PERFORMANCE OF POLYPHENYLSULFONE/COPPER BENZENETRICARBOXYLATE FRAMEWORK NANOFILTRATION MEMBRANE FOR ORGANIC SOLVENTS SEPARATION

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This thesis is dedicated to my beloved husband

(Ridzuan bin Aliman)

my son

(Anas Hakimi)

my parents

(Abdullah Sani bin Ramli and Marbiah binti Mohamad)

my siblings

(Nur Ilyana, Nurul Iffah, Nur Syazana and Muhammad Hirzi)

and friends, who have been constants when everything else was variable

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ABSTRACT

Over the years, the importance of solvent separation emerges to minimize the energy consumption and provide better solvent recovery. The limitation of current technologies has called for new solvents recovery using membrane technology. Hence, the primary focus of this study was to prepare and evaluate the performance of polyphenylsulfone (PPSU) nanofiltration (NF) membranes for organic solvents separation. In the first phase, PPSU membranes with different polymer concentrations in the range of 17 to 25 wt% were fabricated. The experimental results showed that the polymer concentration has great impact not only on the membrane morphology but also its separation characteristics. The obtained results revealed that the PPSU membrane made of 17 wt% polymer concentration (PPSU 17) was the best performing membrane (molecular weight cut off (MWCO) 612 g/mol) due to its promising methanol flux (16.8 $L/m^2.h$) coupled with good rejection of dye (Methyl Blue dye: 92%) at 6 bar. Further investigation using different solvents such as ethanol and isopropanol showed that apart from viscosity, molecular weight and molecular size of the solvent, the affinity between the solvent and the membrane plays a significant role in affecting the transport rate of the solvent through the membrane. In the second phase, PPSU 17 was used to investigate the influence of membrane pretreatment conditions on the membrane properties and performance. It was found that the membrane performance was negatively affected with longer immersion period in methanol solution (14 days) prior to separation experiment, attributed to the rearrangement of the polymer chain which result in membrane swelling and/or change of membrane surface hydrophilicity. In the third phase, the performance of PPSU 17 membrane was further enhanced by incorporating the membrane with copper-1,3,5-benzenetricarboxylate (Cu-BTC) particles at different loadings (0.5 to 3 wt%). The results indicated that when 0.8 wt% Cu-BTC was incorporated into PPSU membrane (designated as PPSU/0.8Cu-BTC), the methanol flux increased by 43% while membrane MWCO decreased by 18% in comparison with the neat PPSU membrane, when both were tested using 10 ppm of methanol-dyes solution at 6 bar. The improvement in membrane flux and dye rejection could be attributed to the good dispersion of the Cu-BTC particles in the membrane matrix coupled with their improved interfacial contact with the membrane. In addition, the incorporation of Cu-BTC showed a great improvement in terms of resistance to compaction, indicating the importance of Cu-BTC in increasing membrane rigidity and strength.

