dual-layer
DLS	Dynamic light scattering
DMAc	Dimethylacetamide
DMF	N,N-dimethyl formamide
EDX	Energy dispersive X-ray
EMBR	Extractive membrane bioreactor
ENM	Electrospun nanofibrous membrane
et al.	Et alii
etc.	Et cetera
FESEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared
h	Hour
HL	Hydraulic boundary layer
h_d	Dry membrane thickness
HPDMS	Hydroxyl-terminated polydimethylsiloxane

h_w	Wet membrane thickness (knife gap setting)
J_s	NaCl flux
k_0	Overall mass transfer coefficient
LiCl	Lithium chloride
MARS	Membrane aromatic recovery system
MBR	Membrane bioreactor
MMM	Mixed-matrix membrane
MOF	Metal-organic framework
nm	Nanometer
OMTC	Overall mass transfer coefficient
PA	Polyamide
PAN	Polyacrylonitrile
PC	Polycarbonate
PDMS	Polydimethylsiloxane
PDMS-MHS	Poly(dimethylsiloxane-co-methylhydrosiloxane)
PEI	Polyetherimide
PEO	Poly(ethyleneoxide)
PES	Polyethersulfone
PET	Poly(ethylene terephthalate)
pH	Potential of hydrogen
PI	Polyimides
PLA	Poly lactide
PMMA	Poly(methyl methacrylate)
ppb	Parts-per-billion

ppm	Parts-per-million
PRO	Pressure retarded osmosis
PS	Polystyrene
Pt	Platinum
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVA	Poly(vinylalcohol)
PVC	Poly(vinyl chloride)
PVDF	Polyvinylidene fluoride
PVMS	Poly(vinylmethylsiloxane)
PVP	Polyvinylpyrrolidone
RH	Relative humidity
S184 kit	Sylgard® 184 silicone elastomer kit
Si	Silicon
Si-O	Siloxane
SL	Single-layer
THF	Tetrahydrofuran
TEOS	Tetraethyl orthosilicate
TFC	Thin film composite
TFC-HF	Thin film composite hollow fiber
US EPA	United States Environmental Protection Agency
VOC	Volatile organic compound
VPDMS	Vinyl-terminated polydimethylsiloxane
wt	Weight

XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZIF-8	Zeolitic imidazolate framework-8
Greek	
Δc	Change of NaCl concentrations in the receiving solution
μm	Micrometer
ρ_d	Dry membrane density
ρ_w	Coating solution density

ABSTRACT

Treatment of organic-containing wastewater has drawn increasing attention in recent years. Among the major pollutants, phenol has become a rising concern due to its high toxicity and carcinogenicity. On the other hand, phenol is recognized as a valuable chemical for industrial application such as production of phenolic resins. Hence, research and development of treatment processes for effective removal and recovery of phenol from wastewater before discharge is of high interest. Among all the existing technologies, membrane process, particularly, the membrane-based aqueous-aqueous extractive process, has been evidenced to be a promising technology ascribed to its appealing features including independent operation of the receiving solutions, point-source treatment of industrial effluents and low energy consumption. However, one of the main challenges that impedes the application of the aqueous-aqueous extractive processes is the shortage of specially designed membranes capable of extracting the organic compounds into the receiving medium with high efficiency and excellent stability.

This study aims to develop high-performance nanofibrous composite membranes for phenol removal in the aqueous-aqueous extractive processes. Three generations of polydimethylsiloxane/polyvinylidene fluoride (PDMS/PVDF) nanofibrous composite membranes have been developed with focus on fabrication of highly porous tiered electrospun nanofibrous membranes (ENMs) as the supportive layers, optimization of the PDMS macromolecular architectures through different cross-linking pathways, and incorporation of ZIF-

8 as transport fillers in the PDMS matrix, respectively. The developed nanofibrous composite membranes exhibited progressive enhancement in k_0 (overall mass transfer coefficient, OMTC) values from $4.1 \pm 0.3 \times 10^{-7}$ m/s in the 1st-generation membrane, $18.3 \pm 1.3 \times 10^{-7}$ m/s in the 2nd-generation membrane, to $35.7 \pm 1.1 \times 10^{-7}$ m/s in the 3rd-generation membrane for phenol removal from wastewater. In addition, the effects of PDMS coating solution preparation, pre-wetting agent for substrate, PDMS precursor molecular weight, cross-linker amount, ZIF-8 addition protocol, and ZIF-8 loading on the phenol removal efficiency were studied systematically. In conclusion, this thesis presents a detailed study on the design and development of high-performance nanofibrous composite membranes for phenol removal in the aqueous-aqueous extractive processes. The findings obtained from this study provide insights and guidelines for fabricating highly efficient membrane materials for organic removal and recovery in various membrane extractive processes.

CHAPTER 1. Introduction

1.1. Background

The increasing scarcity of water resources as well as contamination of waters by organic pollutants have drawn more and more attention in recent years [1]. A USA research reported that 80% of the studied streams were contaminated by organic pollutants [2]. Among the major contaminants, phenol has become a rising concern. Phenol exists in the effluents of many industries such as petrochemicals (2.8-1220 ppm), coal manufacturing (9-6800 ppm), paper industries (0.1-1600 ppm), coking processing (28-3900 ppm), oil refineries (6-500 ppm), plastics, textile, paint, wood products, resin manufacturing and pharmaceuticals [3-5]. Due to its high toxicity and carcinogenicity, phenol has been listed as a top priority pollutant by United States Environmental Protection Agency (US EPA) [6, 7]. Some water purity standards for phenol are <0.1 ppm in non-chlorinated water, <1-2 ppb in chlorinated water, <1-2 ppb in surface water and <0.5 ppb in drinking water [7-11]. On the other hand, phenol is regarded as a valuable chemical in various industrial application such as production of polycarbonates, epoxies, nylon, detergents, herbicides, phenolic resins and pharmaceutical drugs [12, 13]. Therefore, utilizing economically feasible and reliable technologies for efficient removal and recovery of phenol from wastewater streams before discharge is highly demanded.

Technologies currently available for phenol treatment include: (1) traditional methods such as distillation [14, 15], extraction [16], adsorption [17],

chemical oxidation [18, 19], and biodegradation [20]; (2) advanced methods such as photo oxidation processes [21, 22] and membrane separation technologies [23, 24]; and (3) hybrid systems which combine traditional and advanced techniques, for example, reverse osmosis coupled with adsorption process [25], membrane bioreactor (MBR) [26], extractive membrane bioreactor (EMBR) [27-29], membrane aromatic recovery system (MARS) [30] and membrane pervaporation [31]. As presented in **Figure 1-1** which displays the number of publications on organic removal from wastewater streams reported from Jan. 2007 to Dec. 2016, research and development on treatment of organic-containing wastewaters has attracted increasing attention over the past decade with approximately 19% dealing with treatment of phenolic pollutants. However, less than 10% of the published papers utilized membrane technologies to treat the phenol-containing wastewaters. Thus, there is much room for research and development on processes making use of membrane separation technologies for phenol treatment.

Figure 1-1. Growth of research activities on organic removal from wastewater streams presented by the number of publications recorded in referred database (Science Direct) per year.

Among all the membrane technologies, the aqueous-aqueous extractive process has been recognized as a promising technology for removal and recovery of toxic and recalcitrant organic contaminants in wastewaters [32, 33]. This process exhibits advantages including low energy consumption, low operating costs and easy scalability. One typical variation of the aqueous-aqueous extractive process is an EMBR system with biomedium as the receiving solution [1, 29, 34, 35]. Owing to its special configuration, EMBR offers unique features such as operation at ambient temperature and pressure, independent biodegradation of permeated organic pollutants under optimum conditions, and generation of effluents with small quantity [27]. One of the main technical challenges that impedes application of the aqueous-aqueous extractive processes, especially the EMBR process, is the shortage of specially designed membranes

capable of extracting the target organic compounds into the receiving solution with high efficiencies and excellent stabilities. Silicone rubber, particularly polydimethylsiloxane (PDMS), has been employed as the dominant membrane material in most aqueous-aqueous extractive processes due to its organophilicity and hydrophobicity allowing preferential transfer of organics while rejecting water and inorganics [32, 34, 36, 37]. However, the mass transfer efficiency of the PDMS-based membranes is far from satisfaction and should be improved significantly.

The PDMS-based composite membranes are generally more efficient than the PDMS dense membranes as the overall membrane resistance is greatly reduced by employing the porous membrane substrates. One conventional method used to fabricate the porous substrate is the phase inversion technique, but it is difficult to produce a substrate with a highly porous structure while maintaining membrane robustness and integrity [38]. As an alternative, electrospinning is a versatile and simple technique to generate highly porous nanofibrous substrates [39-42]. Notable features of electrospun nanofibrous membranes (ENMs) include interconnected pore structure and large porosity, which can reduce the membrane resistance significantly. The membrane property and structure could be easily tuned by adjusting the polymer dope formulation and varying the electrospinning parameters [41]. To date, nanofibrous substrates have been utilized as scaffold-like highly porous supports to prepare thin film composite (TFC) membranes for various membrane processes such as ultrafiltration, nanofiltration, forward osmosis and pressure retarded osmosis [42-47]. In this research, nanofibrous composite membranes comprising a PDMS-

based dense selective layer and a highly porous polyvinylidene fluoride (PVDF) electrospun nanofibrous support were designed, fabricated and evaluated for phenol removal in aqueous-aqueous extractive processes and an EMBR process as a typical example.

1.2. Research objectives

This research aims to develop nanofibrous composite membranes for phenol removal in aqueous-aqueous extractive processes and an EMBR process as a typical example. Specifically, the primary objectives of the study include:

- (1) To construct nanofibrous composite membranes making use of highly porous tiered ENMs as the supports for phenol removal in an EMBR process as a first trial:
 - To investigate the impact of substrate pore size on preparing composite membranes by fabricating a single-layer symmetric nanofibrous support and a dual-layer nanofibrous support with tiered structure;
 - To study the effect of PDMS pre-cross-linking on the composite membrane fabrication by developing different PDMS preparation methods;

- To examine the influence of pre-wetting treatment on the mitigation of PDMS intrusion into substrate pores by employing different pre-wetting agents.
- (2) To develop high-performance nanofibrous composite membranes by optimizing PDMS macromolecular structures for phenol removal in an aqueous-aqueous extractive process:
- To fabricate dense PDMS membranes with different macromolecular structures by varying cross-linking reaction pathways;
 - To confirm the PDMS macromolecular structures by ATR-FTIR and XPS analyses;
 - To optimize the phenol extraction efficiency of the dense PDMS membranes by varying PDMS precursor molecular weight and cross-linker amount;
- (3) To develop highly efficient nanofibrous composite membranes by incorporating ZIF-8 in the PDMS matrix for phenol removal in an aqueous-aqueous extractive process:
- To realize nanoscale dispersion of ZIF-8 via a facile confinement-assisted in situ self-assembly strategy;

- To optimize the membrane extraction efficiency by varying the ZIF-8 loading;
- To image the phenol transport behaviour across the membrane by proposing a pseudo “tri-mode” transport mechanism.

1.3. Thesis outline

This thesis contains six chapters, which are highlighted as follows:

Chapter 1: *Introduction* – Background information and the objectives of this research are provided.

Chapter 2: *Literature review* – A concise literature review is presented in three areas. Firstly, the aqueous-aqueous extractive process is briefly introduced, followed by detailed elaboration of a typical EMBR process, which includes EMBR concept and advantages, EMBR applications and challenges, and current status of EMBR membranes. Secondly, PDMS membranes are reviewed based on the preparation of PDMS membranes, development of filled PDMS mixed-matrix membranes (MMMs), and development of PDMS-based composite membranes. Thirdly, the state of the art of ENMs are presented. Advantages of ENMs are introduced, followed by fabrication of ENMs, and design and development of ENMs via manipulation of fabrication parameters and exploitation of electrospinning techniques.

Chapter 3: *Fabrication of nanofibrous composite membranes for phenol removal in an extractive membrane bioreactor* – PDMS-coated nanofibrous composite membranes making use of highly porous tiered PVDF ENMs as the supports are fabricated for phenol removal in an EMBR process. The effects of substrate pore size, coating solution preparation and pre-wetting agent on the phenol removal efficiency in an EMBR process and on the mechanical properties of the resultant composite membranes are systematically investigated.

Chapter 4: *Development of high-performance nanofibrous composite membranes by optimizing polydimethylsiloxane architectures for phenol removal* – Three types of cross-linking reactions including condensation, hydrosilylation and commercial kit reactions are adopted to prepare dense PDMS membranes with different polymer architectures. The effects of PDMS precursor molecular weights and cross-linker amounts on the resultant PDMS membrane properties including phenol partition coefficient, mechanical strength and aqueous-aqueous phenol extractive performance are studied systematically. By employing the optimum PDMS formulation, a highly efficient PDMS-coated nanofibrous composite membrane is fabricated and evaluated in aqueous-aqueous phenol extractive tests.

Chapter 5: *Development of highly efficient nanofibrous composite membranes via confinement-assisted in situ self-assembly strategy for phenol removal* – A highly efficient ZIF-8@PDMS/PVDF nanofibrous composite membrane is designed and fabricated via a confinement-assisted in situ self-

assembly technique for phenol removal in an aqueous-aqueous extractive process. Nanoscale dispersion of ZIF-8 is realized by the confinement effect of solvation layers and PDMS chains. The membrane extraction efficiency is optimized by varying the ZIF-8 loading. A pseudo “tri-mode” transport mechanism is proposed to image the phenol transport behaviour across the membrane.

Chapter 6: *Conclusions and recommendations* – The key findings of this research are summarized, followed by recommendations for future work, including development of new nanofibrous composite membranes and exploitation of new applications for nanofibrous composite membranes.

CHAPTER 2. Literature review

2.1. Aqueous-aqueous extractive process

2.1.1. Introduction

Treatment of organic-containing wastewater has drawn increasing attention in recent years [1]. Existing technologies for organic treatment include adsorption, solvent extraction, thermal decomposition, biodegradation, oxidation and membrane separation [1]. Among them, the membrane-based aqueous-aqueous extractive process has been evidenced to be a promising technology ascribed to its appealing features, which include: (1) the separation of the feed and receiving solutions by the membrane that allows independent operation of the latter under optimized conditions regardless of the wastewater compositions. The superiority of this configuration is exemplified by an EMBR where the receiving solution is biomedium [28, 29, 37]; (2) the capability to offer more specific and efficient point-source treatment of individual industrial effluent unlike the centralized classical techniques [37, 48]; and (3) the low energy consumption due to operation at room temperature and atmospheric pressure [28, 29, 37, 49].

Figure 2-1 shows the schematic diagram of an aqueous-aqueous extractive process. In the process, the target organic compounds transfer from the feed wastewater to the aqueous receiving solution through a dense membrane according to the solution-diffusion mechanism [28, 49, 50]. A variety of receiving solutions such as biological cultures and alkaline (or acidic) solutions

can be employed to strip the permeated organics, maintaining the organic concentration driving force imperative for mass transfer across the membrane [28, 29, 50]. The ideal characteristics of the dense membrane for the aqueous-aqueous extractive process should comprise three aspects: (1) high organophilicity to extract the target organics from the aqueous feed effectively; (2) strong hydrophobicity to completely reject water and inorganic components; and (3) low resistance to ensure efficient organic passage. Hence, design and development of membranes with enhancement in either or all aspects is desired in order to enhance the membrane extractive performance for the targeted organic compounds.

Figure 2-1. Schematic of an aqueous-aqueous extractive process.

In order to get a deeper understanding of the aqueous-aqueous extractive systems, a specific process, namely an EMBR process with biomedium as the

receiving solution, is selected for detailed elaboration in the following section. As one of the most attractive and promising variations, the understanding of the EMBR process will provide insights into developing more advanced and efficient aqueous-aqueous extractive systems for treatment of diverse organic-containing wastewaters.

2.1.2. Extractive Membrane Bioreactor (EMBR)

2.1.2.1. Concept and advantages of EMBR

EMBR was first developed by Professor Andrew Guy Livingston and co-workers in 1993 as a novel system to extract and biodegrade recalcitrant organic pollutants present in wastewater [37, 51]. EMBR is a combination of a membrane process and a biological process, which differs from the conventional membrane bioreactor (MBR) in the function of the membrane. In an EMBR, the membrane operates to selectively transfer the organic pollutants from the wastewater feed side to the permeate side via an aqueous-aqueous extractive process, rejecting water or inorganic components. The permselectivity of the extractive membrane is based on solution-diffusion mechanism in which the organic compounds have a higher affinity towards the membrane than water or inorganic compounds and thus could be preferentially adsorbed to the membrane and then diffuse to the permeate side for subsequent biodegradation. Through the removal of permeated organics in the receiving solution, the biodegradation also helps generate and maintain a high concentration gradient across the membrane, driving the organic mass transfer.

The EMBR configuration possesses several advantageous and unique features including:

- (1) Operation at room temperature and atmospheric pressure;
- (2) The separation of the specialized microbial organisms from the wastewater feed by the membrane. This allows the biodegradation of the transferred organics to be performed under independent and optimized conditions through pH control and nutrient addition, etc., without interference from the wastewater feed which usually exhibits high salinity, extreme pH and strong corrosiveness. It is noted that, by employing this configuration, pre-treatment (such as dilution and neutralization) of the feed wastewater stream could be eliminated;
- (3) Consistently high organic concentration difference across the membrane due to ongoing biodegradation on the receiving side;
- (4) Longer cell residence time due to separation of the biological medium from the wastewater stream, which allows complete biodegradation of the organic compounds to take place;
- (5) Biodegradation of only extracted organics instead of treating the whole volume of the wastewater in the case of MBR. This makes the working volume of an EMBR much smaller than that of an MBR;

- (6) A more efficient biodegradation process as only trace or small amounts of organic compounds are treated; and
- (7) Production of only a small amount of effluents ($< 1\%$ of the feed solution), which lowers the burden for post-treatment and subsequent waste discharge [32, 34, 36, 37, 48, 52-54].

The above-mentioned characteristics of the EMBR system make it a promising treatment technique for wastewater streams contaminated with recalcitrant organic pollutants.

2.1.2.2. EMBR applications and challenges

As a result of the above-mentioned advantages, the EMBR process has been demonstrated to be of high value to treat industrial wastewater streams which are acidic, alkaline, saline or contain hostile inorganic salts impairing the functioning of microorganism. EMBR can be employed to treat a great number of toxic organic pollutants ranging from aromatic compounds (e.g. phenol [28, 29, 37], nitrobenzenes [35, 51], anilines [34, 48, 55] and monochlorobenzene [54]) to aliphatic compounds (e.g. dichloroethane [52, 56], 1,3-dichloropropene [57] and dichloromethane [58, 59]). Most of these compounds studied are hydrophobic or marginally soluble organic chemicals. The EMBR application for treatment of wastewaters containing volatile organic compounds (VOCs) has been successfully extended to treating VOC-contaminated waste gases, and superior volumetric removal efficiency has been achieved compared to an alternative bioscrubbing process [56]. A variation of the EMBR used an

anaerobic bioprocess to treat tetrachloroethene in a synthetic wastewater [60]. In order to enhance mass transfer by reducing the biofilm growth on the membrane, an anoxic extractive membrane bioreactor employing nitrate as an electron acceptor rather than oxygen was developed [61]. In addition, a modified EMBR with sulfate-reducing bacteria was applied to treat heavy metal contaminated wastewaters [62].

Despite its great potential in removal of organics, EMBR has not been applied in industry largely due to: (1) the lack of an efficient extractive membrane that can selectively transfer the organic contaminants with enhanced mass transport efficiency and stable performance while entirely rejecting water and inorganics; (2) the lack of proper microorganisms that can biodegrade the toxic and recalcitrant organic pollutants extensively and effectively; and (3) the poor organic trans-membrane efficiency resulting from excessive biofilm growth on the membrane surface [1]. Significant efforts are required to overcome these challenges for commercial applications of EMBR. In particular, design and fabrication of novel extractive membranes are of high value, as the membranes are recognized as the rate-limiting step in the EMBR process.

2.1.2.3. Current status of EMBR membranes

➤ *Silicon-based rubbers*

The membranes utilized in EMBR processes should be able to extract the target organic compounds into the receiving biomedium with high efficiencies and excellent stabilities while being impermeable to water and inorganics. Owing

to its organophilicity and hydrophobicity, silicone rubber has been employed as the dominant membrane in most EMBR processes [32, 34, 36, 63]. Silicone rubber, particularly polydimethylsiloxane (PDMS), comprising siloxane (Si-O) backbones with methyl groups substituted on Si atoms, can serve as a barrier to water, inorganic salts and other harsh components (e.g. acids and carried-over catalysts), while preferentially extracting organic chemicals present in the aqueous feed solutions [37, 51]. Organic molecules can transport through the free volume of PDMS by the solution-diffusion mechanism, which involves three steps: adsorption at the upstream boundary, diffusion through the bulk membrane and desorption away from the downstream boundary [29].