ABSTRAK

Selama bertahun-tahun, pemisahan pelarut muncul untuk mengurangkan penggunaan tenaga dan menyediakan perolehan pelarut yang lebih baik. Batasan teknologi semasa bagi perolehan pelarut memerlukan penggunaan teknologi membran. Oleh sebab itu, fokus utama kajian ini adalah untuk menyediakan dan menilai prestasi membran turasan-nano (NF) polifenilsulfona (PPSU) untuk pemisahan pelarut organik. Pada fasa pertama kajian ini, membran PPSU dengan kepekatan polimer yang berbeza-beza dalam julat antara 17 hingga 25% berat telah dihasilkan. Hasil kajian mendapati bahawa kepekatan polimer mempunyai kesan yang besar terhadap bukan sahaja morfologi membran tetapi juga sifat pemisahannya. Keputusan yang diperolehi mendedahkan bahawa membran PPSU dengan kepekatan polimer sebanyak 17% berat (PPSU 17) merupakan membran berprestasi paling baik (potongan berat molekul (MWCO) 612 g/mol) kerana kadar fluks metanol yang memberangsangkan (16.8 L/m^2.h) serta penolakan pewarna yang baik (Pewarna Metil Biru: 92%) pada tekanan 6 bar. Kajian selanjutnya menggunakan pelarut yang berbeza-beza seperti etanol dan isopropanol telah menunjukkan bahawa selain dari kelikatan, berat molekul dan saiz molekul pelarut, tarikan antara pelarut dan membran juga berperanan penting dalam mempengaruhi kadar pengangkutan pelarut melalui membran. Pada fasa kedua, PPSU 17 telah digunakan untuk mengkaji pengaruh keadaan prarawatan membran tehadap sifat-sifat dan prestasi membran. Keputusan kajian mendapati bahawa prestasi membran terjejas dengan tempoh rendaman yang lama dalam larutan metanol (14 hari) sebelum proses pemisahan disebabkan oleh penyusunan semula rantai polimer yang mengakibatkan pembengkakan membran dan/atau perubahan kehidrofilikan permukaan membran. Pada fasa ketiga, prestasi membran PPSU 17 seterusnya ditingkatkan dengan menggabungkan membran dengan partikel kuprum-1,3,5,-benzenatrikarboksilat (Cu-BTC) dengan muatan yang berbeza-beza (0.5 hingga 3% berat). Keputusan kajian menunjukkan apabila 0.8% berat Cu-BTC digabungkan ke dalam membran PPSU (dilabelkan sebagai PPSU/0.8Cu-BTC), kadar fluks metanol meningkat sebanyak 43% manakala MWCO membran menurun sebanyak 18% berbanding dengan membran PPSU tanpa partikel Cu-BTC, apabila keduanya diuji menggunakan larutan 10 ppm metanol-pewarna pada 6 bar. Peningkatan kadar fluks dan penyingkiran pewarna adalah disebabkan oleh serakan yang baik partikel Cu-BTC dalam matrik membran ditambah pula dengan persentuhan antara muka yang lebih baik dengan membran. Tambahan pula, penggabungan dengan Cu-BTC menunjukkan peningkatan dari segi ketahanan mampatan, disebabkan oleh kepentingan Cu-BTC dalam meningkatkan kekuatan dan ketegaran membran.

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LIST OF ABBREVIATIONS

6PDA	-	2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride
AFM	-	Atomic force microscopy
APDEMS	-	Aminopropylediethoxymethylsilane
APTMS	-	Aminopropyl trimethoxysilane
BTB	-	Bromothymol Blue
CA	-	Cellulose acetate
CCC	-	Counter-current chromatography
Cu-BTC	-	Copper-1,3,5-benzenetricarboxylate
DBB	-	Dibromobutane
DBX	-	Dibromoxylyne
DCM	-	Dichloromethane
DEO	-	1,2,7,8-diepoxyoctane
DMF	-	Dimethylformamaide
DMSO	-	Dimethylsulfoxide
EDX	-	Energy dispersion X-ray spectrometer
FTIR	-	Fourier transform infrared
GA	-	Glutaraldehyde
IP	-	Interfacial polymerization
MB	-	Methyl Blue
MEK	-	Methyl ethyl ketone
MMM	-	Mixed matrix membrane
Mn	-	Manganese
MOF	-	Metal organic frameworks
MR	-	Methyl Red
M_w	-	Molecular weight
MWCO	-	Molecular weight cut off