In the earlier EMBR studies, typical silicone rubber membranes possessed a rather large thickness (at least 0.2 mm) [37, 61, 64]. When the target organic pollutants were hydrophobic (e.g. benzene and toluene) with a high affinity towards the polymeric membranes, the membrane resistances were relatively small compared to the hydraulic boundary layer (HBL) resistances [35, 51]. However, when treating less hydrophobic organic molecules (e.g. aniline and phenol), the membrane resistances usually dominated over the HBL resistances [34, 37]. The large thickness of silicone rubbers led to a high mass transfer resistance and limited the application of EMBR to remove the less hydrophobic organics such as phenol.

In addition to PDMS, a less commonly used variation of silicon-based rubber, i.e. poly(vinylmethylsiloxane) (PVMS), has also been attempted as the membrane material [65]. Compared to PDMS, PVMS offered higher diffusion

rate and removal efficiency for the model compound (phenol molecules). This phenomenon could be ascribed to the different polymeric structures of the two rubbers. Larger steric hindrance was present in PVMS, giving rise to increased number of the molecular level micropores and thus the enhanced phenol diffusion efficiency. However, pinholes were observed in PVMS after a 3-month operation in basic solution ($\text{pH} = 13.5$) while structural changes were not detected in PDMS after a similar operation period. This revealed that PVMS was not suitable for application in the long-term process under harsh conditions (e.g. strong base).

➤ *Thin film composite (TFC) membranes*

As mentioned above, one drawback of the silicone rubber membranes is the large membrane thickness resulting in a high mass transfer resistance. In consideration of reducing the membrane resistance and improving the mass transfer efficiency, TFC membranes comprising a top selective layer and a bottom support layer have been developed [29, 33]. The top selective layer should be thin, dense and hydrophobic, as required by its function to extract organic pollutants while rejecting water and inorganic components in the wastewater feed side. The bottom support layer should be highly porous and as thin as possible to reduce the mass transfer resistance for organic removal, while still providing sufficient mechanical support. In addition, the support layer should adhere well to the top selective layer to maintain the membrane integrity.

Cocchini et al. studied the organic mass transfer through TFC membranes (X-Flow BV, The Netherlands) [33]. The membranes comprised a 2- μm thick PDMS skin layer coated on the inner surface of a tubular polyethersulfone (PES)

support with an asymmetric microporous structure. The PES support was highly porous (up to 85% bulk porosity) and possessed large pore size (0.1-10 μm), giving rise to high wettability and large cross-sectional area for the organic transport. The TFC membranes were employed to extract various organic compounds including toluene, 2-nitrotoluene, 1,3-dichloropropene, 3-chloro-2-methylaniline, 2-chloroaniline, phenol and 1,3-dichloropropan-2-ol from aqueous solutions. It was shown that the affinity of the organic compounds towards the PDMS layer had negligible impact on the organic transfer rate across the TFC membranes, which could be ascribed to the insignificant mass transfer resistance contributed from the thin PDMS layer. As a result, under the same operation conditions, the TFC membranes displayed an overall mass transfer coefficient (OMTC, k_o) that was up to one order of magnitude higher than that of the 350- μm thick PDMS membranes for the extraction of less hydrophobic compounds [32, 33]. In addition, it was found that TFC membranes behaved asymmetrically when the feed solution had a high ionic strength. Higher organic flux was obtained when the saline feed solution was circulated on the active PDMS-coated side than the porous substrate side of the membrane. This implied the significance of operation and design of TFC membrane processes for the removal of organic contaminants from saline feed solutions.

Recently, Loh et al. have developed a series of thin film composite hollow fiber (TFC-HF) membranes to study the phenol mass transfer in EMBR process [29]. The TFC-HF membranes were prepared by coating a thin PDMS layer onto a polyetherimide (PEI) HF substrate, and coating parameters were varied to prepare membranes with different PDMS intrusion levels. It was demonstrated

that the partial PDMS-intruded composite membrane performed around 3 times better than the completely PDMS-intruded counterpart. This was due to the fact that PDMS intrusion into the substrate pores led to a denser membrane structure and thus increased the membrane resistance. Nevertheless, a slight PDMS penetration into the substrate was necessary and beneficial to maintain composite membrane integrity and stability. The TFC-HF membranes exhibited a stabilized OMTC of about 7.5×10^{-7} m/s for phenol removal in the long-term (more than 250 h) EMBR operation, outperforming the commercial silicone rubber tubular membranes with 7.5-time enhancement [32]. However, thick biofilm was observed on the receiving side of the composite membranes, resulting in decreased mass transfer efficiency in the EMBR operation. This had implications in process optimization to control biofilm growth so as to improve organic removal efficiency in EMBR system.

2.2. Polydimethylsiloxane (PDMS) membranes

2.2.1. Preparation of PDMS membranes

Generally, two types of cross-linking reaction pathways exist for PDMS preparation [66-68]:

- (1) In the condensation reaction pathway, hydroxyl-terminated PDMS (HPDMS) precursors react with multi-functional cross-linkers such as tetraethyl orthosilicate (TEOS) under catalysis (e.g. dibutyltin dilaurate, DBTDL) to form the PDMS membranes. As depicted in **Figure 2-2A**, the TEOS cross-linkers bridge the di-functional linear PDMS precursors as

four-armed junction points, resulting in a three-dimensional network structure. Depending on the amount ratios between precursors and cross-linkers, the four active ethoxy groups in each TEOS could be fully or partially replaced by the hydroxyl-terminated PDMS precursors;

- (2) In the pathway of hydrosilylation reaction, the PDMS membranes can be synthesized by reacting vinyl-terminated PDMS (VPDMS) precursors with hydrosilyl-containing cross-linkers such as trimethylsilyl-terminated poly(dimethylsiloxane-co-methylhydrosiloxane) (PDMS-MHS) under Pt catalysis. A linear structure linked by $\text{CH}_2\text{-CH}_2$ groups is obtained for the membranes as shown in **Figure 2-2B**.

Both methods have been adopted to prepare PDMS-based membranes for applications such as gas separation [66], pervaporation [67] and solvent-resistant nanofiltration [68].

comprises a vinyl-type PDMS precursor and a hydrosilyl-type cross-linker [68]. Hence, it could be inferred that a hydrosilylation reaction similar to that depicted in **Figure 2-2B** should be involved in the kit method. Structures including linear, branch or a combination of these two could exist in the kit-prepared PDMS membranes dictated by the exact formulation of the commercial kit.

2.2.2. Development of filled PDMS mixed-matrix membranes (MMMs)

Although PDMS macromolecular structures can be tailored by employing different types of cross-linking reactions, the resultant property and membrane purification performance of the pristine PDMS membranes are still far from satisfaction, due to the intrinsic organophilicity and polymer chain mobility of PDMS [71].

The technique of MMMs with incorporation of transport fillers into the polymer matrix has emerged as one promising synthetic strategy to develop high-performance membrane materials by combining the flexibility and easy processability of polymer materials with the inherent superior separation properties of filler materials [72]. Particularly, filler particles such as carbonaceous frameworks [73, 74], silica [75, 76], zeolite [77], silicalite [78, 79] and metal-organic frameworks (MOFs) [80, 81] have been incorporated into the PDMS matrix to fabricate MMMs for utilization in many membrane processes such as pervaporation with improved performance.

Among all types of fillers, MOFs, comprising inorganic units bridged by organic ligands, are being recognized as the most fascinating candidates

attributed to their high surface area, large porosity and pore volume, tunable pore size and shape, facile functionalization, and good compatibility with polymers [82-84]. As porous fillers, MOFs can improve permeate transport efficiency by two major mechanisms: (1) elongating the transport pathways via the interface created between the fillers and the polymeric phase, which is similar to the usual mechanism involved in the case of solid fillers (such as silica), and (2) providing additional pathways for permeating molecules to pass through their internal cages, which can contribute significantly to the permeation enhancement [85, 86]. The comparison of permeate transport pathways offered by solid and porous fillers is illustrated in a schematic diagram as depicted in **Figure 2-3**.

Figure 2-3. Comparison of permeate transport process in a (A) solid-particle filled and (B) a porous-particle filled PDMS MMM.

Although MOFs are promising transport fillers for membrane performance enhancement, the fabrication of MOF filled PDMS MMMs must

conquer several challenges so as to afford the desired morphology, mechanical strength, chemical stability and membrane purification properties. Three major challenges exist including: (1) homogeneous dispersion of MOF particles in PDMS matrix with minimum agglomeration; (2) good membrane integrity with defect-free MOF/PDMS interface; and (3) good compatibility of MOF with PDMS [87]. Several methods such as one-pot MMM synthesis via a common solvent [88], addition of ionic liquid to strengthen the particle-polymer interactions [89], particle fusion approach [90] and in situ particle crystallization in the polymer system [91] have been developed to tackle the challenges in MMM fabrication. Although good dispersion and compatibility of MOFs in the MMMs can be realized by these synthetic strategies, the required pre-treatments greatly complicate the overall membrane fabrication procedures and thus limit the practical implementation of the protocols [92, 93]. In addition, MOFs have relatively high costs which could impede the utilization in the development of MOF filled MMMs [94, 95]. Therefore, developing facile, simple and, conducive and cost-effective methods for the synthesis of defect-free and uniform MMMs with high separation performance is still a scientific and practical challenge.

2.2.3. Development of PDMS-based composite membranes

As mentioned in **Section 2.1.3**, PDMS-based composite membranes are regarded as a favourable alternative to the silicone rubber membranes attributed to the better fulfilment of practical requirements and enhancement of membrane performance. The PDMS-based composite membranes are usually fabricated by means of coating a thin PDMS skin layer onto a porous substrate, which is

capable of reducing the overall membrane resistance significantly. To ensure the formation of defect-free selective layers, a stable and reproducible method to coat the PDMS layers on the porous substrates is essential [28, 49]. Several coating methods have been reported in the literatures to fabricate composite membranes including:

- (1) Dip coating: dip coating is the most common and convenient approach to prepare the selective layers in both the research laboratories and industrial plants. It offers the advantages of simplicity, low cost, free of waste and easy scalability. In the dip-coating process, the substrate is dipped into the coating solution sequentially and withdrawn at a fixed velocity. After evaporation of the solvent, a thin layer of the non-volatile species is deposited on the substrate. The coating layer thickness is dictated by the coating solution surface tension, concentration and viscosity, as well as the dipping time and withdrawal speed. Coating thickness of 50-500 nm could be obtained. Repeated dipping can be performed to produce thicker coatings though-peeling usually occurs during drying of these successive layers. In addition, it is difficult to fabricate coating layers with uniform thickness especially when the solvent is too volatile or has a high surface tension. Moreover, it is very challenging to coat on highly porous substrates as penetration of the coating solution into the substrate pores often occurs resulting in denser membrane structures and higher membrane resistance [96-100];

- (2) Spin coating: spin coating is a fast and simple technique to fabricate thin and uniform top selective layers with well controlled thickness (0.2-2 μm), and it has numerous applications in areas such as nanotechnology and electronics. The coating thickness is largely affected by parameters including spinning rate and time, coating solution viscosity and density, solution concentration as well as the solvent volatility. In the spin-coating process, excessive coating solution is first applied on the substrate surface. The substrate is subsequently spun up to a certain rotational speed generating centrifugal forces which lead to radial coating outwards. The excess coating solution is spun off the substrate from the edge. The film thinning continues until the equilibrium thickness is reached. Finally, the spinning slows down and the coating layer thinning is controlled by solvent evaporation. Although thin and uniform coating layers could be obtained by the spin-coating technique, the scalability of the process is limited [97, 99, 101-104];
- (3) Knife coating (casting): knife-coating method is a facile coating technique, and the membrane thickness could be controlled by adjusting the gap setting of the coating knife. In the coating process, the flat-sheet substrate is first fixed onto a clean glass plate with a tape. Subsequently, the coating solution is spread onto the substrate surface using an automatic film applicator with a pre-determined coating knife height. The dry membrane thickness could be controlled by adjusting the knife gap setting based on the following empirical equation:

$$h_d \times \rho_d = 0.5 \times c \times \rho_w \times h_w \quad \text{Eq. 2-1}$$

where h_d (μm) and h_w (μm) are the dry membrane thickness and wet membrane thickness (knife gap setting), respectively, ρ_d (g/cm^3) and ρ_w (g/cm^3) are the dry membrane and coating solution densities, respectively, c is the total solid concentration (by weight) of the coating solution. After coating, the solvent of the coating solution is evaporated by drying the membrane in a fume hood at room temperature for a certain time. Subsequent treatment such as heat cure is conducted if necessary, which completes the composite membrane fabrication [105-107];

- (4) Spray coating: spray coating has emerged as a versatile technique to produce a thin and uniform coating layer in a simple, fast and reproducible way. The whole spray coating process can be conducted in an automatic manner utilizing an automatic dispenser robot programmable through a teaching pendant, which ensures the high reproducibility of this technique. In the spray-coating process, a substrate is first mounted onto a glass plate and fixed by tapes. The glass plate is then placed horizontally inside the spray coating machine. The coating solutions are injected via a syringe pump to an air atomizing nozzle and/or an ultrasonic atomizing nozzle through which fine polymer mists are generated and sprayed onto the horizontal-situated substrate. The coating solutions can be sprayed in such patterns as rectangle, where parameters including horizontal spraying speed, spacing between spraying lines,

vertical distance between the substrate and the spraying nozzles, and syringe pump flow rate are finely tuned in order to produce a uniform and defect-free coating layer. More coating cycles can be applied if it is necessary to cover the surface defects. The coated membrane is dried in a fume hood for certain time to evaporate the remaining solvent at room temperature, and is then post-treated, if necessary, for completion of the membrane fabrication [80, 108-111].

Depending on the specific characteristics of the PDMS coating solutions and the desired specifications of the resultant composite membranes, an appropriate coating technique can be adopted to fabricate the targeted PDMS-based composite membranes for application in various water purification processes.

2.3. Electrospun nanofibrous membranes (ENMs)

2.3.1. Advantages of ENMs

As discussed in **Section 2.2.3**, from the practical point of view, it is highly valuable to develop an asymmetric PDMS membrane supported by a substrate for further performance enhancement. The composite membrane should be designed to combine the perm-selective property of the PDMS membrane and the highly permeable feature of a porous membrane, such that the overall membrane resistance could be significantly reduced while maintaining the selective transfer of the target molecules.

One conventional method used to fabricate a porous membrane is the phase inversion technique [38], but it is difficult to produce a membrane with a highly porous structure while maintaining membrane robustness and integrity. As an alternative, electrospinning is a versatile and simple technique to generate highly porous nanofibrous membranes with interconnected pore structures, controllable pore sizes, large surface area to volume ratio and excellent mechanical strengths [28, 41]. These unique features, especially the high porosity, make the ENMs attractive materials as membrane supports to prepare high-performance composite membranes with reduced overall membrane resistance for application in various membrane purification processes such as ultrafiltration, nanofiltration, pressure retarded osmosis and forward osmosis [42-47].

2.3.2. *Fabrication of ENMs*

Prior to electrospinning, a polymer dope solution is prepared by dissolving a pre-determined amount of the selected polymer in a solvent. Additives such as LiCl are usually added in order to improve the dope conductivity. The dope solution is stirred at elevated temperature for some time until a homogeneous mixture is formed. Subsequently, the dope solution is cooled down to room temperature and degassed overnight before use [28, 40-42, 112].

Nanofibrous membrane formation via electrospinning technique entails the self-assembly of polymer nanofibers initiated by an electric field. As shown in **Figure 2-4**, a typical electrospinning setup consists of three parts: a dope transmission line (including syringes installed on syringe pumps, tubing, feeding

pipe sets and nozzles), a grounded collector and a high voltage supply. The operation steps and important notes are described as follows:

- (1) During the process of electrospinning, the dope solution is injected by a syringe pump at a certain flow rate, through a series of thin PTFE tubing into the feeding pipe and finally the nozzles;
- (2) A high voltage of up to 40 kV is applied between the nozzles and the grounded collector. When the applied voltage exceeds the surface tension of the dope solution, electrically charged jets of polymer solution are pulled out of the nozzles;
- (3) Solvent in the jets starts to evaporate during flight, forming the nascent polymer nanofibers which are deposited on the non-woven textile pre-fixed on the collecting cylinder;
- (4) Horizontal repetitive motion of the collector has been activated to ensure a uniform nanofiber deposition, while the distance between the nozzles and the collector is maintained at an optimum value in order to precisely collect the generated polymer nanofibers;
- (5) After a pre-set operation time, an integrated piece of overlapped and interconnected nanofibrous membrane is produced on the collector;

- (6) The maximum membrane area is limited by the dimensions of the rotating collector and varied by the electrospinning parameters such as horizontal movement stroke;
- (7) To fully remove the leftover solvent in the nascent membrane, the as-spun nanofibrous membrane is placed in a fume hood at ambient temperature for certain time to ensure complete drying;
- (8) Finally, heat-press post-treatment at a temperature just below the melting point of the polymer material is conducted on the dried membrane in order to enhance the membrane integrity and mechanical strength [28, 40-42, 112-114].

Figure 2-4. Schematic diagram of an electrospinning setup.

2.3.3. Design and development of ENMs

2.3.3.1. Manipulation of fabrication parameters

In principal, ENMs can be fabricated from any polymer that is fusible or soluble, provided that all the fabrication parameters are appropriately tuned. The prepared ENMs are three-dimensional networks consisting of overlapped and interconnected nanofibers. As a result, the quality of the electrospun nanofibers will directly influence the structures and properties of the resultant ENMs.

Generally, fabrication parameters incurred in an electrospinning process can be classified into two categories including molecular parameters and process parameters, both of which are of high significance in controlling the nanofiber formation [115, 116]. Therefore, empirical knowledge as well as theoretical analysis of these parameters can well offer insights into the tailoring of ENMs with a variety of appealing structures and properties for application in various membrane purification processes. The effects of the fabrication parameters on nanofiber formation are listed in **Table 2-1** and discussed in details as follows.

Table 2-1. Effects of fabrication parameters on nanofiber formation [115, 116].

Fabrication parameters			Effects on nanofiber formation
Molecular parameters	Intrinsic properties of polymer material	Molecular weight	Determining the nanofiber morphologies together with the solvent (refer to “Dope solution properties”).
		Molecular weight distribution	
		Solubility	
		Crystallization velocity	
		Melting point	
		Glass transition temperature	
		Entanglement density	
	Intrinsic properties of solvent	Vapor pressure	Determining the nanofiber morphologies together with the polymer material (refer to “Dope solution properties”).
		Boiling point	
		Polarity	
		Surface tension	
		pH	

Fabrication parameters			Effects on nanofiber formation
Process parameters	Dope solution properties	Concentration	Higher polymer concentration: thicker and more uniform nanofibers with cylindrical morphology; Lower polymer concentration: thinner nanofibers, with additional beads usually produced along the nanofiber axis; Very low polymer concentration (high dilution): nanofibers not formed.
		Viscosity	Higher solution viscosity: thicker nanofibers; Lower solution viscosity: more uniform nanofibers; Very high solution viscosity (above optimum range): high solution cohesiveness, unstable flow, prohibiting electrospinning process; Very low solution viscosity (below optimum range): polymer droplets generated.
		Electrical conductivity	Higher electrical conductivity: thinner nanofibers, fewer or no beads, ultrathin bead-free nanofibers with diameters down to a few nanometers attainable via filler addition.
		Surface tension	Lower surface tension: fewer or no beads in the nanofibers.
		Viscoelasticity	Solution viscoelasticity: modulated by surfactant addition, affording nanofibers with defect-free morphologies.

Fabrication parameters			Effects on nanofiber formation
Process parameters	Operational conditions	Electric field strength	Stronger electrical field: polymer jets split more easily, thinner nanofibers; increased fluid ejection, larger polymer jets, thickening nanofibers; rougher nanofibers, bead-free and smooth nanofibers not guaranteed.
		Dope pumping rate	Lower dope pumping rates: smaller polymer jets, thinner nanofibers.
		Nozzle-to-collector distance	Optimum distance: ensuring sufficient flight of the polymer jets for solvent evaporation and jet solidification; beads generated at either too large or too small separation.
	Ambient conditions	Electrode geometry	Smaller nozzle diameter: smaller polymer jets, thinner nanofibers.
		Relative humidity	Higher relative humidity: retarded solvent evaporation and slower jet solidification, thinner nanofibers with a fiber-sticking structure.
		Temperature	Lower temperature: slower solvent evaporation and jet solidification, enhanced jet elongation, thinner nanofibers; Higher temperature: lower viscosity of the dope solution, more uniform nanofibers.