NF	-	Nanofiltration
NMP	-	N-methyl-2-pyrrolidone
n-TFC	-	Nano thin film composite
PA	-	polyamide
PANI	-	Polyaniline
PBI	-	Polybenzimidazole
Pd	-	Palladium
PDMS	-	Polydimethylsiloxane
PEG	-	Polyethyleneglcol
PEG	-	Polyethylene glycol
PEI	-	Polyetherimide
PES	-	Polyethersulfone
PI	-	Polyimide
PIB	-	Polyisobutylene
PPSU	-	Polyphenylsulfone
PSF	-	Polysulfone
PVDF	-	Polyvinylidenefluoride
RO	-	Reverse osmosis
RO16	-	Reactive Orange 16
RR120	-	Reactive Red 120
Ru	-	Ruthenium
SEM	-	Scanning electron microscopy
SRNF	-	Solvent resistant nanofiltration
TEM	-	Transmission electron microscopy
TFC	-	Thin film composite
TFN	-	Thin film nanocomposite
TGA	-	Thermal gravimetric analysis
THF	-	Terahydrofuran
THF	-	Tetrahydrofuran
TiO_2	-	Titanium dioxide
XRD	-	X-ray diffraction

LIST OF SYMBOLS

A	-	Membrane effective area (m^2)
c_f	-	Solute concentration in the feed (ppm)
c_p	-	Solute concentration in the retentate (ppm)
D_{AB}	-	Diffusion coefficient of solute A in solvent B (m^2/s)
d_A	-	Effective solute diameter (nm)
J	-	Membrane flux ($L/m^2.h$)
k	-	Boltzmann coefficient (J/K)
R	-	Membrane rejection (%)
R_a	-	Mean roughness (nm)
R_q	-	Root mean square of Z data (nm)
T	-	Temperature (K)
t	-	Time (h)
V	-	Volume of permeate (L)
V_A	-	Solute molar volume (m^3/kg.mol)
V_m	-	Molar volume (cm^3/mol)
$\emptyset$	-	Association parameter of solvent (dimensionless)
μ	-	Viscosity (mPa.s)
λ	-	Wavelength
δ	-	Solubility parameter ($Mpa^{1/2}$)
θ	-	Diffraction angle
$\sum E_{coh}$	-	Cohesive energy (J/mol)

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CHAPTER 1

INTRODUCTION

1.1 Membrane separation processes

Separation processes are of the utmost importance in pharmaceutical industry, consuming 40 to 90% of both capital and operating cost (Buonomenna and Bae, 2014). In addition, most pharmaceutical syntheses are solvent-based processes and its final products require separation and purification from the solvents. Besides synthesis, the solvents are also used as a cleaning agent. The solvent-product separation and solvent recovery (from cleaning process) are normally carried out using distillation, evaporation and extraction. However, these separation techniques are energy intensive (Vandezande *et al.*, 2008; Marchetti *et al.*, 2014). Since 1960s, membrane separation processes have been gradually applied in the industry. They are feasible alternatives and could be integrated with conventional separation processes such as distillation, evaporation, adsorption, extraction, and chromatography. Such integrations are reported to improve the process in terms of economy, environment, and safety. Unfortunately, its implementation has been limited to aqueous applications (Baker, 2004; Hilal *et al.*, 2004).

The membrane is a semi-permeable and selective barrier. It selectively allows certain species to permeate through, whilst hinders the others making it possible to perform separation. A schematic representation of membrane separation is given in Figure 1.1. Transport through the membrane takes place because of differences in physical and/or chemical properties between the membrane and the permeating components. The driving force for the transport of species is provided by a pressure, concentration, temperature and electrical potential difference between the feed and permeate at each side of the membrane. (Mulder, 1996). Other than the driving force, the membrane itself is the principle factor determining the selectivity and flux. In fact, the nature of the membrane, i.e. structure and material, determines the type of application, ranging from the separation of macroscopic particles to the separation of molecules of an identical size and shape (Baker, 2004).

Several types of membrane separation processes have been developed for specific industrial applications such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). As shown in Figure 2.1**Figure 2.2**, distinction between these processes is primarily made on the basis of (1) the pressure required for the separation; (2) the size of the rejected solute or, in turn the size of the pore; (3) the molecular weight cut off (MWCO); and (4) the transport mechanism governing the separation (Vandezande *et al.*, 2008; Marchetti *et al.*, 2014). Among various membrane processes, NF membranes have been proved useful in many application such water softening, removal of pesticide and micro-pollutants from ground water, treatment of textile wastewater, virus and bacteria removal, decontamination and recycling of industrial wastewater and removal of heavy metal ions from ground water (Zhang *et al.*, 2006; Lau and Ismail, 2009; Lau *et al.*, 2013; Miralles-Cuevas *et al.*, 2014; Chen *et al.*, 2015). The success of NF in aqueous systems has triggered expansion to organic solvent. In the late 1990s, a new spin-off of NF so called solvent resistant nanofiltration (SRNF) emerged.