➤ *Molecular parameters*

In the fabrication of ENMs, the first factor to consider is usually the polymer material which is selected based on the required membrane properties (such as mechanical resilience, hydrophilicity/hydrophobicity, chemoselectivity, electrical conductivity and adhesiveness) and the electrospinning criteria (such as processability). As a result, the intrinsic properties of the polymer including molecular weight and distribution, solubility, crystallization velocity, melting point, glass transition temperature and entanglement density are important parameters to be taken into account for the choice of polymer material.

Up to date, a variety of polymer materials such as biopolymers, water-soluble polymers, solvent-based polymers and multiphase polymers have been employed for electrospinning. Representative examples include cellulose, cellulose acetate (CA), lipase, collagen, chitosan, poly(ethyleneoxide) (PEO), poly(vinylalcohol) (PVA), polyvinylpyrrolidone (PVP), polyacrylamide, polyelectrolytes, polystyrene (PS), polyacrylonitrile (PAN), polyamide (PA), polycarbonate (PC), poly(ethylene terephthalate) (PET), polyurethane (PU), poly(vinylidene fluoride) (PVDF), polyimides (PI), polylactide (PLA), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), polymer blends such as PET/poly(ethylene naphthalate), polyaniline/PS (or PEO), polysulfone/PU, chitosan/PLA and PVC/PU, block copolymers such as PLA-*b*-PEO, PS-*b*-polybutadiene-*b*-PS, PS-*b*-polyisoprene, poly(lactide-co-glycolide)-*b*-PEO and PS-*b*-polydimethylsiloxane, graft copolymers such as PS-*b*-poly(4-vinylpyridine)(3-*n*-pentadecylphenol)_{1.0}, polymer composites such as PEO/Au,

PVA/LiCl/Mn(OAc)₂, PVP/Ag, PU/MnZnNi, PAN/Ag, PMMA/Co, PAN/CNT and PVA/ZrO₂ [115, 116].

Moreover, to dissolve the selected polymer material, a proper solvent needs to be identified. It has been reported that the solvent compositions can significantly affect the morphologies of the electrospun nanofibers. A single- or mixed-solvent system can be adopted, and selection of the solvent is largely based on the intrinsic properties of the solvent such as vapor pressure, boiling point, polarity, surface tension and pH. Among all the parameters, the electrolytic tendency of the solvent is recognized as the most influential factor to be taken into account for the electrospinning process.

Common solvents that have been utilized in electrospinning include distilled water, hydrochloric acid, formic acid, acetic acid, camphorsulfonic acid, silk aqueous solutions, methylene chloride, acetone, ethanol, hexafluoro-2-propanol, toluene, dimethylacetamide (DMAc), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), dichloromethane, chloroform, mixed-solvents such as chloroform/methanol, DMF/toluene, dichloromethane/trifluoroacetic acid, distilled water/ethanol, distilled water/chloroform, distilled water/isopropanol and DMF/THF [115-117].

In addition to the intrinsic properties of the polymer and solvent, the characteristics of the combined polymer-solvent system along with many other process parameters are also crucial factors affecting the electrospinning process and the morphologies of the resultant nanofibers, which will be presented below.

➤ *Process parameters*

In the process of electrospinning, three categories of parameters including dope solution properties (such as concentration, viscosity, viscoelasticity, electrical conductivity and surface tension), operational conditions (such as dope pumping rate, distance between nozzles and collector, electric field strength and electrode geometry) and ambient conditions (such as relative humidity and temperature) need to be taken into account for the design and development of ENMs with desired structures and properties [115, 116].

Among all the process parameters, dope solution properties play a major role in determining the dimensions and architectures of the produced nanofibers. As nanofibers are generated by solvent evaporation and subsequent solidification of the polymer fluid jets, the diameters of the nanofibers are dictated primarily by the sizes and contents of the polymer jets:

- (1) Thicker and more uniform nanofibers with cylindrical morphology are formed at higher polymer concentration. Nanofiber diameters can be reduced significantly by decreasing the polymer concentration, whereas additional beads are usually produced along the nanofiber axis. For very dilute dope solutions, nanofibers cannot be generated [115, 116];
- (2) Higher solution viscosity produces nanofibers with larger diameters, whereas more uniform nanofibers are formed by lowering the viscosity of the dope solution [115, 116];

- (3) Bead formation can be mitigated by enhancing the dope electrical conductivity via addition of filler materials, affording ultrathin nanofibers (diameters of a few nanometers) [115, 116];
- (4) Lowering the surface tension of the dope solutions also tends to form nanofibers free of beads [115, 116];
- (5) Solution viscoelasticity can be modulated by addition of surfactants, affording nanofibers with defect-free morphologies [115, 116];
- (6) On the other hand, viscosity largely dictates the spinnability of the polymer dope solutions. Usually, the values of viscosity fall into a certain range for a spinnable dope solution. At values above the range, solution cohesiveness is very high and the flow becomes unstable, prohibiting the electrospinning process; while polymer droplets are generated when the values are below the range [115, 116, 118].

The electrospinning operational conditions are also important parameters in the control of the diameters and morphologies of the forming nanofibers:

- (1) Stronger electrical field can split the polymer jets more easily, producing nanofibers with smaller diameters. However, higher voltage supply could also generate larger polymer jets due to increased fluid ejection, thickening the nanofibers. On the other hand, higher electrical field does

not guarantee formation of bead-free and smooth nanofibers, and rougher nanofibers can be produced [115, 116];

- (2) In addition, the distance between nozzles and collector need to be properly adjusted to ensure sufficient flight of the polymer jets for solvent evaporation and jet solidification. Otherwise, beads can be generated if the separation is either too large or too small [115, 116];
- (3) Besides, smaller nozzle diameters and lower dope pumping rates produce smaller polymer jets, leading to thinner nanofibers [115, 116, 119-124].

Besides the above-mentioned parameters, ambient conditions also affect the architectures of the resulting nanofibers:

- (1) At lower temperatures, solvent evaporation and jet solidification are slower, leading to enhanced elongation of the polymer jets and thus thinner nanofibers. However, more uniform nanofibers are obtained at higher temperatures attributed to lowered viscosity of the dope solution [115, 116];
- (2) Furthermore, thinner nanofibers with a fiber-sticking structure are produced at higher relative humidity, as a result of the retarded solvent evaporation and slower jet solidification [115, 116, 118, 120, 121, 125, 126].

From the above review, it is clear that the process parameters of dope solution properties, operational conditions and ambient conditions function jointly, resulting in the ultimate structures of the formed nanofibers. These parameters need to be carefully tuned on the base of empirical knowledge as well as theoretical analysis in order to fabricate ENMs with desired properties.

2.3.3.2. Exploitation of electrospinning techniques

As presented above, manipulating the fabrication parameters of electrospinning offers enormous possibilities for tuning the structures and properties of ENMs. The variety of ENMs can be boosted to an even greater extent by exploring new electrospinning techniques. Apart from conventional single-jet electrospinning systems, multi-jet electrospinning techniques can be developed to fabricate diverse types of ENMs with novel architectures and appealing properties [115, 127-130].

Normally, an ENM with a symmetric structure is fabricated from a single material. However, to enhance the membrane transport properties, ENMs with gradient pore sizes are desirable in many applications. This can be realized by sequential electrospinning of different dope solutions prepared from the same material with variation in solvents or concentrations, affording multi-layer ENMs with layers made of nanofibers with different diameters [115, 131-133]. This implies the successful fabrication of heterogeneously structured ENMs with layers of different pore sizes.

In addition to single-phase ENMs, chemically inhomogeneous ENMs can be constructed by either sequential or simultaneous electrospinning of various dope solutions prepared from different types of materials. This produces either tiered ENMs with each layer made of one type of material or hybrid ENMs with different types of materials overlapped and integrated with each other. Integrity of the resultant tiered or hybrid ENMs can be secured by physical adhesion, chemical interaction or a combination of the two forces among the constituent materials [127-130].

From this section, it is understood that electrospinning is a highly versatile yet intricate process. A multitude of parameters govern the formation of electrospun nanofibers. A variety of ENMs can thus be designed and developed by adjusting various fabrication parameters as well as exploiting advanced electrospinning techniques. The electrospinning technology offers access to completely new materials which can be utilized in diverse areas both academically and industrially.

CHAPTER 3. Fabrication of nanofibrous composite membranes for phenol removal in an extractive membrane bioreactor

3.1. Introduction

As mentioned in **Section 2.1.2**, one of the main challenges that impedes EMBR application is the shortage of specially designed membranes capable of extracting the target organic compounds into the receiving biomedium with high efficiencies and excellent stabilities. The hydrophobic silicone rubber, particularly PDMS, has very flexible polymer chains, large free volume and good affinity towards organic compounds, rendering it the dominant and most favourable membrane material in EMBR processes [32, 34, 36, 63]. Although efforts have been made to develop alternative silicone polymers such as poly(diphenylsiloxane) (PDPS), the resulting membrane performance is unsatisfactory largely due to decreased flexibility of the polysiloxane backbone [134]. One drawback of silicone rubber is high thickness (at least 0.2 mm), which results in rather low organic mass transfer efficiency [37, 61, 64].

In order to lower the membrane resistance and enhance the mass transfer efficiency, composite hollow fiber membranes were developed [29, 33]. The composite membranes (X-Flow BV, The Netherlands) [33] utilized by Cocchini et al. displayed an OMTC that was up to one order of magnitude higher than that of the 350- μm thick PDMS membranes for the extraction of less hydrophobic

compounds in aqueous-aqueous extractive processes, largely owing to the thin PDMS skin layer (2 μm) of the TFC membranes [32, 33]. However, the tubular PES support of the composite membranes possessed a high thickness of 0.4 mm and a tortuosity of 1.5-2.0 which created unfavourable mass transfer resistance [33, 135]. The TFC-HF membranes developed by Loh et al. [29] outperformed the commercial silicone rubber tubular membranes with 7.5-time enhancement of OMTC for phenol removal in EMBR operation [32]. However, thick biofilm was observed on the receiving side of the composite membranes, resulting in decreased mass transfer efficiency in the EMBR operation. Therefore, development of new supportive layers with properties such as thin thickness, small tortuosity and lowered/controlled biofouling is highly desirable to enhance the overall composite membrane performance.

In consideration of the versatility and superior features of ENMs as introduced in **Section 2.3**, it is of high interest to construct novel composite membranes making use of the highly porous ENMs as the membrane supports for reduction of overall membrane resistance. To the best of our knowledge, no research has been presented regarding to the fabrication of PDMS-coated nanofibrous composite membranes for EMBR processes, probably due to the large surface pore size of nanofibrous membranes. Majority of the ENMs prepared by other researchers possess an average nanofiber diameter of greater than 200 nm [43-46]. It seems that the nanofiber diameter must be reduced so as to reduce the surface pore size of the substrate if it would be used to prepare a uniform PDMS surface coating for EMBR application.

On the other hand, the top selective layer of a composite membrane has a critical role in determining the membrane performance. It is desirable to fabricate uniform selective layers without defects. Moreover, the intrusion of top selective layer must be well controlled to avoid an extra mass transfer resistance in addition to those caused by the top layer and the original support layer. Shi et al. have previously studied the effect of PDMS intrusion on pervaporation performance by PDMS composite membranes [136]. It was observed that a thin PDMS intrusion layer into the substrate near the interface could cause a significant adverse impact on the permeation performance, which was associated with the structure of the formed binding interfaces. Recently, Loh, C. H. et al. have prepared TFC hollow fiber membranes with different PDMS intrusion levels by varying coating parameters for phenol removal in an EMBR process [29]. It was demonstrated that the partially PDMS-intruded composite membrane performed around 3 times better than the completely PDMS-intruded counterpart. However, more comprehensive approaches to mitigate the intrusion issue so as to enhance the organic removal efficiency of the composite membranes have not yet been well addressed in details.

Generally, the suggested techniques to mitigate intrusion include: (1) optimization of substrate surface properties (i.e. pore size); (2) control of the coating solution concentration and viscosity; and (3) selection of an appropriate pre-wetting agent to fill the substrate pores before coating [28]. In this work, the effects of substrate pore size, coating solution preparation and pre-wetting agent on the phenol removal efficiency in EMBR process and on the mechanical properties of the resultant composite membranes were systematically

investigated. The composite membranes were fabricated by coating a dense PDMS selective layer onto an electrospun PVDF nanofibrous substrate with a highly porous and tiered structure, of which the top was made by ultrafine nanofibers. PVDF was chosen due to its good chemical resistance, ready processability and low cost [137]. This work will bring insight into the essential factors in fabricating ultrafine PVDF nanofibers and designing highly efficient extractive membranes. The developed nanofibrous composite membrane could emerge as a promising extractive membrane candidate to be applied in the EMBR process.

3.2. Experimental

3.2.1. Materials and chemicals

The substrate material PVDF (Kynar HSV900) was supplied by Arkema. Sylgard® 184 Silicone Elastomer Kit was supplied by Dow Corning. The kit consisting of polymer base and curing agent requires manual mixing in a 10 (base): 1 (curing agent) weight ratio. N,N-dimethyl formamide (DMF, Merck chemicals), acetone (Fisher Scientific) and *n*-hexane (Merck chemicals) were employed as solvents. Anhydrous lithium chloride (LiCl, Merck chemicals) was selected as an additive to prepare polymer dope solutions for membrane fabrication. Acetic acid ($\geq 99\%$, Sigma Aldrich), glycerol (85% aqueous solution, Merck chemicals) and deionized water (DI water, purified by a Milli-Q system, Millipore Co. Singapore) were used as the pre-wetting agents for substrates. Phenol ($\geq 99\%$, Sigma Aldrich), sodium chloride (Merck chemicals) and hydrochloric acid (fuming 37%, Merck chemicals) were used to prepare synthetic

wastewater. All the reagents were used directly without any treatment. For the EMBR experiment, a type of sludge acclimated to 750 ppm phenol was inoculated into a 4 liter liquid medium comprising DI water and essential inorganic nutrients (200 mg/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 840 mg/L KH_2PO_4 , 750 mg/L K_2HPO_4 , 100 mg/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 1200 mg/L NH_4Cl and trace amount of FeCl_3) at the start of the EMBR operation [37, 138]. The pH of biomedium was maintained at optimum value (6.9 ± 0.4) for biodegradation of the extracted phenol throughout the EMBR operation.

3.2.2. Preparation of PVDF ENMs

Certain amounts of PVDF and LiCl were dissolved in solvents to prepare PVDF dope solutions. All the solutions were stirred at 60 °C for one day to afford homogeneous dopes. In order to study the effect of substrate pore size on the preparation of composite membranes, two types of PVDF ENMs were fabricated: a single-layer symmetric nanofibrous support (denoted as SL), and a dual-layer nanofibrous support with tiered structure (denoted as DL). The dope compositions for electrospinning these nanofibrous substrates are listed in **Table 3-1**. As shown in the table, the SL support was electrospun by an 8 wt% PVDF dope solution, while the DL support comprised a thinner nanofiber top layer by electrospinning a 3 wt% PVDF dope solution and a coarser nanofiber bottom layer by electrospinning an 8 wt% PVDF dope solution. The electrospinning process was conducted using Nanospinner 24 (Inovenso, Turkey). A distance of 150 mm was set between the nozzles and grounded collecting cylinder where a high voltage of 30-35 kV was applied. Heat-press (Carver Inc, USA) post-

treatment was conducted at 155 °C for 30 min to enhance the membrane integrity and mechanical strength. The as-prepared PVDF nanofibrous membranes were immersed sequentially in 80 wt% ethanol aqueous solution, DI water and lastly the corresponding pre-wetting agent prior to the PDMS coating procedure.

Table 3-1. Dope compositions and characteristics of PVDF nanofibrous substrates.

Parameter		SL	DL
Dope composition (wt%)	Top layer	N.A.	PVDF/LiCl/DMF/Acetone (3/0.01/38.8/58.2)
	Bottom layer	PVDF/LiCl/DMF (8/0.004/92)	PVDF/LiCl/DMF (8/0.004/92)
Mean pore size (μm)		0.57 ± 0.01	0.29 ± 0.02
Max pore size (μm)		0.89 ± 0.01	0.37 ± 0.03
Water contact angle (°)		135 ± 1	130 ± 1
Thickness (μm)		56 ± 1	55 ± 1
Bulk porosity (%)		81 ± 3	80 ± 1
Surface fiber diameter (nm)		129 ± 13	61 ± 12
Tensile modulus (MPa)		83 ± 3	84 ± 2
Tensile at break (MPa)		11 ± 1	10 ± 1
Strain at break (%)		70 ± 3	45 ± 4

3.2.3. Preparation of PDMS-coated PVDF nanofibrous composite membranes with tiered structures

To investigate the effect of PDMS pre-crosslinking on the resultant composite membrane performance, two methods were developed to prepare the PDMS coating solutions with dilute concentration (5 wt% PDMS in *n*-hexane). Method A was the direct method where base polymer and curing agent were mixed in solvent and stirred at room temperature for 1 h prior to coating. Method B was a two-step partially pre-crosslinking method: (1) a 50 wt% PDMS solution was prepared firstly by mixing base polymer and curing agent in *n*-hexane and stirred at room temperature. It was observed that the stirred solution became gels after 2 days. Thus, a shorter reaction time of 42 h was adopted to prepare the highly crosslinked yet homogeneous PDMS solution; (2) the resultant partially pre-crosslinked 50 wt% PDMS solution was diluted into the desired concentration (5 wt%) for membrane coating.

The coating protocol for preparing the PDMS-coated PVDF composite membranes with tiered structure was depicted in **Figure 3-1**. The pre-wetted substrate was fixed between a set of Teflon plate and frame, and coated by directly pouring the as-prepared PDMS solution onto it. After complete solvent evaporation, the coated membrane was heated in an oven at 80 °C for 2 days to allow complete crosslinking of the PDMS layer. The resultant composite membrane was detached from the Teflon mold, and immersed in 80 wt% ethanol aqueous solution followed by DI water until usage.

Figure 3-1. The coating protocol for preparing the PDMS-coated PVDF composite membranes with tiered structures.

3.2.4. Membrane characterizations

Surface and cross-sectional morphologies of the membranes were observed by a field emission scanning electron microscope (FE-SEM, JSM-7600F) supplied by JEOL Asia Pte Ltd, Japan. Nanofiber diameter was determined based on the FE-SEM images. PDMS intrusion thicknesses were estimated from the FE-SEM images of the composite membranes. Membrane thickness was recorded by a Vernier micrometer. Membrane pore sizes (mean and maximum pore sizes) were measured using a capillary flow porometer (CFP-1500A) supplied from Porous Materials, Inc., Singapore. Membrane porosity was measured by a gravimetric method. Water contact angles were determined by a goniometer using sessile drop methodology (Contact Angle System OCA) obtained from Data Physics Instruments GmbH, Singapore. For each test, 5 μL DI water was injected onto a horizontal membrane surface. Mechanical strengths of the membranes were determined using a Zwick/Roell universal testing machine at room temperature.

3.2.5. Leakage test

Leakage test in a cross-flow configuration was carried out to examine the rejections of water and inorganic salts by the resultant composite membranes. The set-up was akin to that of an aqueous-aqueous phenol extractive test adopted in our previous study but without inflow or overflow sections [29]. The feed solution consisted of 50 g/L NaCl in DI water, and the receiving solution was DI water. The membrane was mounted into a flat sheet membrane module with an effective membrane area of 30 cm². NaCl flux was determined by the equation:

$$J_s = \Delta c * V / (\Delta t * A) \quad \text{Eq. 3-1}$$

where J_s (mg/m²·h) is the NaCl flux, Δc (mg/L) is the change of NaCl concentrations in the receiving solution with volume V (L) during time interval Δt (h), and A (m²) is the effective membrane area. NaCl concentrations were recorded by an Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES).

3.2.6. Aqueous-aqueous extractive tests

An aqueous-aqueous phenol extractive test was conducted to measure the membrane's phenol extractive performance [29]. The feed solution (1 L) contained 1000 ppm phenol, 1 M HCl and 50 g/L NaCl in DI water while the receiving solution (1 L) was DI water. An inflow DI water and an overflow solution were pumped into and out of the receiving solution respectively at a flow

rate of 15 mL/min. The phenol mass transfer efficiency was characterized by OMTC, i.e. k_0 (m/s), which was calculated by the following equation:

$$k_0 = (\frac{dC_r}{dt} * V_r + C_r * Q_{out}) / (A * (C_f - C_r)) \quad \text{Eq. 3-2}$$

where C_r and C_f (g/m³) are the phenol concentrations at the receiving and feed sides respectively at time t (s), V_r (m³) is the receiving solution volume, Q_{out} (m³/s) is the overflow rate, A (m²) is the effective membrane area.

To investigate membrane stability, long-term aqueous-aqueous phenol extractive test was conducted using the membrane with best performance. Compared with short-term test, the feed solution contained highly concentrated phenol (2000 ppm), 1 M HCl and 50 g/L NaCl in DI water. Both the feed and receiving solutions were refreshed daily to maintain phenol concentration gradient. k_0 (m/s) was calculated similarly to equation (3-2) with Q_{out} set to 0.

3.2.7. Extractive membrane bioreactor tests

The as-prepared composite membrane was then tested in an extractive membrane bioreactor (EMBR) process for two weeks. The feed solution (1 L) contained 1000 ppm phenol and 5 g/L NaCl in DI water, and the receiving solution (4 L) was the biomedium described in **Section 3.2.1**. The feed solution was refreshed daily. 25 mL of the receiving solution was withdrawn and replaced with 25 mL of the biomedium described in **Section 3.2.1**, in order to replenish the nutrient supply in the biological growth medium. Losses from evaporation

were made up by adding distilled water. Since phenol concentration in the biomedium was maintained at zero during the entire EMBR operation, k_0 (m/s) was calculated as follows:

$$k_0 = \frac{dC_f}{dt} * V_f / (A * C_f) \quad \text{Eq. 3-3}$$

where V_f (m³) is the feed solution volume.

Phenol concentrations were recorded by a high performance liquid chromatography (HPLC) purchased from Shimadzu Corporation (Inertsil OD-3 C18 column). For each phenol extractive test, flow rates at feed and receiving sides were set at 500 mL/min. The Reynolds number was calculated by the equation:

$$R_e = Q * D_H / (\nu * A_c) \quad \text{Eq. 3-4}$$

where R_e stands for the Reynolds number, Q (m³/s) is the volumetric flow rate, ν (m²/s) is the kinematic viscosity of the flow, A_c (m²) is the area of the flow cross-section, D_H (m) is the hydraulic diameter of the flow and is defined as $D_H = 4A_c/P$ with P (m) being the wetted perimeter of the cross section of the flow. At ambient temperature of 20 °C, ν of water is c.a. 1 cSt, that is, 10⁻⁶ m²/s. P is 0.084 m for the flat sheet membrane module used in this system. When Q was 500 mL/min, the Reynolds number was thus calculated to be 397.

3.3. Results and discussion

3.3.1. Characterization of PVDF ENMs

To identify a suitable substrate for preparing the composite membranes, two types of PVDF ENMs were fabricated. As shown in **Figure 3-2**, both supports consist of overlapped and interconnected nanofibers, generating three-dimensional integrated networks. The single layer (SL) PVDF support shows a uniform nanofibrous structure with nanofiber diameter of 129 ± 13 nm and thickness of 56 ± 1 μ m. The dual layer (DL) PVDF support possesses an additional ultrafine top layer with nanofiber diameter of 61 ± 12 nm, which was fabricated by enhancing the dope conductivity and optimizing the polymer concentration. A higher concentration of LiCl in the initial dope can assist in creating higher conductive pathways along the polymer jets and thus accelerate the stretching of nanofibers along the longitudinal fiber directions during the electrospinning process, leading to the production of finer nanofibers. The FE-SEM images of the DL substrate are shown in **Figure 3-2B**. It can be observed that a 2.6- μ m thick finer fiber layer is situated above a 52- μ m thick coarser layer, clearly displaying the tiered structure.

Figure 3-2. FE-SEM images of PVDF electrospun nanofibrous membranes (ENMs): SL (A1: surface; A2: cross section; A3: enlarged cross section) and DL (B1: surface; B2: cross section; B3: enlarged cross section).

As tabulated in **Table 3-1**, the mean pore sizes of SL and DL supports are 0.57 μm and 0.29 μm , respectively. The smaller pore size of DL support should be due to the top ultrafine nanofibrous layer, which formed smaller interconnected membrane pores. Both supports possess high bulk porosity over 80% attributed to the nanofibrous structure, and have high water contact angle above 130° ascribed to high surface roughness [139, 140]. The two supports have similar tensile modulus and tensile at break. However, the DL support displays a 35% lower strain at break than the SL support. The possible reason is that the polymer crystalline and molecular orientation are enhanced by reducing the nanofiber diameter, which thus increase the nanofiber stiffness [141].

3.3.2. Optimization of the composite membranes with tiered structure

3.3.2.1. Effect of substrate pore size on composite membrane preparation

To investigate the impact of substrate pore size on preparing composite membranes, PDMS coating was performed on both SL and DL nanofibrous supports using the same preparation condition. That is, both supports were pre-wetted by DI water and PDMS coating solutions were prepared via method A without pre-crosslinking. It turned out that when the SL support was selected as the substrate, the resultant composite membrane (coded as SL-A-DI) showed significant salt solution leakage during the leakage test with NaCl flux of $569 \pm 21 \text{ mg/m}^2\cdot\text{h}$, as shown in **Table 3-2**. The defects with uncovered surface could be observed from the FE-SEM images as shown in **Figures 3-3A1** and **3-3A2**. In contrast, the composite membrane prepared based on the DL support (coded as DL-A-DI) was essentially defect-free with NaCl flux less than $10 \text{ mg/m}^2\cdot\text{h}$. A uniform and smooth PDMS layer can be observed on resultant membrane surface as displayed in **Figure 3-3B**. These results showed that substrate with a smaller pore size could effectively support a more uniform coating on the top and produce a defect-free composite membrane [142]. Thus, the DL support was chosen as the substrate for all studies discussed below.

Table 3-2. Effects of substrate pore size, PDMS preparation method and pre-wetting agent.

Parameter	SL-A-DI	DL-A-DI	DL-B-DI	DL-B-AA	DL-B-DG21	DL-B-DG11
Substrate	SL	DL	DL	DL	DL	DL
Pre-wetting agent	DI water	DI water	DI water	acetic acid	DI water: glycerol (2:1)	DI water: glycerol (1:1)
PDMS preparation method	Method A	Method A	Method B	Method B	Method B	Method B
PDMS intrusion level	Complete	Complete	Complete	Complete	Partial	Partial
NaCl flux (mg/m ² ·h) *	569 ± 21	< 10	< 10	< 10	< 10	< 10
Water contact angle (°)	116 ± 1	116 ± 1	118 ± 1	117 ± 1	119 ± 1	118 ± 1

* SL-A-DI: data collected from leakage test; others: data collected from aqueous-aqueous phenol extractive tests.

Figure 3-3. Surface morphologies of PDMS-coated PVDF composite membranes made from different substrates: SL-A-DI (A1; A2: enlarged surface displaying the defects) and DL-A-DI (B: smooth surface completely covered by PDMS).

3.3.2.2. *Effect of PDMS preparation method on composite membrane preparation*

In the studies discussed above, the PDMS coating solutions were prepared via method A (direct method) and severe intrusion of PDMS solutions into the substrate pores was observed for both composite membranes (**Table 3-2**, SL-A-DI and DL-A-DI). In order to mitigate the intrusion, a PDMS coating solution with higher viscosity is more desirable. One approach to enhance the solution viscosity is to increase the polymer concentration. However, this will usually result in a thicker coating layer, raising the overall membrane resistance. Thus, a partially pre-crosslinking method (method B) was developed to prepare the PDMS coating solution. By this method, the solution viscosity could be increased while the PDMS concentration was maintained. The coating was performed on the DL support pre-wetted by DI water. Although the intrusion of PDMS solution was still observed for the resultant composite membrane (**Table 3-2**, DL-B-DI), the intrusion extent was smaller than that of DL-A-DI. As shown in **Figures 3-**

4A (DL-A-DI morphologies) and **3-4B** (DL-B-DI morphologies), a thin PDMS top layer besides the intruded intermediate layer between PVDF nanofibrous support and PDMS selective layer could be observed for membrane DL-B-DI, while the PDMS coating solution was intruded into the DL substrate completely without a distinct PDMS top layer for membrane DL-A-DI. Furthermore, the bottom surface of membrane DL-A-DI was fully filled and covered by PDMS, implying severe and complete PDMS intrusion into the substrate pores, while only partial PDMS coverage was observed for membrane DL-B-DI.

In addition, the thickness of composite membrane DL-B-DI is 83 μm while that of DL-A-DI is 64 μm , which confirms that a distinct PDMS layer has been coated on the substrate surface for DL-B-DI. Although DL-B-DI has a larger thickness, it still possesses a higher OMTc (6.0×10^{-7} m/s) than DL-A-DI does (4.8×10^{-7} m/s). This implies that an intermediate layer arising from intrusion could raise the membrane resistance more significantly than a distinct coating layer on the top of the substrate, leading to lower mass transfer efficiency. It can be concluded that the use of more viscous PDMS solution prepared from the partially pre-crosslinking method (method B) can reduce PDMS intrusion. This gives rise to a composite membrane with a smaller overall resistance and thus a larger overall mass transfer coefficient for phenol removal.

Figure 3-4. FE-SEM images of PDMS-coated PVDF composite membranes fabricated by different PDMS preparation methods or pre-wetting agents, with varied PDMS intrusion levels. A1-A3: membrane DL-A-DI; B1-B3: membrane DL-B-DI; C1-C3: membrane DL-B-AA; D1-D3: membrane DL-B-DG21; E1-E3: membrane DL-B-DG11. A1-E1: cross sections, yellow arrows indicate location of PDMS (top distinct layers and intermediate layers); A2-E2: enlarged cross sections at the boundaries between top distinct PDMS layers and the intermediate layers; A3-E3: bottom surfaces.

3.3.2.3. Effect of pre-wetting agent on composite membrane preparation

Although increasing the PDMS coating solution viscosity can help reduce the extent of intrusion, the impact is not significant. Therefore, it is necessary to explore other techniques such as utilization of pre-wetting agents to further reduce the level of PDMS intrusion. Fundamentally, a good pre-wetting agent should fulfil the following criteria: (1) it should not swell or dissolve the substrate; (2) it should not be miscible to the coating solution solvent; (3) it should have a suitable boiling point to keep stable inside the substrate pores during coating; (4) it should be able to wet the substrate and cover all the pores on the substrate surface [143]. Based on the above criteria, DI water, glycerol aqueous solutions and acetic acid were chosen as the pre-wetting agents for analysis in this work.

As shown in **Table 3-2** (columns 4-7), all the resultant composite membranes could reject salt solutions effectively with negligible NaCl flux ($< 10 \text{ mg/m}^2\cdot\text{h}$). Different levels of PDMS intrusion were observed from their respective FE-SEM images (**Figure 3-4**). Compared with DL-B-DI pre-wetted by DI water, DL-B-AA pre-wetted by acetic acid displayed a greater extent of intrusion and the bottom surface of the membrane was almost fully covered by PDMS (**Figure 3-4C**). In contrast, partial intrusion was observed for the composite membranes DL-B-DG21 and DL-B-DG11, which were pre-wetted by 33 wt% and 50 wt% glycerol aqueous solutions, respectively. As shown in **Figures 3-4D1** and **3-4E1**, distinct top layers of PDMS were formed on the surfaces of DL-B-DG21 and DL-B-DG11, below which were the intermediate layers and intact nanofibrous supports. The bottom surfaces of these two composite membranes remained highly porous (**Figures 3-4D3** and **3-4E3**). Membrane DL-B-DG11 had the smallest extent of intrusion and most part of the substrate remained porous (**Figures 3-4E1** and **3-4E2**). The observed phenomena should be due to the varied physical properties of different pre-wetting agents. The boiling points of water, acetic acid and glycerol are 100°C [143], 118°C [144] and 290°C [145], respectively. Therefore, glycerol aqueous solution is the least volatile liquid and could stay in the substrate pores for the longest time. In addition, at 20°C , the viscosity of 50 wt% glycerol aqueous solution ($6.00 \text{ mPa}\cdot\text{s}$) is much higher than that of water ($1.01 \text{ mPa}\cdot\text{s}$) or acetic acid ($1.21 \text{ mPa}\cdot\text{s}$) [146, 147]. This makes glycerol aqueous solution retain in the substrate pores more easily and thus more effectively limit the intrusion of the PDMS coating solution.

The levels of PDMS intrusion were also reflected by the thicknesses of the composite membranes. As illustrated by **Figure 3-5A**, membrane DL-B-AA with the most severe PDMS intrusion had the smallest thickness of 59 μm . Considering that the DL substrate had a thickness of 55 μm , it seemed that almost all the PDMS had penetrated into the substrate matrix, forming an integrated compact layer (**Figure 3-4C**). By contrast, the largest thickness of 110 μm was obtained for membrane with the least level of PDMS intrusion as the PDMS formed a distinct layer on the top of the substrate (**Figure 3-4E**, DL-B-DG11). Besides, the overall mass transfer coefficients (k_0 's) of various composite membranes tested in an aqueous-aqueous extractive process also increased with the decreasing levels of PDMS intrusion as shown in **Figure 3-5B**. The most PDMS-intruded membrane DL-B-AA presented the smallest k_0 ($5.1 \pm 1.4 \times 10^{-7}$ m/s), while the least PDMS-intruded membrane DL-B-DG11 exhibited the largest k_0 ($9.3 \pm 0.8 \times 10^{-7}$ m/s). To explain this observation, a resistance model was proposed as shown in **Figure 3-6B** using a schematic diagram and in **Figure 3-6C** using an electrical circuit analog [148].

Figure 3-5. Comparisons of (A) thickness, (B) OMTC, or k_0 , and (C) tensile modulus of various PDMS-coated PVDF composite membranes prepared using different pre-wetting agents.

From **Figure 3-6B**, the overall composite membrane resistance comprises 5 parts, including: (1) R_1 : the resistance of the PDMS top selective layer with thickness L_1 and surface area A_1 ; (2) R_2 : the resistance contributed by the intruded PDMS portion of the intermediate layer with thickness L_2 and surface area A_1 ; (3) R_3 : the resistance contributed by the “dense” nanofibrous substrate portion of the intermediate layer with thickness L_2 and surface area A_2 ; (4) R_4 : the resistance of the top ultrafine nanofibrous substrate with thickness L_3 ; (5) R_5 : the resistance of

the bottom coarser nanofibrous substrate with thickness L_4 . As shown in Figure 6C, the overall resistance of the composite membrane (R) is expressed as:

$$R = R_1 + \frac{R_2 R_3}{R_2 + R_3} + R_4 + R_5 \quad \text{Eq. 3-5}$$

In this model, the membrane resistance is defined as $R = \frac{L}{P \times A}$, where P is the intrinsic permeability of the membrane material to the permeate. Thus, the resistance of the intermediate layer, L_2 , is as follows:

$$\frac{R_2 R_3}{R_2 + R_3} = \frac{1}{\frac{1}{R_2} + \frac{1}{R_3}} = \frac{1}{\left(\frac{P_1}{L_2}\right) A_1 + \left(\frac{P_2}{L_2}\right) A_2} \quad \text{Eq. 3-6}$$

where P_1 and P_2 are the intrinsic permeability of PDMS and PVDF to phenol compound, respectively. As PDMS is much more permeable to phenol than PVDF is ($P_1 \gg P_2$), and the resistances of the intact top ultrafine as well as the bottom coarser nanofibrous substrate are negligible compared with that of the PDMS layer ($R_4 \ll R_1$, $R_5 \ll R_1$), equation (3-5) can be simplified as:

$$R = R_1 + \frac{L_2}{P_1 A_1} \quad \text{Eq. 3-7}$$

Thus, according to equation (3-7), the overall composite membrane resistance R increases with the increase of the intrusion thickness L_2 . This relation is in accordance with the empirical findings depicted in **Figure 3-6A**, where the

OMTC was found to decrease with the increase of the intrusion thickness for composite membranes prepared with different pre-wetting agents.

Figure 3-6. (A) Correlation of PDMS intrusion thickness and k_0 for composite membranes prepared with different pre-wetting agents; (B) schematic diagram showing the membrane resistance contributed by different layers of a tiered composite membrane; and (C) the electrical circuit analog for the resistance model.

Furthermore, the intrusion of PDMS showed an effect on mechanical properties of resultant composite membranes. It could be seen in **Figure 3-5C** that DL-B-AA with a complete PDMS intrusion level possessed the highest tensile modulus. The strong mechanical interlocking between PDMS and PVDF nanofibers in the PDMS-intruded nanofiber interface contributed to the strong membrane strength. Nevertheless, membrane DL-B-DG11 with the smallest

tensile modulus was still strong enough to perform steadily in the long-term operation as demonstrated in **Section 3.3.3**.

Clearly, the pre-wetting treatment is proven to be a very effective technique to reduce PDMS intrusion, rendering a smaller overall membrane resistance for phenol removal. In particular, 50 wt% glycerol aqueous solution was identified to be the most effective pre-wetting agent for this work because of its highest boiling point and viscosity, making it most easily retain in the substrate pores to prevent the PDMS intrusion.

3.3.3. Long term performance in an aqueous-aqueous extractive test

The stability of the newly developed tiered composite membrane was studied by performing a long-term aqueous-aqueous phenol extractive test over a prolonged operation time. Membrane DL-B-DG11 exhibiting the highest overall mass transfer coefficient was selected for the test. As shown in **Figure 3-7A**, k_o of the membrane DL-B-DG11 did not vary significantly throughout the entire testing period and had an average daily value of $7.1 \pm 0.7 \times 10^{-7}$ m/s. Moreover, the membrane remained defect-free with insignificant NaCl flux (< 10 mg/m²·h). This demonstrated that membrane DL-B-DG11 possessed stable structural integrity leading to steady performance over a long operation period, and thus could be considered as a potential candidate to be tested in an EMBR process.

Figure 3-7. (A) Long term performance of aqueous-aqueous phenol extractive test, (B) EMBR performance, and (C) biofilm growth profile during EMBR test for membrane DL-B-DG11.

3.3.4. EMBR process

After confirming its steady performance in the long-term aqueous-aqueous phenol extractive process, membrane DL-B-DG11 was applied in an EMBR process for two weeks. Conductivity in the biomedium remained unchanged during the whole operation period, implying negligible NaCl flux from the wastewater feed side. As shown in **Figure 3-7B**, the membrane had a steady performance in the first week with average daily k_0 of $5.8 \pm 0.4 \times 10^{-7}$ m/s. This initial k_0 value was lower than that obtained from the long-term test ($7.1 \pm 0.7 \times 10^{-7}$ m/s). The discrepancy in k_0 could be attributed to the following reason: from the onset of the EMBR process, some amount of phenol was extracted by

the composite membrane from the wastewater side to the receiving side where biomedium degraded the incoming phenol, leading to biofilm growth on the receiving side of the membrane. This developed biofilm on the membrane contributed to an elevated mass transfer resistance for phenol removal, resulting in a lower k_0 from the beginning of the EMBR process.

It was observed that starting from the second week of the EMBR operation, k_0 began to drop (below 5.0×10^{-7} m/s) and stabilized at around $4.1 \pm 0.3 \times 10^{-7}$ m/s at the end of the process. The drop in k_0 was largely due to substantial biofilm growth on the receiving side of the membrane, giving rise to larger mass transfer resistance in the process. It was also evident from **Figure 3-7C** that biofilm had grown to a significant amount on the seventh day when drop in k_0 was detected. The receiving side of the membrane was almost fully covered by the biofilm at the end of the experiment when the biofilm concentration (measured in terms of total suspended solids) was determined to be 5.2 ± 0.2 mgTSS/cm². Nevertheless, the percentage decline in k_0 (29%) was much smaller than that observed in an earlier study (74% k_0 decline) where higher organic flux likely led to larger biofilm growth and thus greater k_0 decline [29].

Although k_0 dropped with biofilm growth, the stabilized k_0 (after biofilm growth, $4.1 \pm 0.3 \times 10^{-7}$ m/s) of our composite membrane was still over 4 times larger than that of the commercial silicone tubular membranes (without biofilm growth, 1×10^{-7} m/s) studied in an earlier work [32]. This encouraging result reveals that the composite membrane developed in this work could be a potentially attractive candidate to be used in EMBR systems.

3.3.5. Comparison of phenol extractive performance of various membranes

The phenol extractive performance of the composite membrane DL-B-DG11 was compared with that of a commercial tubular silicone rubber membrane [32], a PDMS-PES TFC-HF membrane [33] and a PDMS-PEI TFC-HF membrane [29] as tabulated in **Table 3-3**. It could be seen that the composite membrane prepared in this work outperformed the commercial tubular silicone rubber membrane in both aqueous-aqueous phenol extractive process and EMBR process. On the other hand, the TFC-HF membranes showed a higher performance than our membrane, which could be attributed to the much higher Reynolds numbers (higher operational flow rates) employed in their studies. In addition, compared with hollow fiber membranes, the bubbling cleaning method utilized in MBR processes to control biofilm growth is more effective for membranes with flat sheet configuration [1, 54]. Thus, the PDMS-coated PVDF composite membrane with tiered structure developed in this work provided an alternative option to be employed in an EMBR process, especially in practical operations.

Table 3-3. Phenol extractive performance of various membranes.