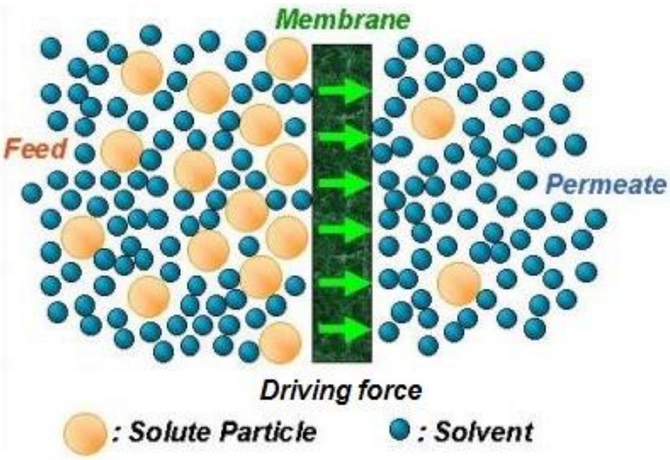

Figure 2.1 Schematic representation of filtration using membrane (Mulder, 1996).

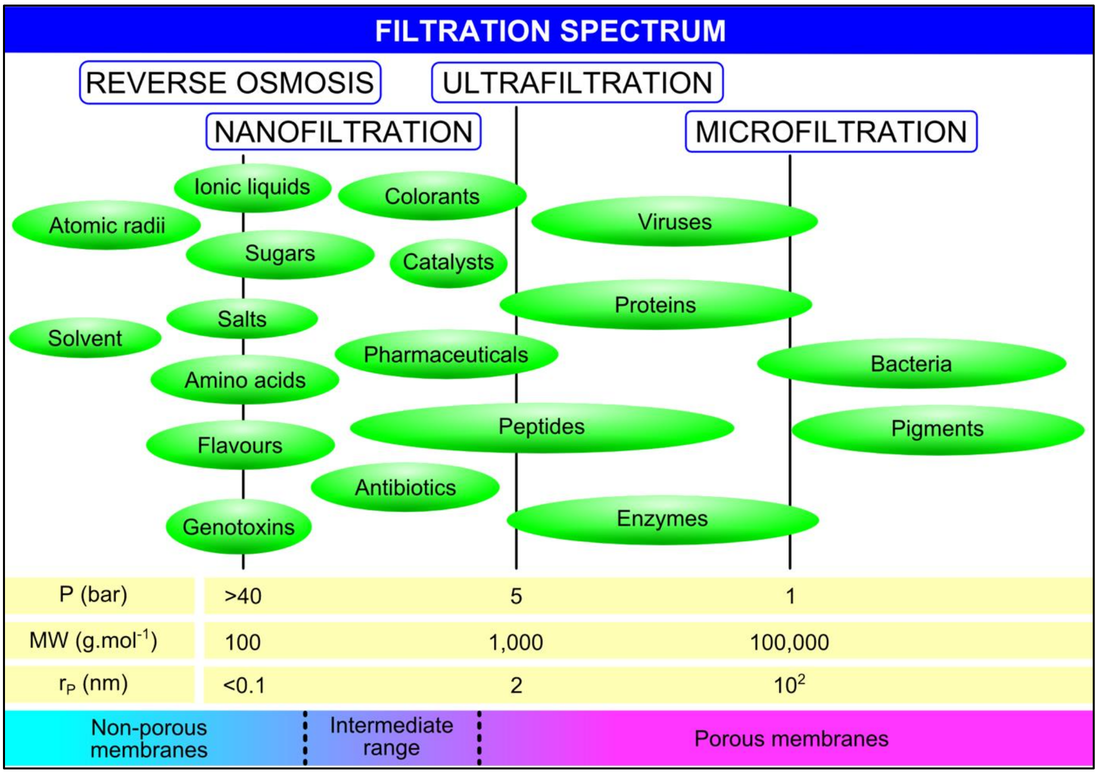

Figure 2.2 Classification of membrane processes according to operating pressure, retained solute/pore size (nm), MWCO (g/mol), transport mechanism, and examples of applications (Marchetti *et al.*, 2014).

1.2 Solvent resistant nanofiltration (SRNF)

NF of non-aqueous system or SRNF is a relatively young membrane separation technology that holds enormous potential as it allows separation of small compounds with M_w ranging from 200 to 1400 g/mol from organic solvents. SRNF-based technology has been proven to be significant in expanding the spectrum of membrane applications from aqueous systems primarily for water purification and other water-related treatments to filtration and concentration of organic solutions. In addition to solvent recovery in pharmaceutical industry, SRNF-based technologies can be applied for recovery of solvents from dewaxed lube oil filtrates, organometallic complexes recovery from various organic solvents, separation of phase transfer catalyst from toluene, deacidification of vegetable oils and concentration of pharmaceuticals (Raman *et al.*, 1996; Subramanian *et al.*, 1998; White and Nitsch, 2000; Luthra *et al.*, 2002; Scarpello *et al.*, 2002; Sheth *et al.*, 2003; Geens *et al.*, 2007; Tylkowski *et al.*, 2011). The incentives to apply SRNF are numerous. Its lower energy consumption than the conventional techniques and ease of scaling-up and retrofitting make it particularly attractive for pharmaceutical process (Vandezande *et al.*, 2008). The pharmaceutical process has low process temperature to prevent thermal degradation of sensitive substance, thus very suitable for SRNF. By having the SRNF, the solvent recovery process could offer significant benefits with regards to reduce purchase, storage and discharge costs. However, most current NF membranes are designed specifically for aqueous which are completely unfit for organic solvents recovery. The typical NF would suffer from excessive swelling or even complete dissolution of the membrane material resulting loss of selectivity (Van der Bruggen *et al.*, 2002b; Vanherck *et al.*, 2008). Therefore, the development of advanced SRNF has been initiated.