Substrate	Process	Operation conditions			OMTC, k_0 (E-07 m/s)	Membrane configuration
		Feed solution	Receiving solution	Reynolds number		
N.A.	Aq-aq	1000 ppm phenol solution	DI water	12000 (feed side) 4700 (receiving side)	1.0	Tubular [32]
PES	Aq-aq	phenol solution	DI water	7500 (feed side) 2700 (receiving side)	12	TFC-HF [33]
PEI	Aq-aq	1000 ppm phenol, 50 g/L NaCl solution	DI water	1000 (both sides)	32	TFC-HF [29]
PVDF	Aq-aq	1000 ppm phenol, 1 M HCl, 50 g/L NaCl solution	DI water	400 (both sides)	9.3	Composite (this work)
N.A.	EMBR	1000 ppm phenol, 1 M HCl, 50 g/L NaCl solution	Biomedium	N.A.	2.1	Tubular [37]
PEI	EMBR	1000 ppm phenol, 50 g/L NaCl solution	Biomedium	1000 (both sides)	7.5	TFC-HF [29]
PVDF	EMBR	1000 ppm phenol, 5 g/L NaCl solution	Biomedium	400 (both sides)	4.1	Composite (this work)

3.4. Conclusions

This study focused on the development of PDMS-coated PVDF nanofibrous composite membranes applied in extractive membrane bioreactor (EMBR) systems for phenol removal. The membranes consisted of a nanofibrous substrate with tiered structure fabricated by electrospinning PVDF dope solutions with differed concentrations, and a top PDMS selective layer prepared via a coating method.

The effects of membrane substrate pore size, coating solution preparation method and pre-wetting agent on the properties of resultant composite membranes were systematically studied. It was found that the dual-layer PVDF nanofibrous substrate with ultrafine nanofibers on the top could better support a uniform coating, and thus produced a defect-free composite membrane. A PDMS coating solution with higher viscosity, which was prepared by a partially pre-cross-linking method, could assist in mitigating PDMS intrusion into the substrate pores. Moreover, 50 wt% glycerol aqueous solution was identified to be the most effective pre-wetting agent due to its highest boiling point and viscosity. It could retain in the substrate pores most easily to help alleviate the PDMS intrusion. With reduction of PDMS intrusion depth, the overall resistance of a composite membrane decreased based on the resistance model, leading to an enhanced overall mass transfer coefficient for phenol removal.

With the above-mentioned factors taken into account, the first PDMS-coated PVDF nanofibrous composite membrane was fabricated for EMBR

system. The OMTC of resultant membrane for phenol removal exhibited a stable value of $4.1 \pm 0.3 \times 10^{-7}$ m/s after two-week operation, which was 4 times higher than that of the commercial silicone rubber. This indicated that the composite membrane developed in this work could be a promising extractive membrane candidate to be utilized in EMBR systems. The techniques studied in this work to mitigate PDMS intrusion could be further extended to the fabrication of a series of analogous composite membranes employed in such processes as pervaporation, gas separation and solvent-resistant nanofiltration. New coating methods such as spray coating (Chapter 4) and knife coating (Chapter 5) are being exploited in order to reduce the PDMS selective layer thickness and consequently enhance the overall mass transfer efficiency.

CHAPTER 4. Development of high-performance nanofibrous composite membranes by optimizing polydimethylsiloxane architectures for phenol removal

4.1. Introduction

The PDMS-coated PVDF nanofibrous composite membranes fabricated in Chapter 3 demonstrated the superiority of electrospun nanofibrous membranes as porous substrates for preparing composite membranes with reduced overall membrane resistances. The overall mass transfer coefficient (OMTC, k_0) of the resultant nanofibrous composite membrane exhibited a stable value of $4.1 \pm 0.3 \times 10^{-7}$ m/s for phenol removal in a two-week EMBR operation, which was 4 times higher than that of the commercial silicone rubber. Although a performance improvement has been made, the obtained k_0 value is still far from satisfaction, impeding the practical application of the membrane.

As described in **Section 2.1**, in an aqueous-aqueous extractive process, the target organic compounds transfer from the feed wastewater to the aqueous receiving solution through a dense membrane on the basis of the solution-diffusion mechanism [28, 49, 50]. The solution-diffusion mechanism involves three steps: adsorption at the upstream boundary, diffusion through the bulk membrane and desorption away from the downstream boundary [149]. The

control of the adsorption, diffusion and desorption of the small molecules by engineering the polymer macromolecular structures, free volumes and functional groups to optimize mass transfer efficiency is of great value.

As introduced in **Section 2.2**, two types of cross-linking reaction pathways generally exist for PDMS preparation [66-68]. In the pathway of hydrosilylation reaction, a linear PDMS polymer structure can be formed by reacting vinyl-terminated PDMS precursors with hydrosilyl-containing cross-linkers under Pt catalysis; while in the condensation reaction pathway, hydroxyl-terminated PDMS precursors react with multi-functional cross-linkers under catalysis to generate a three-dimensional network [66-68]. Both methods have been adopted to prepare PDMS-based membranes for applications such as gas separation [66], pervaporation [67] and solvent-resistant nanofiltration [68]. However, to the best of our knowledge, the effects of PDMS cross-linking conditions and resultant polymer architectures on phenol transport behavior have not yet been studied systematically.

Additionally, the mechanical properties of the PDMS membrane are critical for practical applications, especially for the development of composite membranes. Although PDMS membranes have high organic affinity, they usually display unsatisfactory mechanical strength resulting from the intrinsic weak intermolecular interactions among the polymer chains [150] as well as the thin PDMS thickness ($< 10\ \mu\text{m}$) for reducing the membrane resistance [29, 151]. Moreover, if the PDMS membranes are developed for pressure-driven processes such as gas separation, the mechanical strength needs to be further boosted so as

to withstand the elevated pressure (> 100 bar) [152]. For the purpose of preparing high strength PDMS, a number of reinforcing fillers such as fumed silica and montmorillonite clays have been incorporated into the PDMS matrix [153-156]. However, pre-treatments such as surface modification of fillers [153, 155, 156] and functionalization of PDMS [154] are usually required so as to achieve adequate interfacial interactions between the fillers and PDMS matrix [156]. Alternatively, PDMS mechanical strength could be enhanced by optimizing the cross-linking methods and thus controlling the polymer architectures, which is considered to be more promising, convenient, economically valuable and practical [157]. However, the consequences of the architecture changes on the membrane separation performance, particularly, the phenol removal efficiency in extractive processes, have not been studied in details. Therefore, it is of high importance to systematically investigate the correlations among the cross-linking regimes, mechanical strength and phenol extractive performance of dense PDMS membranes.

Moreover, as presented in **Chapter 3**, a simple and straightforward coating method, that is, the direct pouring of PDMS coating solution onto the substrate fixed in a Teflon mold, was adopted to fabricate the nanofibrous composite membranes on the first attempt. Although a relatively thin PDMS layer had been achieved by reducing the concentration and coating amount of the PDMS solution, the obtained PDMS thickness ($55\text{ }\mu\text{m}$) was still high, resulting in appreciable membrane resistance and moderate k_{θ} . As the thickness of the selective layer is limited by the selected coating method, other coating techniques need to be explored in order to fabricate a thin and defect-free selective layer.

Several coating methods have been reported in the literatures to fabricate thin film composite membranes, which include dip coating, spin coating, knife coating (casting) and spray coating (**Section 2.2.3**). Among them, spray coating has emerged as a versatile technique to produce a thin and uniform coating layer in a simple, fast and reproducible way [80]. In addition, the whole spray coating process can be conducted in an automatic manner which ensures the high reproducibility of this technique [80]. Thus, a spray-coating technique has been selected in this study as an attempt to fabricate PDMS-coated nanofibrous composite membranes with high phenol mass transfer efficiency in an aqueous-aqueous extractive process.

In this work, condensation, hydrosilylation and commercial kit reactions were adopted to prepare dense PDMS membranes with various polymer architectures. The corresponding PDMS structures were confirmed by ATR-FTIR and XPS analyses. Phenol partition coefficients of resultant dense PDMS membranes were examined. Moreover, PDMS precursor molecular weights as well as cross-linker amounts were varied to investigate their impacts on phenol partition efficiencies and mechanical strengths. Aqueous-aqueous phenol extractive tests were conducted to examine the phenol mass transfer efficiencies of selected dense PDMS membranes, from which the optimum formulation was identified to prepare the final composite membrane. An electrospun dual-layer PVDF nanofibrous membrane with a tiered structure was utilized as the substrate to prepare PDMS-coated nanofibrous composite membranes. The morphologies of the resultant nanofibrous composite membranes were confirmed by FESEM and EDX. The phenol extractive performances of the composite membranes were

examined in aqueous-aqueous phenol extractive tests. DI water, instead of the biomedium (i.e. EMBR), was used as the receiving solution to avoid complication of the testing process resulted from biofouling on the membranes.

4.2. Experimental

4.2.1. Materials and chemicals

Vinyl-terminated polydimethylsiloxane (VPDMS, average molecular weight: 25000, viscosity: 850-1150 cSt), hydroxyl-terminated polydimethylsiloxane (HPDMS, viscosity: 750 cSt, 3500 cSt and 18000-22000 cSt, respectively), tetraethyl orthosilicate (TEOS), dibutyltin dilaurate (DBTDL), trimethylsilyl terminated poly(dimethylsiloxane-co-methylhydrosiloxane) (PDMS-MHS) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Pt. catalyst, 0.05 M in vinyl terminated PDMS) were supplied by Sigma Aldrich. All the other chemicals including a two-component Sylgard® 184 silicone elastomer kit, PVDF, acetone, *n*-hexane, DMF, glycerol, DI water, sodium chloride and phenol were described in **Section 3.2.1**. All the reagents were used directly without further treatment.

4.2.2. Preparation of dense PDMS membranes

To investigate the effect of polymer architectures on phenol extractive performances of dense PDMS membranes, three methods were used to prepare them. In the first method (condensation reaction), 10 wt% HPDMS was first dissolved and stirred in *n*-hexane at room temperature for 1 h. Desired amounts of cross-linker TEOS and catalyst DBTDL were added subsequently into the

solution and stirred vigorously for 3 min. In order to identify the optimum formulation, HPDMS precursors with different molecular weights (reflected as viscosities: 750 cSt, 3500 cSt and 18000-22000 cSt) and TEOS with different amounts (3 wt%, 5 wt%, 10 wt% and 20 wt%) were used for the membrane preparation. The dense PDMS membrane fabricated by this method was denoted as PA. In the second method (hydrosilylation reaction), 10 wt% VPDMS and 3.5 wt% PDMS-MHS were dissolved and stirred in *n*-hexane at room temperature for 1 h, followed by adding 100 ppm Pt. catalyst. The dense PDMS membrane prepared by VPDMS and PDMS-MHS in the second method was named as PB. The PDMS prepared by commercial S184 kit method was chosen as a reference, which was designated as PK. In this kit method, 10 wt% vinyl-type PDMS precursor was mixed with 1 wt% hydrosilyl-type cross-linker in *n*-hexane and stirred at room temperature for 1 h. For all methods, PDMS solutions were poured into Teflon moulds immediately after preparation. The complete evaporation of the solvent at room temperature followed by heat cure in an oven at 80 °C for 2 days resulted in the dense PDMS membranes.

4.2.3. Preparation of a tiered PVDF electrospun nanofibrous substrate

A dual-layer nanofibrous membrane with a tiered structure was fabricated by electrospinning and post-treated as described in **Section 3.2.2**. The nanofibrous substrate was then immersed sequentially in an 80 wt% ethanol aqueous solution, DI water and the pre-wetting agent (75 wt% glycerol aqueous solution) before the PDMS coating was conducted.

4.2.4. Preparation of nanofibrous composite membranes via spray coating

The PDMS-coated nanofibrous composite membranes were fabricated by spraying the PDMS solutions prepared by the condensation reaction or reference kit method onto nanofibrous substrate surfaces. An automatic spray coating machine (Model 7400, Spraying Systems Co., Singapore) was utilized to conduct the whole spraying process in a facile and reproducible manner. The coating solutions were injected via a syringe pump to an air atomizing nozzle through which the polymeric solutions were atomized and sprayed onto the horizontal-situated substrates. The coated membranes were dried in the open air for 30 min to evaporate the remaining solvent, and were then cured in an oven at 80 °C for two days in order to fully cross-link the PDMS layer. The resultant PDMS-coated nanofibrous composite membranes were detached from the glass plate, and immersed in an 80 wt% ethanol aqueous solution for 10 min followed by DI water prior to evaluation.

4.2.5. Membrane characterizations

Energy dispersive X-ray (EDX) spectroscopy was employed to analyze the PDMS intrusion level into the substrates. The chemical structures of the dense PDMS membranes were confirmed by a Fourier transform infrared (FTIR) spectrophotometer (IRPrestige-21 FTIR, Shimadzu, Japan) in attenuated total reflectance (ATR) mode with a resolution of 4 cm⁻¹ and 45 scans. X-ray photoelectron spectroscopy (XPS: PHI Quantera II) with an Al K α X-ray source was performed after 5 nm sputtering for the dense PDMS membrane samples to analyze the detailed membrane compositions, and the binding energy scale was

calibrated by setting the C 1s core level peak at 284.8 eV [158]. The surface and cross-sectional morphologies, thickness and mechanical properties of the membranes were determined by the same methods as described in **Section 3.2.4**.

4.2.6. Partition coefficient measurements

The partition coefficients of phenol between the aqueous phase and different dense PDMS membranes were measured according to the procedure reported in the literature [32]. Briefly, dense PDMS membranes with various volumes were soaked in different volumes of phenol solutions (200 ppm) in several containers. These containers were then put in a shaker for at least 3 days until equilibria were reached. The partition coefficient K was given by the following equation:

$$C_0/C_{eq} - 1 = K * (V_m/V_f) \quad \text{Eq. 4-1}$$

where V_f was the volume of phenol solution, V_m was the volume of dense PDMS membrane, C_0 was the initial phenol solution concentration, and C_{eq} was the phenol solution concentration at equilibrium. The plot of $(C_0/C_{eq} - 1)$ against (V_m/V_f) provided a linear line with the partition coefficient K as the gradient.

4.2.7. Aqueous-aqueous extractive tests

The aqueous-aqueous phenol extractive tests were conducted for selected dense PDMS membranes and PDMS-coated nanofibrous composite membranes for 24 h [29]. The feed solution consisted of 1000 ppm phenol and 5 g/L NaCl in

DI water while the receiving solution was DI water. The membranes were mounted into flat sheet membrane modules with an effective membrane area of 9 cm² for dense PDMS membrane and 36 cm² for nanofibrous composite membrane. The phenol mass transfer efficiency was characterized by k_0 as described in **Section 3.2.6**. To examine membrane stability, a long-term aqueous-aqueous phenol extractive experiment was conducted for 2 weeks using the best nanofibrous composite membrane.

4.3. Results and discussion

4.3.1. Characterization of different dense PDMS membranes

The dense PDMS membranes are typically cross-linked from linear precursors, and their performances are intrinsically determined by respective chemical reaction. The cross-linking reactions conducted in this work and simplified schematic diagrams of the as-synthesized dense PDMS membranes are drawn in **Figure 4-1**. In the method for PA preparation (**Figure 4-1A**), a condensation reaction was carried out between the hydroxyl-terminated PDMS precursor and the cross-linker TEOS with the aid of a catalyst DBTDL [67]. As depicted in **Figure 4-1B**, the TEOS cross-linkers bridged the di-functional linear PDMS precursors as four-armed junction points, resulting in a three-dimensional network structure. Depending on the amount ratios between precursors and cross-linkers, the four active ethoxy groups in each TEOS could be fully or partially replaced by the hydroxyl-terminated PDMS precursors. In the method for synthesizing PB (**Figure 4-1C**), the vinyl-terminated PDMS precursor reacted with the hydrosilyl-containing cross-linker under Pt catalysis through a

hydrosilylation reaction pathway [159]. A linear structure linked by $\text{CH}_2\text{-CH}_2$ groups was obtained for PB as shown in **Figure 4-1D**. According to the manufacturer information, the commercial S184 kit comprised a vinyl-type PDMS precursor and a hydrosilyl-type cross-linker [68]. Hence, it could be inferred that a hydrosilylation reaction similar to that for PB should be involved in the kit method. Structures including linear, branch or a combination of these two could exist in the kit-prepared PDMS membrane (PK) dictated by the exact formulation of the commercial kit.

Figure 4-1. Reaction pathways and schematic diagrams of the as-synthesized dense PDMS membranes PA (A and B) and PB (C and D).

The chemical structure characterizations of different dense PDMS membranes were performed by both ATR-FTIR and XPS. ATR-FTIR can provide qualitative information while XPS is well-suited to provide quantitative chemical analysis. All the as-developed dense PDMS membranes display similar ATR-FTIR spectra as presented in **Figure 4-2**, which comply well with the literatures [160, 161]. The peak between 2950 and 2970 cm^{-1} corresponds to methyl stretching in $\text{Si}-(\text{CH}_3)_2$, while the methyl deformation vibration is observed in the range of 1400-1420 and 1245-1270 cm^{-1} . A broad and shouldered peak between 930 and 1200 cm^{-1} represents Si-O-Si asymmetric deformation. The Si-C band is found in the range of 825-865 cm^{-1} . In addition, a strong peak observed between 785 and 815 cm^{-1} corresponds to CH_3 rocking in $\text{Si}-(\text{CH}_3)_2$. The ATR-FTIR has demonstrated the successful cross-linking of the dense PDMS membranes.

Figure 4-2. ATR-FTIR spectrum of the dense PDMS membranes.

Figure 4-3 shows the XPS results, which analyze the chemical groups on PDMS surfaces in details. As shown in **Figure 4-3A**, in a polysiloxane system, a silicon atom could exist in four kinds of chemical groups resulting in increasing Si binding energies with increasing oxygen atoms replacing the methyl groups [162, 163]. The chemical structures are denoted as M [mono-siloxy: $(\text{CH}_3)_3\text{-Si-O}_{1/2}$], D [di-siloxy: $(\text{CH}_3)_2\text{-Si-O}_{2/2}$], T [tri-siloxy: $(\text{CH}_3)\text{-Si-O}_{3/2}$] and Q [quaternary-siloxy: $\text{Si-O}_{4/2}$]. As a result, the Si 2p XPS spectrum of each PDMS membrane could be resolved into components corresponding to the chemical structures as presented in **Figures 4-3B, 4-3C and 4-3D** [158, 162, 163].

Figure 4-3. (A) Chemical structures of the siloxy units present in polysiloxanes; Si 2p XPS spectra for the dense PDMS membranes: (B) PA, (C) PB and (D) PK.

As shown in **Figure 4-3B**, the decomposed Si 2p XPS spectrum of PA contains a peak at 101.79 eV assigned to the D structure, corresponding to the dimethylsiloxane backbones of the PDMS membrane [158]. The Q structure presented at 103.00 eV demonstrates that the four-armed quaternary-siloxy units

[Si-O_{4/2}] are formed as the linkages during the cross-linking reaction, confirming the three-dimensional network structure of PA as proposed in **Figure 4-1B** [158]. In contrast, only the di-siloxy D structure is observed for the PDMS membrane PB (**Figure 4-3C**), illustrating that a linear structure with dimethylsiloxane backbones is adopted by PB as presented in **Figure 4-1D**. For the commercial PDMS membrane PK made via the kit method, both D and T structures (at 102.40 eV) exist (**Figure 4-3D**) [158], implying that PK exhibits a chemical structure combining both linear and branch architectures. The presence of T structure should be ascribed to the fillers added in the kit formulation [68].

4.3.2. Phenol partition coefficients of dense PDMS membranes

A variety of mechanistic and phenomenological models have been developed to explain the mass transfer behavior encountered in porous and dense membranes [164]. Regarding the dense membranes, the solution-diffusion model is the most popular one in which the solutes partition from the feed solutions into the polymeric bulk of the dense membranes, then diffuse through the membrane bulk and are finally released into the permeate streams [29]. Most of the solute transport research does not account for the solute partitioning rate into the polymeric dense membranes [164]. However, the phenol partition coefficient (K) has been identified as an essential parameter to determine the membrane mass transfer resistance [32].

In this work, the phenol partition coefficients of resultant dense PDMS membranes with different polymer architectures were examined at room temperature and pressure. As depicted in **Figure 4-4**, a linear partitioning of

phenol into the dense PDMS membranes can be observed. The dense membrane PA with a three-dimensional network architecture exhibits the highest phenol partition coefficient ($K = 1.145 \pm 0.021$), while the dense membrane PB with a linear structure obtains a K of 0.280 ± 0.013 . Besides, the membrane PK with a combination of linear and branch architectures made by the S184 kit method shows a K of 0.322 ± 0.001 . The phenol partition coefficient of PA exceeds that obtained from the commercial PK for over 3 times, revealing the significant improvement of phenol partition efficiency due to polymer macromolecular structure optimization.

Figure 4-4. Phenol partition coefficients (K , gradients of the linear lines) of dense PDMS membranes prepared with condensation reaction (PA), hydrosilylation reaction (PB) and commercial S184 kit method (PK).