1.3 Problem statements

Currently, majority of SRNF membranes are made of polymeric materials. Polymers provide wide choices, relatively easy processing and good reproducibility. It is also much easier to tailor polymeric membrane to the application as compared with ceramic membranes. However, literature reveals that polymeric membranes suffer from severe performance loss in organic solvents due to their chemical instability. Being exposed to organic solvents causes infinite flux due to membrane swelling or dissolution, zero flux due to membrane collapse, poor selectivity or rejection and membrane deterioration (Raman *et al.*, 1996; Subramanian *et al.*, 1998; Bridge *et al.*, 2002). Besides, most studies on the SRNF membrane have been performed using commercially available membranes which are typically made for aqueous applications. Hence, in this research work, a new class of polysulfone (PSF) family–polyphenylsulfone (PPSU) was selected for SRNF study. PPSU is known to have superior properties compared to the more frequently used PSF and polyethersulfone (PES). It presents greater resistance to hydrolysis and plasticization. Its moderate thermal and mechanical stability, chemical resistance and ease of manufacturing make PPSU a suitable material as SRNF membranes (Scheirs, 2000; Darvishmanesh *et al.*, 2011a). Therefore, there is a need to evaluate in detail the

PPSU properties and separation performance in solvent particularly methanol before it can be implemented at industrial scale. Methanol was selected as the solvent due to its extensive use in pharmaceutical syntheses. It has good solubility against many organic solutes at high concentrations. Four different types of dyes with molecular weight (M_w) in the range of 269 to 1470 g/mol were selected to represent of pharmaceutical products.