The partition behavior of a given penetrant in a polymer matrix depends on the segmental mobility of the polymer chains, the free volume within the

polymer and the interaction between polymer matrix and the compound, which are affected by the nature of polymer backbones, degree of cross-linking and crystallinity as well as the existence of substituent [165]. Thus, the phenomenon of partition coefficient improvement could be explained by considering the respective polymer backbones and architectures (linear, branch and three-dimensional network) of the dense PDMS membranes, along with their siloxy group (Si-O) densities and corresponding interaction intensity (hydrogen bonding and Van der Waals force) with phenol molecules in a unit volume.

As illustrated in **Figure 4-5A**, the dense membrane PA adopts a three-dimensional network structure with the four-armed quaternary-siloxy units as the junction points connecting the dimethylsiloxane backbones. The [Si-O_{4/2}] siloxy connection points are believed to be able to increase free volume available for the permeating molecules, resulting in an increase of phenol partition. Additionally, the [Si-O_{4/2}] siloxy units could offer extra interactions between the incoming phenol molecules and PDMS via hydrogen bonding, in addition to Van der Waals force provided by the dimethylsiloxane backbones [166, 167]. Moreover, these [Si-O_{4/2}] siloxy connection points produced by TEOS could cross-link to a large extent with themselves, leading to a much higher density of siloxy functional groups throughout the entire dense membrane [168]. Thus, all these effects synergistically enhance the affinity of phenol molecules towards the dense PDMS membrane PA.

On the contrary, the dense PDMS membrane PB is assumed to have a linear structure as a result of the hydrosilylation reaction pathway, where the

polymer chains could arrange irregularly with respect to each other as shown in **Figure 4-5B**. The substitution of the $[\text{Si-O}_{4/2}]$ linkages by $\text{CH}_2\text{-CH}_2$ groups can dramatically reduce the permeability as a result of the increased polymer backbone rigidity and the decreased free volume available for the molecule diffusion [165]. The density of siloxy groups and corresponding intermolecular interactions between PDMS and phenol molecules are weakened as well [167], resulting in a much smaller phenol partition coefficient. The dense PDMS membrane PK prepared by the commercial kit method shows a slightly higher phenol partition coefficient than PB. This could be ascribed to the presence of the branch polymer structure, besides the linear structure (**Figure 4-5C**). The branch polymer chains with tri-siloxy (T) groups can increase polymer free volume as well as hydrogen bonding available for phenol partition.

Figure 4-5. Schematic diagrams showing phenol transport through PDMS unit volume and the primary interactions between phenol molecules and PDMS: (A) PA with network architecture, (B) PB with a linear architecture and (C) PK with a combination of linear and branch architectures.

4.3.3. Optimization of phenol partition coefficients of dense PDMS membranes

As a result of more free volumes and a higher density of functional siloxy groups, the dense PDMS membrane PA developed by condensation reaction has been proved to exhibit a higher phenol partition coefficient. It was reported that both PDMS precursor molecular weight and cross-link density could influence the molecular transport process [164]. Thus, in this part of work, the phenol partition coefficients of PA are further optimized by controlling PDMS precursor molecular weight and cross-linker amount.

It is presumable that the PDMS matrix cross-linked by polymer precursors with longer chains could possess a higher segmental mobility, thus more flexibility, own larger phenol transport channels and more free volumes, leading to higher partition for phenol molecules. When the PDMS precursor molecular weights are varied (**Figure 4-6**), it turns out that only a slightly higher K value is obtained from the membrane fabricated from the high-mass precursor (denoted as PA-H, $K = 1.145 \pm 0.021$) than that from the low-mass precursor (denoted as PA-L, $K = 1.043 \pm 0.003$). These experimental results show that the improvement of phenol partition efficiency by broadening transport channels and enhancing the free volume via increasing PDMS precursor molecular weights is negligible, largely due to the small molecular weight (94.1 g/mol) and volume (355 Å³) of phenol [169].

Figure 4-6. Phenol partition coefficients (K , gradients of the linear lines) of dense PDMS membranes PA prepared with low-mass PDMS precursor (PA-L), middle-mass PDMS precursor (PA-M) and high-mass PDMS precursor (PA-H).

However, the phenol partition coefficients can be improved appreciably with the increase of cross-linker amounts as shown in **Figure 4-7**. The dense PDMS membrane prepared from 20 wt% TEOS (denoted as PA-H-20) shows the highest K of 2.575 ± 0.041 , while that from 3 wt% TEOS (denoted as PA-H-3) exhibits the lowest K of 1.011 ± 0.061 . This result further emphasizes the importance of siloxy group on phenol partition efficiency of the resultant PDMS. As more four-armed junction points of quaternary-siloxo units are produced by increasing TEOS cross-linkers, it would lead to more functional units available for hydrogen bonding with phenol molecules.

Figure 4-7. Phenol partition coefficients (K , gradients of the linear lines) of dense PDMS membranes PA-H prepared with 3 wt% TEOS (PA-H-3), 5 wt% TEOS (PA-H-5), 10 wt% TEOS (PA-H-10) and 20 wt% TEOS (PA-H-20).

In order to confirm the polymer architectures of dense membranes PA prepared with different amounts of TEOS, the curve-fitted C 1s, O 1s and Si 2p

XPS spectra of PA-H-5 and PA-H-20 are presented in **Figure 4-8**. Both PDMS membranes PA-H-5 and PA-H-20 exhibit a single synthetic peak at 284.80 eV for the C 1s core level, as carbon atom is only present in the di-siloxy structure of PDMS (**Figures 4-8A and 4-8B**) [158]. The same three-dimensional network polymeric architecture exists in both dense PDMS membranes PA-H-5 and PA-H-20, reflected by the presence of di-siloxy (D) and quaternary-siloxy (Q) components in the O 1s and Si 2p XPS spectra. As presented in **Figures 4-8C and 4-8D**, the O 1s core-level spectra of both PDMS membranes are decomposed to one peak at binding energy of 532.40 eV for the D unit and another peak at binding energy of 533.20 eV for the Q unit [158]. The structures can be further ascertained by the Si 2p core-level line shapes as shown in **Figures 4-8E and 4-8F**. A good fit to the analysis has been realized using O 1s and Si 2p core-level spectra. The intensities of the four-armed Q groups for PA-H-20 (**Figures 4-8D and 4-8F**) are higher than those for PA-H-5 (**Figures 4-8C and 4-8E**), demonstrating that a larger amount of $[\text{Si-O}_{4/2}]$ siloxy units is obtained by adding more TEOS cross-linkers.

Figure 4-8. C 1s, O 1s and Si 2p XPS spectra of dense PDMS membranes PA-H-5 (A, C and E) and PA-H-20 (B, D and F).

4.3.4. Mechanical properties of dense PDMS membranes

One limitation of dense PDMS membranes is their unsatisfactory mechanical properties. To fulfil the practical operation requirements, the mechanical strengths of dense PDMS membranes PA prepared in this work were evaluated as shown in **Figure 4-9**. **Figure 4-9A** illustrates the stress-strain curves for dense membranes PA prepared from PDMS precursors with different molecular weights. Two typical regions can be observed from the curves, including initial linear and second nonlinear regions: the initial linear region up to the proportional limit indicates the elastic behavior of PDMS and the tensile modulus is derived from the gradient of the linear portion based on Hooke's law, while the second nonlinear region represents strain hardening effect arising from stress-induced plastic deformation of the polymer chains [170, 171]. As shown in the **Figure 4-9A**, the membranes become tougher with smaller precursor

molecular weights as the slopes of linear portions become higher. The highest tensile modulus (1.14 ± 0.05 MPa) and the lowest elongation at break ($169.5 \pm 7.1\%$) are observed for PA-L, as shown in **Figures 4-9A** and **4-9B**. Whereas, the PA-H prepared by PDMS precursor with the highest molecular weight possesses the lowest tensile modulus (0.64 ± 0.02 MPa) and the highest elongation at break ($251.2 \pm 5.4\%$), indicating its best flexibility. This leads to a conclusion that a PDMS matrix utilizing the precursor with a lower molecular weight can be cross-linked more effectively, affording stiffer interaction and higher toughness.

Figure 4-9. Stress-strain curves and tensile moduli of the dense PDMS membranes PA prepared with different PDMS precursor molecular weights (A and B), and TEOS amounts (C and D).

Figure 4-9C shows the effect of the cross-linker TEOS amounts on the mechanical properties of resultant dense PDMS membranes. The PA-H-20 exhibits a tensile modulus of 121.1 ± 1.5 MPa (**Figure 4-9D**) with an increase of more than 200 times with respect to the PA-H-3. It demonstrates that a higher cross-linking degree attributed to increased cross-linker TEOS addition can endow the dense PDMS membrane with a greater mechanical robustness. The incorporation of TEOS replaces the weak polymer-polymer entanglement by the formation of polymer-crosslinker-polymer covalent bonds. These tighter and more effective connections between polymer backbones lead to a more rigid polymer structure. Besides, the stress-strain curve of PA-H-20 shows a steep linear line in **Figure 4-9C** over the full range of strain without appreciable plastic flow before fracture and possesses the lowest elongation of $4.0 \pm 0.4\%$. The loss of flexibility is observed as a consequence of reducing mobility of the polymer chains. The stiffness enhancement with increasing TEOS amount could provide an important implication for design and development of strong PDMS materials in other applications.

4.3.5. Overall mass transfer efficiency of dense PDMS membranes

As stated earlier, in the solution-diffusion model, the permeating components desorb from the dense membrane into receiving streams after adsorption and diffusion through the membrane matrix. The removal of target components should be determined by the overall mass transfer efficiency combining the partition efficiency as well as the diffusion velocity. Thus, the three best dense PDMS membranes (PA-H-5, PA-H-10 and PA-H-20) based on

the measurement of phenol partition coefficients and mechanical properties, along with the reference dense PDMS membrane PK, were tested in the aqueous-aqueous phenol extractive processes to obtain the OMTC of phenol. The dense PDMS membranes with thickness around 300 μm were fabricated. The k_0 of each dense PDMS membrane was tabulated in **Table 4-1**. All the PA membranes outperformed the reference dense PDMS membrane PK with over 50% higher k_0 values. This agreed well with the results from the phenol partition coefficient measurements. However, the k_0 values of the dense membranes PA prepared with different TEOS amounts did not differ much from each other, although their phenol partition coefficients varied. This phenomenon could be attributed to the low Reynolds number (270) applied during the operation, such that the liquid boundary layer resistances could dominate over the membrane resistance [32]. Consequently, the expected k_0 enhancement by increasing the quaternary-siloxy units was not fully revealed, leading to similar overall phenol mass transfer coefficients for the dense membranes PA prepared with different TEOS amounts. According to this result, 5 wt% TEOS was applied to prepare the final PDMS-coated nanofibrous composite membranes since the least amount of TEOS was sufficient to achieve high phenol extractive performance.

Table 4-1. Overall mass transfer coefficients, k_0 , of selected dense PDMS membranes from aqueous-aqueous phenol extractive tests.

Membrane	Thickness (μm)	k_0 (E-07 m/s)
PK	271 ± 45	1.54 ± 0.06
PA-H-5	291 ± 16	2.38 ± 0.02
PA-H-10	305 ± 10	2.23 ± 0.21
PA-H-20	299 ± 18	2.47 ± 0.21

4.3.6. Aqueous-aqueous extractive performance of nanofibrous composite membranes

To further reduce the membrane resistance for phenol transfer, the PDMS-coated nanofibrous composite membranes were designed and developed in this work. The FESEM images of the tiered PVDF nanofibrous support is presented in **Figure 4-10**. It can be observed in **Figure 4-10A** that the thickness of the top ultrafine nanofiber layer is around $2.5\ \mu\text{m}$ and that of the bottom coarse nanofiber layer is about $52\ \mu\text{m}$. Moreover, the delamination between the top ultrafine and the bottom coarse nanofibrous layers is not detected, confirming a good adhesion at the interface. As presented in **Figures 4-10B** and **4-10C**, the average diameter of the nanofibers decreases from $148 \pm 16\ \text{nm}$ for the bottom coarse nanofibers to $72 \pm 14\ \text{nm}$ for the top ultrafine nanofibers, due to the enhancement of the dope conductivity and the reduction of dope concentration. This dual-layer nanofibrous substrate is designed to ensure a thin and defect-free PDMS coating layer and provide sufficient mechanical strength for practical operations [28].

Figure 4-10. (A) The cross-sectional images of PVDF nanofibrous support with a tiered structure; the surface morphologies of (B) a top ultrafine PVDF nanofibrous layer and (C) a bottom coarse PVDF nanofibrous layer.

The spray coating method was utilized to fabricate a thin and uniform PDMS layer on the PVDF nanofibrous substrate. In order to mitigate PDMS intrusion into the substrate pores, PDMS solutions with increased viscosity were prepared via a partially pre-crosslinking technique prior to spray coating [28]. The nanofibrous composite membrane coated by the PDMS solution prepared with the PA-H-5 formulation was denoted as M1, while the composite membrane coated by the PDMS solution prepared via the kit method was denoted as M2. By applying the same spray coating parameters, uniform and defect-free PDMS top selective layers were obtained for both nanofibrous composite membranes as observed in the FESEM surface images (**Figures 4-11A1 and 4-11B1**). The thin PDMS layers had similar thicknesses of 7 μm (**Figures 4-11A2 and 4-11B2**). Moreover, the elemental analyses for prepared nanofibrous composite membranes were carried out using EDX as shown in **Figures 4-11A3-A4 and 4-11B3-B4**. The blue color denoted the presence of silicon element while the green color denoted the distribution of fluorine element, which were detected to identify the intrusion level of PDMS into PVDF nanofibrous substrates. It was found that, for both nanofibrous composite membranes M1 and M2, silicon was only observed on the substrate surfaces, rather than the bulk regions of the substrates. In other words, the intrusion of the top PDMS layers was mitigated effectively for both membranes.

Figure 4-11. Surface and cross-section FESEM images of PDMS-coated nanofibrous composite membranes M1 (A1 and A2) and M2 (B1 and B2); EDX images of PDMS-coated nanofibrous composite membranes M1 (A3 and A4) and M2 (B3 and B4) showing levels of PDMS intrusion into PVDF substrate pores, blue color denotes the presence of Si element, and green color denotes the presence of F element.

When the composite membranes were subjected to the aqueous-aqueous phenol extractive tests, M1 with an optimized PDMS coating layer developed in this work displayed a higher k_0 ($18.3 \pm 1.3 \times 10^{-7}$ m/s) than M2 coated with the commercial PDMS ($12.6 \pm 0.6 \times 10^{-7}$ m/s) as illustrated in **Table 4-2**. The significantly higher k_0 of membrane M1 should be attributed to the more efficient PDMS skin layer on the nanofibrous composite membrane surface. Additionally, salt flux was not detected for M1, revealing that the nanofibrous composite membrane spray-coated by the newly developed PDMS was defect-free and only allowed the partition and diffusion of phenol across the membrane during the extractive process.

Table 4-2. Aqueous-aqueous phenol extractive performances of PDMS-coated nanofibrous composite membranes.

Membrane Code	PDMS preparation method	Top thickness (μm)	k_o (E-07 m/s)
M1	PA-H-5 formulation	7.1 ± 0.6	18.3 ± 1.3
M2	Kit method	6.9 ± 0.4	12.6 ± 0.6

Futhermore, the nanofibrous composite membrane M1 was continuously run in an aqueous-aqueous phenol extractive test for a total of 364 h to examine the membrane robustness and stability. As observed in **Figure 4-12**, it performed steadily throughout the whole testing period and exhibited an average daily k_o of $18.8 \pm 0.2 \times 10^{-7}$ m/s. In addition, insignificant NaCl flux ($< 10 \text{ mg/m}^2\cdot\text{h}$) was detected for the membrane M1, which demonstrated that M1 had stable structural integrity, giving rise to steady performance over a prolonged operation period.

Figure 4-12. Long term performance of the nanofibrous composite membrane M1.

The aqueous-aqueous phenol extractive performance of as-prepared nanofibrous composite membrane M1 was compared with that of a commercial tubular silicone rubber membrane [32], PDMS-coated thin film composite tubular and hollow fiber membranes [29, 33] and a PDMS-coated PVDF nanofibrous composite membrane developed in our previous study [28], as tabulated in **Table 4-3**. It could be seen that the composite membrane developed in this work outperformed most of the membranes reported in the literatures. One of the thin film composite hollow fiber membranes showed a higher performance, which could be due to a thinner PDMS selective layer. Compared with our previous nanofibrous composite membrane, the composite membrane developed in this work possessed a doubled k_0 due to a novel-developed thin and highly effective PDMS layer. The nanofibrous composite membrane fabricated in this work can emerge as a promising membrane candidate to be utilized in extractive processes to remove phenol contaminants.

Table 4-3. Comparison of aqueous-aqueous phenol extractive performance of various membranes.

Membrane	PDMS thickness	Feed solution condition	Reynolds number	OMTC, k_0 (E-07 m/s)
Tubular silicone rubber membrane [32]	0.5 mm	1000 ppm phenol solution	12000 (feed side) 4700 (receiving side)	1.0
Tubular silicone rubber membrane [32]	0.25 mm	1000 ppm phenol solution	12000 (feed side) 4700 (receiving side)	1.7
PDMS-PES TFC-HF membrane [33]	2 μ m	phenol solution	7500 (feed side) 2700 (receiving side)	12
PDMS-PEI TFC-HF membrane [29]	0.5-2 μ m	1000 ppm phenol, 50 g/L NaCl	1000 (both sides)	32
PDMS-PVDF nanofibrous composite membrane [28]	55 μ m	1000 ppm phenol, 1 M HCl, 50 g/L NaCl	400 (both sides)	9.3
PDMS-PVDF nanofibrous composite membrane (this work)	7 μ m	1000 ppm phenol, 5 g/L NaCl	270 (both sides)	18

4.4. Conclusions

In this work, three cross-linking reactions were adopted to prepare dense PDMS membranes with different polymer architectures. The condensation-cured membranes PA fabricated from hydroxyl-terminated PDMS precursors and TEOS cross-linkers exhibited a three-dimensional network structure. The hydrosilylation-cured membrane PB with a linear architecture was prepared from a vinyl-terminated PDMS precursor and a hydrosilyl-type cross-linker, while the membrane PK with a linear and branch structure was developed by a commercial kit method. It was found that the four-armed quaternary-siloxy groups formed as the junction points in PA played a critical role in enhancing available free volume for phenol passage and affording additional hydrogen bonding between phenol and PDMS matrix, which contributed to a significant increase of phenol partition efficiency.

Additionally, the effects of PDMS precursor molecular weights and cross-linker amounts on the resultant PDMS membrane properties including phenol partition coefficient, mechanical strength and aqueous-aqueous phenol extractive performance were studied systematically. As phenol exhibited a small molecular size, the influence of broadening transport channels via lengthening the polymer chains on phenol partition was negligible. The phenol partition efficiency was improved greatly by increasing the cross-linker amount. High-mass PDMS precursor and 5 wt% TEOS used in the condensation reaction were found to be optimum considering the phenol partition coefficient, mechanical strength and aqueous-aqueous phenol extractive performance.

By employing the optimum PDMS preparation method, a highly efficient PDMS-coated nanofibrous composite membrane was fabricated via a spray coating technique. The overall mass transfer coefficient of the resultant membrane achieved a high value of $18.3 \pm 1.3 \times 10^{-7}$ m/s in the aqueous-aqueous extractive process. This surpassed the nanofibrous composite membrane coated by the commercial kit method with 45% increment. In addition, the as-developed nanofibrous composite membrane displayed a stable performance in a 2-week long-term operation with an average daily k_0 of $18.8 \pm 0.2 \times 10^{-7}$ m/s and insignificant NaCl flux. This promising result demonstrated that the PDMS prepared by the optimized cross-linking condition could be utilized as a highly effective selective layer for composite membrane fabrication.

CHAPTER 5. Development of highly efficient nanofibrous composite membranes via confinement-assisted in situ self-assembly strategy for phenol removal

5.1. Introduction

As manifested in **Chapter 4**, optimizing PDMS macromolecular structures could enhance the membrane performance in aqueous-aqueous phenol extractive processes. The developed PDMS/PVDF nanofibrous composite membrane exhibited a high k_0 of $18.3 \pm 1.3 \times 10^{-7}$ m/s, attributed to the enhanced PDMS free volume and strengthened hydrogen bonding for phenol transport. This offers insights into design and development of highly efficient new-generation membrane materials by engineering the intrinsic structures of the membranes [172, 173].

As discussed in **Section 2.2.2**, the technique of MMMs with incorporation of transport fillers into the polymer matrix has emerged as one promising synthetic strategy to develop high-performance membrane materials [72]. Among all types of fillers, MOFs are being regarded as the most fascinating candidates attributed to their appealing features such as large porosity and pore volume, high surface area, tunable pore size and shape, facile functionalization, and good compatibility with polymers [82-84]. For example, $\text{Zn}_4\text{O}_{13}\text{C}_{24}\text{H}_{12}$

framework known as MOF-5 is one of the best-known prototypical MOFs, which belongs to the IRMOF-n series [174]. In MOF-5, benzene struts link octahedral Zn-O-C clusters to form a primitive cubic framework, resulting in highly rigid and porous structure [174]. More importantly, the three-dimensional porous structure could be functionalized with various organic groups to afford different pore size ranges, which are essential for potential application in storage of gases such as CO₂, H₂ and methane [175-177]. Cu₃(BTC)₂, also named HKUST-1, is a hydrophilic MOF which has been used to fabricate MMMs to separate water from ethanol [178, 179]. Due to its sorption property for H₂ and CO₂, HKUST-1 has been intensively studied for gas separation membranes [180]. Besides, the possibility of utilizing HKUST-1 in the development of organic solvent nanofiltration MMMs has been explored [181, 182]. Zeolitic imidazolate framework-8 (ZIF-8), a widely-known MOF material, exhibits exceptional chemical and thermal stabilities, as well as strong framework flexibility and hydrophobicity [183, 184]. In the ZIF-8 structure, zinc ions are interconnected by 2-methylimidazole linker molecules forming a sodalite topology with a nominal crystallographic aperture size of c.a. 3.4 Å [184]. Owing to the flexible nature of ZIF-8 framework, dynamic structural transformations (e.g. “gate-opening” and “breathing”) can take place upon external stimuli such as temperature, pressure and guest molecules [185, 186]. This structural flexibility allows the access of ZIF-8 inner cages by much larger molecules such as 1,2,4-trimethylbenzene whose molecular size (7.6 Å) has been approximated as the limiting aperture size of ZIF-8 [184]. Therefore, it is speculated that phenol molecules (5.1 Å) [187] can transport through the ZIF-8 inner channels, which can serve as expressways with small mass transfer resistance. Moreover, ZIF-8

can interact with phenol through hydrogen bonding and π - π stacking, which can significantly increase the phenol affinity of the MMM [188]. If ZIF-8 can be effectively incorporated into the PDMS matrix to synthesize a defect-free MMM, it is expected to make a significant breakthrough in extraction efficiency for phenol removal.

Although ZIF-8 has good compatibility with most of the organic polymers owing to the hydrophobic nature of ZIF-8 framework, two major challenges exist for fabricating ZIF-8-based MMMs including: (1) uniform dispersion of ZIF-8 in polymer matrix with minimum agglomeration and (2) good membrane integrity with defect-free ZIF-8/polymer interface [87]. Several methods have been developed to tackle the challenges in MMM fabrication. Zhang et al. [189] proposed a coordination-driven in situ self-assembly method to prepare ZIF-8/poly(sodium 4-styrene-sulfonate (PSS) hybrid membranes. Uniform dispersion and good compatibility of ZIF-8 in the membrane were achieved through in situ growth of ZIF-8 into the polymer, driven by simultaneous coordination of metal ions with both ligands and functionalized polymer. Wang et al. [190] adopted a bio-inspired interfacial design technique to fabricate ZIF-8-polyimide (PI) MMMs. Polydopamine (PD) surface coating on ZIF-8 improved the interfacial compatibility between ZIF-8 and PI matrix, alleviating the void defects in the MMMs. Although good dispersion and compatibility of ZIF-8 in the MMMs could be realized by these synthetic strategies, the required pre-treatments of the fillers and/or polymers complicated the overall membrane fabrication procedures and thus limited the practical implementation of the protocols [92, 93]. Therefore, developing facile, simple

and conducive methods for the synthesis of defect-free and uniform MMMs with high separation performance is still a scientific and practical challenge.

Herein, a facile confinement-assisted in situ self-assembly method (**Figure 5-1**) was proposed to prepare high-efficiency ZIF-8@PDMS/PVDF nanofibrous composite membranes for phenol removal in aqueous-aqueous extractive processes. The newly-grown ZIF-8 nanoparticles in wet state were directly introduced into the PDMS solution without intermediate drying process. Nanoscale dispersion of ZIF-8 could be achieved that was ascribed to the confinement effect of solvation layers and PDMS chains. The resultant ZIF-8@PDMS MMMs were characterized by FESEM, FTIR and XRD to study the membrane morphologies and chemico-physical properties. Aqueous-aqueous phenol extractive tests were carried out to study the impact of ZIF-8 loading. A pseudo “tri-mode” transport mechanism was proposed to image the phenol transport process through the MMMs. The newly-developed ZIF-8@PDMS/PVDF nanofibrous composite membrane was analyzed by FESEM and EDX, and evaluated in aqueous-aqueous phenol extractive tests. For the first time, this work presented the development of highly efficient ZIF-8@PDMS/PVDF nanofibrous composite membranes for phenol removal in aqueous-aqueous extractive processes.

Figure 5-1. Schematic illustration of confinement-assisted in situ self-assembly strategy for preparation of ZIF-8@PDMS/PVDF nanofibrous composite membranes.

5.2. Experimental

5.2.1. Materials and chemicals

Zinc nitrate hexahydrate (reagent grade, 98%), 2-methylimidazole (green alternative, 99%) and ethanol (EMSURE® ACS, ISO, Reag. Ph Eur.) were supplied by Sigma Aldrich. All the other chemicals including PVDF, hydroxyl-terminated PDMS (viscosity: 18000-22000 cSt), TEOS, DBTDL, acetone, *n*-hexane, DMF, glycerol, DI water, sodium chloride and phenol were described in **Sections 3.2.1 and 4.2.1**. All the reagents were used directly without further treatment.

5.2.2. Synthesis of ZIF-8 nanoparticles

ZIF-8 nanoparticles were synthesized according to a modified literature procedure [191]. Briefly, a clear solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.11 g) in ethanol (25 mL) was poured into another clear solution of 2-methylimidazole (Hmim, 2.27 g) in ethanol (50 mL) under stirring, which was continued and stopped after 5 h to afford a homogeneous ZIF-8 suspension. The as-prepared ZIF-8/ethanol suspension was centrifuged and washed with fresh ethanol for three times to remove residues of unreacted reagents and by-products. It was further washed with fresh *n*-hexane and centrifuged for three times in order to enhance the compatibility with the PDMS/*n*-hexane solution. Subsequently, without the drying step, the as-washed ZIF-8 nanoparticles were directly re-dispersed in *n*-hexane with a pre-determined concentration for later usage. For comparison, a batch of the as-washed ZIF-8 nanoparticles was dried under vacuum at 50 °C overnight to afford the pre-formed ZIF-8 nanoparticles.

5.2.3. Preparation of ZIF-8@PDMS MMMs

10 wt% PDMS precursor was first dissolved in *n*-hexane and stirred at room temperature for 1 h. Pre-determined amount of the as-prepared homogeneous ZIF-8/*n*-hexane suspension was transferred into a separate glass bottle, followed by adding the PDMS precursor/*n*-hexane solution dropwise into the same glass bottle under stirring via a “prime” technique [87]. The mixed ZIF-8/PDMS suspension was stirred vigorously for another 1 h. Subsequently, the cross-linker TEOS (5 wt%) and catalyst DBTDL (1 wt%) were added into the suspension and stirred vigorously for several minutes until the suspension

became viscous. The mixture was immediately poured into an aluminum petri dish. Complete solvent evaporation at room temperature followed by heat cure in an oven at 80 °C for 24 h afforded the ZIF-8@PDMS MMM which was peeled off the petri dish for subsequent study. The fabrication protocol for ZIF-8@PDMS MMMs was summarized in **Figure 5-2**. For comparison, the pristine PDMS dense membrane was prepared using the same method.

Figure 5-2. Schematic diagram of fabrication protocol for ZIF-8@PDMS MMMs.

5.2.4. Preparation of ZIF-8@PDMS/PVDF nanofibrous composite membranes

A tiered PVDF nanofibrous membrane was fabricated by electrospinning and used as the membrane substrate [28]. The resultant electrospun nanofibrous substrate was pre-wetted by sequential immersion in 80 wt% ethanol aqueous solution, DI water and 75 wt% glycerol aqueous solution (final pre-wetting

agent). The pre-wetted substrate was then fixed onto a clean glass plate with a tape, while the residual pre-wetting liquid on the substrate surface was quickly removed by a filter paper. Meantime, the coating solution (ZIF-8/PDMS suspension, 5 wt% PDMS) was being prepared following the protocol described above for the MMM fabrication. The coating solution was partially pre-cross-linked to reach an optimum viscosity, in order to ensure a thorough and homogeneous mixing of ZIF-8 nanoparticles and PDMS, and to mitigate solution intrusion into the substrate pores upon coating [28, 49]. Subsequently, the partially pre-cross-linked viscous coating solution was spread onto the substrate surface immediately using an automatic film applicator (Elcometer 4340, Elcometer Asia Pte. Ltd.) with a knife height of 50 μm . Evaporation of the solvent residue in a fumehood for 30 min followed by curing in an oven at 80 $^{\circ}\text{C}$ for 24 h afforded the ZIF-8@PDMS/PVDF nanofibrous composite membrane. The resultant composite membrane was detached from the glass plate, and immersed in an 80 wt% ethanol aqueous solution (10 min) followed by DI water prior to usage. For comparison, the pristine PDMS/PVDF nanofibrous composite membrane was fabricated in the same way.

5.2.5. Membrane characterizations

The ZIF-8 particle size distribution in ethanol at 25 $^{\circ}\text{C}$ was measured by a dynamic light scattering (DLS) device (Malvern Zetasizer Nano, DKSH Technology Pte Ltd). X-ray diffraction (XRD) patterns of the ZIF-8 nanoparticles and membranes were determined on a Bruker D8 Advance diffractometer (Cu-K α X-ray radiation, $\lambda = 1.54 \text{ \AA}$) over 5-50 $^{\circ}$ with a 0.02 $^{\circ}$ step size. The energy

dispersive X-ray spectroscopy (EDX) equipment was employed to study the distribution of ZIF-8 nanoparticles in the PDMS matrix as well as the PDMS intrusion degree into the substrate pores. A Fourier transform infrared (FTIR) spectrophotometer (IRPrestige-21 FTIR, Shimadzu, Japan) was employed to analyze the chemical structures of the ZIF-8 nanoparticles (KBr mode: compacted powder tablet, 1 wt% sample + 99 wt% KBr) and membranes (ATR mode: attenuated total reflectance) with a resolution of 4 cm⁻¹ and 45 scans. The ZIF-8 nanoparticles were dried under vacuum at 50 °C for 24 h prior to XRD and FTIR tests. The surface and cross-sectional morphologies, and the thickness of the membranes were determined by the same methods as described in **Section 3.2.4**.

5.2.6. Aqueous-aqueous extractive experiments

The fabricated membranes with effective membrane area of 9 cm² were evaluated in aqueous-aqueous phenol extractive tests as described in **Section 4.2.7**. NaCl flux was determined by the same method as mentioned in **Section 3.2.5**.

5.3. Results and discussion

5.3.1. Confinement effect on dispersion of ZIF-8 nanoparticles

Nanoscale dispersion of ZIF-8 facilitates the formation of a homogeneous ZIF-8/PDMS suspension. As a result, it is imperative to examine the dispersion of ZIF-8 nanoparticles prior to the addition of PDMS solution. Confinement effect on ZIF-8 dispersion in colloidal suspensions was thus examined, as shown

in **Figure 5-3**. It could be observed that the ZIF-8 colloidal suspension prepared by confinement-assisted in situ self-assembly strategy (without drying) was translucent with uniform ZIF-8 dispersion stable for at least 12 h at room temperature. According to the DLS and FESEM analyses (**Figures 5-3A1** and **5-3A2**), the prepared ZIF-8 suspension exhibited a narrow mono-modal particle size distribution with a centered hydrodynamic diameter of c.a. 180 nm, indicating nanoscale dispersion of ZIF-8 without aggregation. In contrast, the ZIF-8 colloidal suspension prepared by the conventional drying and redispersion process generated severe agglomeration and sedimentation within 30 min of preparation. As shown in **Figures 5-3B1** and **5-3B2**, the resultant ZIF-8 suspension displayed a bi-modal particle size distributoin with hydrodynamic diameters ranging from 200-1100 nm, implying significant ZIF-8 aggregation.

Figure 5-3. DLS and FESEM analyses of ZIF-8 colloidal suspensions prepared by (A1) and (A2) confinement-assisted in situ self-assembly strategy and (B1) and (B2) conventional drying and redispersion process.

The better uniformity of the ZIF-8 colloidal suspension prepared by the confinement-assisted in situ self-assembly strategy can be attributed to confinement effect of solvent as explained below: the newly-grown ZIF-8 nanoparticles are surrounded by solvation layers since nucleation, which provide steric hinderance and prevent interaction and collision of the randomly-moved nanoparticles with each other. Consequently, particle aggregation is avoided, affording nanoscale-dispersed ZIF-8 suspension [192-194]. Conversely, ZIF-8 nanoparticles tend to agglomerate during drying process arising from high surface energy of the naked nanoparticles [195]. However, the formed aggregates cannot be easily separated upon subsequent redispersion of the nanoparticles, leading to significant agglomeration and sedimentation in the ZIF-8 colloidal suspension prepared by the conventional drying and redispersion process [192, 193]. From the above analyses, it could be concluded that the confinement-assisted in situ self-assembly technique is superior in the preparation of nanoscale-dispersed ZIF-8 suspension which is critical in the subsequent development of ZIF-8@PDMS MMMs with high uniformity, sound structural integrity and excellent mass transfer properties.

5.3.2. Chemico-physical characterization of ZIF-8@PDMS MMMs

The ZIF-8@PDMS MMMs with various ZIF-8 loadings (0, 1, 4 and 8 wt%), namely ZIF-8@PDMS-0 (pristine PDMS membrane), ZIF-8@PDMS-1, ZIF-8@PDMS-4 and ZIF-8@PDMS-8, were fabricated to investigate the interfacial interactions between ZIF-8 and PDMS matrix. As observed in the surface FESEM image (**Figure 5-4A**), the pristine PDMS membrane possessed

a smooth surface. After adding 1 wt% ZIF-8, the MMM (ZIF-8@PDMS-1) with a low coverage of nano-sized ZIF-8 particles wrapped in the PDMS matrix was obtained (**Figure 5-4B**). When the amount of ZIF-8 was increased to 4 wt%, more ZIF-8 nanoparticles (200-300 nm) were embedded and homogeneously distributed in the PDMS matrix, forming a continuous membrane structure (**Figure 5-4C**). Moreover, it should be noted that the nanoparticles were essentially integrated with the polymer phase without obvious interfacial defects, implying excellent compatibility between ZIF-8 and PDMS. The absence of interfacial defects was further confirmed by the aqueous-aqueous phenol extractive test which showed negligible NaCl flux (discussed in **Section 5.3.3**). However, by incremental addition of ZIF-8 to 8 wt%, micrometer-sized ZIF-8 particles (1-2 μm) were observed in the membrane (ZIF-8@PDMS-8), as shown in **Figure 5-4D**. The formation of large ZIF-8 particles could be attributed to particle aggregation at high ZIF-8 loading, where the probability of particle-particle interaction and collision was increased in the mother ZIF-8/PDMS suspension, leading to increased particle aggregation in the resultant MMM. The results implied that a moderate ZIF-8 loading of 4 wt% was optimum for the fabrication of uniform ZIF-8@PDMS MMMs without significant particle aggregation.

Figure 5-4. Surface FESEM images of the ZIF-8@PDMS MMMs: (A) ZIF-8@PDMS-0 (pristine PDMS membrane); (B) ZIF-8@PDMS-1 (1 wt% ZIF-8); (C) ZIF-8@PDMS-4 (4 wt% ZIF-8) and (D) ZIF-8@PDMS-8 (8 wt% ZIF-8).

XRD and FTIR characterizations (**Figure 5-5**) were carried out to further examine the physical and chemical properties of ZIF-8@PDMS-4. As presented in **Figure 5-5A**, the XRD pattern confirmed that the synthesized ZIF-8 was crystalline, corresponding to a typical sodalite structure [183]. The shift of peak at $2\theta = 18.3^\circ$ in ZIF-8@PDMS-4, relative to the pure ZIF-8 with index (222), could be attributed to the preferential orientation of the nanocrystals in the polymer matrix [196, 197]. In the FTIR pattern of ZIF-8@PDMS-4 (**Figure 5-5B**), the signature bands of both ZIF-8 and PDMS could be identified. The in-plane bending of the ZIF-8 imidazole ring at $900\text{--}1350\text{ cm}^{-1}$ was not well pronounced as it was masked by the strong Si-O-Si bands of PDMS. Shifts in the bands in the ranges of $2800\text{--}3000\text{ cm}^{-1}$ and $1360\text{--}1580\text{ cm}^{-1}$ were detected for the MMM in comparison with ZIF-8 or pristine PDMS membrane, suggesting the presence of chemical interaction between ZIF-8 and PDMS matrix [80, 198].

Figure 5-5. (A) XRD and (B) FTIR patterns of pristine PDMS membrane, ZIF-8@PDMS-4 and pure ZIF-8 nanocrystals.

5.3.3. Aqueous-aqueous extractive performance of ZIF-8@PDMS MMMs

A ZIF-8@PDMS MMM can be regarded as a two-phase material comprising a dense PDMS phase and a microporous ZIF-8 phase. As illustrated in **Figure 5-6**, a pseudo “tri-mode” transport mechanism could be proposed for phenol transfer through the membrane: (1) a solution-diffusion transport mode is applied in the dense PDMS phase of the MMM (**Figure 5-6A**) akin to that in the pristine PDMS membrane [28, 49, 190]. Due to the organophilicity and hydrophobicity of PDMS, phenol molecules can preferentially transfer through the free volume of the dense PDMS phase where water molecules and salts are essentially retained; (2) a pore-flow transport mode is feasible in the microporous ZIF-8 phase of the MMM (**Figure 5-6B**) [184]. Owing to the structural flexibility of ZIF-8, phenol molecules can access the ZIF-8 inner channels via “gate-opening” or “breathing” mechanism [185, 186]. On the other hand, transfer of the smaller water molecules through the ZIF-8 channels is not favored ascribed to the intrinsic hydrophobic nature of ZIF-8 inner cages [184]. This molecular

sieving effect based on hydrophobicity difference ensures the exclusive passage of phenol through the ZIF-8 cages which supposedly possess much smaller mass transfer resistance than the dense PDMS phase; and (3) an electrostatic mode is present throughout the entire MMM (**Figure 5-6C**). On the one hand, dense PDMS phase can interact with phenol through hydrogen bonding (O atoms from dimethylsiloxane backbones $[(CH_3)_2Si-O_{2/2}]$ and quaternary-siloxy cross-links $[Si-O_{4/2}]$ of PDMS with hydroxyl groups $[-OH]$ of phenol) and Van der Waals force (dimethylsiloxane backbones of PDMS with phenyl rings of phenol) [49]. On the other hand, hydrogen bonding (N atoms from imidazole rings of ZIF-8 with hydroxyl groups of phenol) as well as π - π stacking (imidazole rings of ZIF-8 with phenyl rings of phenol) exist between microporous ZIF-8 phase and phenol [188]. These electrostatic interactions provided by dense PDMS phase and microporous ZIF-8 phase can play a vital role in enhancing the affinity of phenol towards the MMM. Altogether, synergy of the solution-diffusion, pore-flow and electrostatic modes is expected to significantly improve the phenol transfer efficiency through the ZIF-8@PDMS MMM in comparison with the pristine PDMS membrane where only the solution-diffusion mechanism is present.

Figure 5-6. Schematic diagram of an aqueous-aqueous phenol extractive process based on a pseudo “tri-mode” transport mechanism for a ZIF-8@PDMS MMM.

Various free-standing ZIF-8@PDMS MMMs (c.a. 400- μm thick) were prepared with different ZIF-8 loadings (0, 1, 2, 4 and 8 wt%) and evaluated by aqueous-aqueous phenol extractive tests. As shown in **Figure 5-7**, the k_0 values of the prepared MMMs increased with the incorporation of ZIF-8 from 0-4 wt%, with NaCl flux maintained at a negligible level (c.a. 8 $\text{mg}/\text{m}^2\cdot\text{h}$). In contrast to the pristine PDMS membrane (k_0 , $1.71 \pm 0.04 \times 10^{-7}$ m/s), ZIF-8@PDMS-4 with 4 wt% ZIF-8 loading exhibited a k_0 of $2.61 \pm 0.05 \times 10^{-7}$ m/s with 53% increment. The enhanced phenol mass transfer efficiency of the MMMs could be attributed to the following reasons: (1) as illustrated in the pore-flow transport mode (**Figure 5-6B**), ZIF-8 with a highly ordered porous structure provided additional favorable transport channels for phenol molecules, which lowered the overall mass transfer resistance of the MMMs [199, 200]; (2) owing to the strong electrostatic mode furnished by ZIF-8 (**Figure 5-6C**), phenol exhibited an extraordinary affinity towards ZIF-8, resulting in highly directed transport of

phenol through the ZIF-8 inner cavities facilitated by electrostatic interactions [31]; and (3) due to high surface area of ZIF-8 fillers, the membrane extraction capacity for phenol was increased to a large extent, further improving the overall mass transfer efficiency of the MMMs [201, 202]. The negligible and unchanged NaCl flux upon ZIF-8 incorporation (0-4 wt%) indicated excellent interfacial compatibility between ZIF-8 and PDMS matrix [203] in addition to the strong hydrophobicity of ZIF-8 and PDMS, effectively preventing the transport of water molecules and salts through the MMMs.

Figure 5-7. The effect of ZIF-8 loadings (0, 1, 2, 4 and 8 wt%) on the aqueous-phenol extractive performance of ZIF-8@PDMS MMMs.

However, when the ZIF-8 doping amount was further increased to 8 wt%, a decrease in k_0 ($2.02 \pm 0.04 \times 10^{-7}$ m/s) and a simultaneous increase in NaCl flux ($27 \text{ mg/m}^2\cdot\text{h}$) were observed. The deteriorated extractive performance could be attributed to polymer chain rigidification near the PDMS–ZIF-8 interface as well as partial pore blockage of ZIF-8 by PDMS chains at high ZIF-8 loading [204,

205], hampering the solution-diffusion and pore-flow modes for phenol transport. Moreover, significant ZIF-8 aggregates generated in ZIF-8@PDMS-8 (**Figure 5-4D**) could promote the formation of microscopic non-selective interfacial voids between ZIF-8 and PDMS, leading to increased passage of water molecules and salts [206].

According to this result, it could be concluded that a ZIF-8 loading of 4 wt% is optimum for fabricating a ZIF-8 filled PDMS MMM with the highest k_0 and negligible NaCl flux. This optimum MMM formulation will be adopted for the subsequent development of a high-performance ZIF-8@PDMS/PVDF nanofibrous composite membrane for phenol removal in an aqueous-aqueous extractive process.

5.3.4. Aqueous-aqueous extractive performance of ZIF-8@PDMS/PVDF nanofibrous composite membranes

In order to fulfil such practical requirements as high OMTC and insignificant salt flux in aqueous-aqueous phenol extractive processes, ZIF-8@PDMS/PVDF nanofibrous composite membranes were designed and fabricated in this work. As observed in the surface FESEM image (**Figure 5-8A**), the tiered PVDF electrospun nanofibrous substrate exhibited a highly porous (bulk porosity > 80%) structure with tightened surface of ultrafine nanofibers (diameter 70 ± 15 nm), which would be beneficial to lower the overall composite membrane resistance significantly [28]. Upon coating by a ZIF-8/PDMS suspension (4 wt% ZIF-8), a uniform and defect-free skin layer was obtained on the top of the nanofibrous support as shown in **Figure 5-8B**. The ZIF-8

nanoparticles were embedded and distributed homogeneously in the PDMS matrix without significant agglomeration. This result was further confirmed in the corresponding EDX analyses as discussed in the following paragraph. Moreover, it should be noted that less particle aggregation was achieved for the dense skin layer of the ZIF-8@PDMS-4/PVDF nanofibrous composite membrane (denoted as M1), in comparison to the dense membrane ZIF-8@PDMS-4 (**Figure 5-4C**) with the same ZIF-8 loading (4 wt%). This could be attributed to the lower PDMS concentration (5 wt%) applied for M1 preparation than for MMM preparation (10 wt%), resulting in better ZIF-8 dispersion in M1. As shown in the cross-sectional FESEM image of M1 (**Figure 5-8C**), a coherent and thin (c.a. 9 μm) skin layer was formed on the surface of the highly porous nanofibrous support, with ZIF-8 nanoparticles embedded in the PDMS matrix. Although particle agglomeration was observed, it was not significant and showed improvement in comparison with the MMMs fabricated using the traditional drying and re-dispersing processes for MOF addition [94, 207]. Moreover, intrusion of the skin layer into the substrate pores was effectively alleviated, evidenced by the intact highly porous structure of the support layer.

Figure 5-8. Surface FESEM images of (A) a tiered PVDF electrospun nanofibrous support; (B) ZIF-8@PDMS-4/PVDF nanofibrous composite membrane M1; and (C) cross-sectional FESEM image of M1.

EDX analyses (**Figure 5-9**) were conducted to further examine the ZIF-8 distribution in the composite membrane M1. In the surface EDX maps (**Figure 5-9A**), the continuous carbon and silicon signals represented the PDMS matrix, while the scattered zinc signal indicated the presence of ZIF-8 nanoparticles. The Zn elemental map suggested a homogeneous distribution of ZIF-8 on the membrane surface with insignificant aggregation. This was further verified by the cross-sectional EDX analysis of the composite membrane (**Figure 5-9B**), where the zinc signal was detected in the skin layer with high uniformity. In

addition, silicon was only observed until a depth of c.a. 15 μm from the skin surface, indicating little intrusion of the skin layer into the substrate pores.

Figure 5-9. (A) surface and (B) cross-sectional EDX analyses of ZIF-8@PDMS-4/PVDF nanofibrous composite membrane M1.

When the composite membrane M1 was tested in an aqueous-aqueous phenol extractive process for 24 h, it exhibited an exceptionally high k_0 ($35.7 \pm 1.1 \times 10^{-7} \text{ m/s}$), doubling that obtained from the pristine counterpart (denoted as M2: k_0 , $16.9 \pm 1.3 \times 10^{-7} \text{ m/s}$) tested under the same operating condition (**Table 5-1**). Meantime, NaCl flux of M1 ($12.3 \pm 0.4 \text{ mg/m}^2 \text{ h}$) was maintained at a negligible level similar to M2 ($11.8 \pm 0.4 \text{ mg/m}^2 \text{ h}$). This remarkable performance enhancement further demonstrated the superiority of incorporating ZIF-8 nanoparticles in the PDMS matrix, providing additional transport modes (pore-flow mode and electrostatic mode) for highly efficient and highly selective phenol passage as discussed earlier in **Section 5.3.3**.

Table 5-1. Aqueous-aqueous phenol extractive performance of nanofibrous composite membranes.

Membrane Code	Skin layer	Skin thickness (μm)	k_0 (E-07 m/s)	NaCl flux ($\text{mg}/\text{m}^2\text{h}$)
M1	ZIF-8@PDMS	9.6 ± 0.8	35.7 ± 1.1	12.3 ± 0.4
M2	PDMS	8.8 ± 0.6	16.9 ± 1.3	11.8 ± 0.4

The stability of the developed nanofibrous composite membrane M1 was tested in an aqueous-aqueous phenol extractive process for a prolonged time (> 360 h) and the performance was compared with that of the pristine counterpart M2. As shown in **Figure 5-10**, membrane M1 exhibited a steady performance throughout the whole examining period with an average daily k_0 of $36.0 \pm 0.3 \times 10^{-7}$ m/s, doubling that obtained from the membrane M2 ($16.8 \pm 0.2 \times 10^{-7}$ m/s). Meantime, NaCl flux was maintained at a similarly low level (11.6 ± 1.6 $\text{mg}/\text{m}^2\cdot\text{h}$). This long-term high-performance stability revealed the sound structural integrity of M1 as well as the durability of ZIF-8 as fillers in the PDMS matrix under current testing conditions.

Figure 5-10. Long-term performance of the nanofibrous composite membranes M1 and M2.

5.3.5. Comparison of aqueous-aqueous phenol extractive performance of various membranes

The aqueous-aqueous phenol extractive performance of the newly-developed nanofibrous composite membrane M1 was compared with that of a commercial tubular silicone rubber membrane [32], PDMS-based TFC membranes [29, 33] and PDMS-coated PVDF nanofibrous composite membranes developed in our previous studies [28, 49] (**Table 5-2**). It could be seen that the composite membrane M1 developed in this work excelled all the precedent membranes in the OMTC, being the best-performance membrane to remove phenol in an aqueous-aqueous extractive process up to date. This could be largely attributed to the highly porous ZIF-8 fillers incorporated in the PDMS matrix, offering favorable electro-directed transport channels and high extraction capacity for efficient and exclusive phenol transfer. The remarkable performance

enhancement indicated that the current composite membrane could be a promising membrane candidate to be applied in aqueous-aqueous extractive processes to remove other types of organic pollutants.

Table 5-2. Comparison of aqueous-aqueous phenol extractive performance of various membranes.

Membrane type	PDMS thickness (μm)	Substrate pore size (μm)	Feed solution condition	Reynolds number	OMTC, k_0 (E-07 m/s)	Reference
#1 Tubular silicone rubber membrane	500	N.A.	1000 ppm phenol solution	12000 (feed side) 4700 (receiving side)	1.0	[32], 1995
#2 Tubular silicone rubber membrane	250	N.A.	1000 ppm phenol solution	12000 (feed side) 4700 (receiving side)	1.7	[32], 1995
#3 PDMS/PES TFC tubular membrane	2	0.1-10	phenol solution	7500 (feed side) 2700 (receiving side)	12	[33], 2002
#4 PDMS/PEI TFC-HF membrane	0.5-2	0.05	1000 ppm phenol, 50 g/L NaCl	1000 (both sides)	32	[29], 2016
#5 PDMS/PVDF nanofibrous composite membrane	55	0.3-0.6	1000 ppm phenol, 1 M HCl, 50 g/L NaCl	400 (both sides)	9.3	[28], 2017
#6 PDMS/PVDF nanofibrous composite membrane	7	0.3-0.6	1000 ppm phenol, 5 g/L NaCl	270 (both sides)	18	[49], 2017
#7 ZIF-8@PDMS/PVDF nanofibrous composite membrane	9	0.3-0.6	1000 ppm phenol, 5 g/L NaCl	300 (both sides)	36	Current work

5.4. Conclusions

A highly efficient ZIF-8@PDMS/PVDF nanofibrous composite membrane was designed and fabricated via the confinement-assisted in situ self-assembly method for phenol removal in an aqueous-aqueous extractive process. The proposed method was proven to be effective to enhance the dispersion and compatibility of ZIF-8 within PDMS matrix, in comparison to the conventional drying and redispersion process. Nanoscale dispersion of ZIF-8 was realized that was attributed to the confinement effect of solvation layers and PDMS chains, which created steric hinderance and prevented subsequent interaction and collision of the randomly-moved nanoparticles with each other, effectively alleviating the particle aggregation.

The newly-developed nanofibrous composite membrane exhibited a remarkable k_0 of $35.7 \pm 1.1 \times 10^{-7}$ m/s in an aqueous-aqueous phenol extractive test, doubling that obtained from the pristine counterpart ($16.9 \pm 1.3 \times 10^{-7}$ m/s). The high extractive performance was maintained for more than 360 h without drop in salt rejection. The appealing outcome was realized by furnishing favorable electro-directed transport channels and high extraction capacity in the membrane through effective ZIF-8 incorporation in PDMS matrix. As a result, the pore-flow and electrostatic modes were promoted for efficient and exclusive phenol transport, as explained by a proposed pseudo “tri-mode” transport mechanism. The current study has made a significant progress in developing membrane extraction technology for phenol removal in aqueous-aqueous extractive processes. The facile confinement-assisted in situ self-assembly

strategy for incorporating filler materials in the polymer matrix could contribute to the development of high-performance MMMs for diverse membrane separation processes.

CHAPTER 6. Conclusions and recommendations

6.1. Overall conclusions

Treatment of phenol-containing wastewaters is of high importance due to the health concern and industrial application of phenol. Among the existing technologies, the aqueous-aqueous extractive process has been evidenced to be a promising technology due to advantages such as independent operation of the receiving solution under optimized condition, specific and efficient point-source treatment of individual industrial effluent, low energy consumption, low operating costs and easy scalability. However, one of the main challenges in the aqueous-aqueous extractive process is the shortage of specially designed membranes capable of extracting the target organic compounds into the aqueous receiving medium with high efficiencies and excellent stabilities.

This thesis presented the development of high-performance PDMS-based nanofibrous composite membranes for phenol removal in aqueous-aqueous extractive processes. PDMS was selected as the polymer material to fabricate the dense selective layers of the composite membranes, attributed to its organophilicity and hydrophobicity which allow the preferential transfer of organics while rejecting water and inorganics. PVDF was chosen as the material to prepare the porous supportive layers of the composite membranes, due to its good chemical resistance, ready processability and low cost. Electrospinning technique was employed to fabricate the membrane supports with appealing

features including high porosity, controllable pore sizes, interconnected pore structures, large surface-area-to-volume ratio and excellent mechanical strengths.

On the first attempt (**Chapter 3**), PDMS-coated PVDF nanofibrous composite membranes making use of highly porous tiered ENMs as the supports were fabricated for phenol removal in an EMBR process. The effects of substrate pore size, coating solution preparation and pre-wetting agent on the phenol removal efficiency in an EMBR process and on the mechanical properties of the resultant composite membranes were systematically investigated. In order to improve the overall mass transfer efficiency of the nanofibrous composite membranes, PDMS macromolecular structures were optimized by varying the PDMS cross-linking reactions including condensation, hydrosilylation and commercial kit reactions (**Chapter 4**). The effects of PDMS precursor molecular weight and cross-linker amount on the resultant PDMS membrane properties including phenol partition coefficient, mechanical strength and aqueous-aqueous phenol extractive performance were studied systematically. By employing the optimum PDMS formulation, a highly efficient PDMS-coated nanofibrous composite membrane was fabricated and evaluated in aqueous-aqueous extractive processes. With the purpose of developing highly efficient new-generation nanofibrous composite membranes, ZIF-8 fillers were incorporated into the PDMS matrix via a facile confinement-assisted in situ self-assembly technique (**Chapter 5**). The effects of ZIF-8 loading on the morphologies as well as the aqueous-aqueous phenol extractive performance of the membranes were investigated in details. To explain the significant enhancement of the phenol

extractive performance of the newly-developed membranes, a pseudo “tri-mode” transport mechanism was proposed.

The major outcomes and conclusions obtained in each chapter are summarized as follows:

Chapter 3:

- (1) ENMs with gradient pore sizes can be designed and developed by sequential electrospinning of dope solutions with different polymer concentrations;
- (2) Essential techniques for mitigating PDMS intrusion include:
 - Reducing the substrate surface pore size by fabricating a tiered support with tightened surface;
 - Increasing the coating solution viscosity by preparing partially pre-cross-linked coating solutions;
 - Filling the substrate pores with a pre-wetting agent exhibiting such attributes as high boiling point and viscosity;
- (3) The overall resistance of a composite membrane can be reduced by alleviating the intrusion degree of the coating solution according to the

proposed resistance model, leading to an enhanced overall mass transfer coefficient;

- (4) The 1st-generation PDMS/PVDF nanofibrous composite membrane making use of a highly porous tiered ENM as the support was fabricated, exhibiting a k_0 of $4.1 \pm 0.3 \times 10^{-7}$ m/s for phenol removal in an EMBR process which was 4 times higher than that obtained from the commercial silicone rubber;

Chapter 4:

- (5) PDMS macromolecular architectures can be varied by developing different cross-linking protocols including condensation, hydrosilylation and commercial S184 kit methods;
- (6) The condensation-cured PDMS membrane fabricated from a hydroxyl-terminated PDMS precursor and TEOS cross-linker possesses the largest free volume and the highest siloxy density attributed to the formed three-dimensional network structure with four-armed quaternary-siloxy bridges [Si-O_{4/2}];
- (7) PDMS membranes with greater mechanical robustness can be fabricated by increasing the cross-linker TEOS loading;
- (8) The 2nd-generation PDMS/PVDF nanofibrous composite membrane utilizing PDMS with three-dimensional network structure linked by four-

armed quaternary-siloxy units was developed, exhibiting a high k_0 of $18.3 \pm 1.3 \times 10^{-7}$ m/s for phenol removal in an aqueous-aqueous extractive process which surpassed the commercial counterpart with 45% increment;

Chapter 5:

- (9) The confinement-assisted in situ self-assembly strategy is effective to enhance the dispersion and compatibility of ZIF-8 within PDMS matrix, attributed to the confinement effect of solvation layers and PDMS chains;
- (10) The effective incorporation of ZIF-8 fillers in PDMS matrix furnishes favorable electro-directed transport channels and high extraction capacity in the MMMs;
- (11) A pseudo “tri-mode” transport mechanism, including the solution-diffusion, pore-flow and electrostatic modes, is proposed to study the phenol transport behaviour through the ZIF-8 filled PDMS MMMs;
- (12) The 3rd-generation PDMS-based PVDF nanofibrous composite membrane with ZIF-8 incorporated in the PDMS matrix was developed, exhibiting a remarkable k_0 of $35.7 \pm 1.1 \times 10^{-7}$ m/s for phenol removal in an aqueous-aqueous extractive process which doubled the value obtained from the pristine counterpart.

6.2. Recommendations for future research

6.2.1. *Development of new nanofibrous composite membranes*

➤ Development of dense selective layers

Among all the polymeric materials, PDMS has been recognized as the best-performance material for separating organic compounds. However, due to its intrinsic organophilicity, PDMS displays only modest affinity for organic compounds with higher polarity (e.g. alcohols, amines, ketones, amides and ethers). In order to enhance the membrane permselectivity for polar organics, a variety of functionalized PDMS-based dense membranes can be developed by modifying PDMS structures. Available techniques include: (1) surface modification via physical means (e.g. plasma treatments) or chemical methods (e.g. surface grafting); (2) bulk modification through copolymerization (e.g. block, segmented and graft copolymerization), blending, functionalization (e.g. side-group modification) and synthesizing interpenetrating polymer networks; and (3) other modification through methods such as adjusting the post-curing conditions [208].

In addition, mixed-matrix membranes (MMMs) with incorporation of porous transport fillers in the PDMS matrix can be developed, which further increase the diversity of PDMS-based membranes. Besides ZIF-8 nanoparticles which have been utilized in this work (**Chapter 5**), enormous number of transport fillers can be considered for incorporation in PDMS. Representative examples include zeolites, non-porous silica, activated carbons, graphite, carbon molecular sieves, carbon nanotubes, meso-porous materials and metal organic frameworks

(MOFs) [87]. Moreover, modification of existing porous transport fillers can be conducted to produce new functional materials with targeted transport properties.

Therefore, by modifying the PDMS structures, doping PDMS with porous transport fillers, and combining the former two strategies, it is expected to generate novel PDMS-based dense selective layers with enhanced organophilicity and thus permselectivity for organic compounds, especially those which are more polar and less readily removed.

➤ Development of nanofibrous supportive layers

Besides PVDF which has been utilized as the substrate material in the current work, many other polymeric materials such as polyether ether ketone (PEEK), polyethersulfone (PES), polyimide (PI), polyamideimide (PAI) and polyetherimide (PEI) can be selected as the membrane materials to fabricate nanofibrous supportive layers. These polymers are suggested on the basis of their chemical structures as depicted in **Figure 6-1**. Presence of polar functional groups such as ether, ketone, sulfone, imide and amide in the polymers will improve the organophilicity of the substrates for organic compounds with higher polarity (e.g. alcohols, amines, ketones, amides and ethers), giving rise to enhanced transport efficiency of the organics. Moreover, multiphase polymers including polymer blends, graft copolymers, block copolymers and polymer composites can be developed for electrospinning. This strategy combines the advantages of different materials and increases the variety of functionalized electrospun nanofibrous substrates.

Figure 6-1. Chemical structures of polymeric materials.

6.2.2. *Exploitation of new application for nanofibrous composite membranes*

➤ Removal and recovery of other organic compounds

In the actual industrial wastewater streams, a complex mixture of compounds is usually present. The wastewaters can contain various organic compounds and exhibit high salinity, extreme pH and strong corrosiveness. Hence, it is of high interest to apply the nanofibrous composite membranes developed in this work for the removal and recovery of other organic compounds than phenol in aqueous-aqueous extractive processes. For instance, in a typical phenol-formaldehyde resin manufacturing plant, effluents comprising a mixture of methanol, phenol and formaldehyde are produced [209]. Application of current study in treatment of such a multi-organic-containing wastewater is thus of great importance and particularly relevant in industry.

- Application in an extractive membrane bioreactor (EMBR) system

Majority of this work (**Chapters 4 and 5**) has focused on development of high-performance nanofibrous composite membranes for phenol removal in an aqueous-aqueous extractive process. For the sake of simplicity, DI water has been chosen as the receiving solution. In order to evaluate the performance of current nanofibrous composite membranes more practically, it is of high value to extend their application in a more complex and applicable system such as an EMBR. In an EMBR system, the receiving solution is a biomedium where the specialized microbial organisms are developed for the biodegradation of the permeated organic pollutants. More challenges such as control of biofouling will emerge which may require the development of new nanofibrous composite membranes with antifouling properties.

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