Up to now, most of the SRNF research works have focused on (1) improving membrane stability in various types of solvent, (2) tailoring membrane pore size/MWCO and/or (3) unravelling solvent and solute transport mechanisms. Very little attention is paid to membrane pretreatment, although several researchers have reported that it could enhance or decrease the membrane flux due to the solvent-membrane interactions (Jeżowska *et al.*, 2006; Darvishmanesh *et al.*, 2010a). The purpose of pretreating membrane with organic solvent is to stabilize the membrane prior to any experiment. It is because sudden exposure of membrane to solvent of filtration may result in inconsistent flux and sudden swell of membrane. For this reason, it is necessary to investigate the influence of pretreatment conditions since it would affect membrane properties as well as performance.

Recently, it is reported that low membrane flux and poor solute rejection has become a major obstacle in polymeric membrane separation process. As reported by Gibbins *et al.* (2002) and Siddique *et al.* (2014b), the polymeric membranes often suffer from flux decline over time, caused by pressure induced compaction which leads to rearrangement of the polymer chains in solvent and/or fouling problem. One approach to reduce this problem is by producing hybrid organic/inorganic membranes known as mixed matrix membrane (MMM). Previous research works have shown that the introduction of inorganic fillers into membrane matrix could improve solvent flux and/or enhance mechanical stability, but poor adhesion between polymer and inorganic filler is likely to occur, leading to interface void formation. These voids, that are much larger than solute size, may negatively affect membrane rejection rate. Therefore, metal organic framework (MOF) has been proposed in this work for MMMs fabrication with the aim of minimizing formation of void, reducing flux decline due to compaction, and increasing chemical and mechanical strength of membranes. Of the various MOFs available, copper-1,3,5-benzenetricarboxylate (herein referred to as Cu-BTC) was selected as it has highly affinity to organic linkers of MOFs and polymer chains. This would minimize the formation of voids. Furthermore, Cu-BTC contains nanoscale pore size of around 0.9 nm in diameter, making it suitable to transport most solvents used in SRNF whilst capable of rejecting solute of bigger size (Küsgens *et al.*, 2009; Li *et al.*, 2009). Hence, it is expected that the addition of Cu-BTC into the PPSU membrane matrix could enhance solvent permeability and solute rejection as well as chemical and mechanical stability.

1.4 Objectives of the study

The main focus of this study is to develop SRNF membrane with the sufficient chemical and mechanical stability for solvent separation. The main concerns in the fabrication of the membranes and their properties are the influence of several important parameters, i.e. polymer concentration, inorganic filler loading and operating condition. Hence, the main objectives of the study are:

(i) To study the influence of polymer concentration and solvent properties on the performance of PPSU membranes.

(ii) To investigate the effect of membrane pretreatment conditions on the PPSU membrane properties and separation performance.

(iii) To investigate the influence of Cu-BTC loading on the PPSU-based membrane properties and separation performance.

(iv) To investigate the influence of solvents exposure and operating conditions on the performance of PPSU and PPSU/Cu-BTC membrane.

1.5 Scopes of the study

In order to meet the objectives of this study, following scopes of work have been performed:

(i) Preparing the PPSU membrane solution at three different polymer concentrations ranging from 17 to 25 wt% *via* phase inversion method.

(ii) Investigating the effect of solvent properties using methanol, ethanol and isopropanol on the separation performance of selected PPSU membrane.

(iii) Identifying the ideal polymer concentration for membrane pretreatment process and preparation of MMM for methanol filtration.

(iv) Investigating the effect of membrane pretreatment conditions on the membrane properties and separation performance with respect to pure methanol flux and dye rejection using selected PPSU membrane.

(v) Synthesizing Cu-BTC powder *via* precipitation method using copper nitrate and 1,3,5-benzenetricarboxylate acid.

(vi) Characterizing the Cu-BTC using X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), N_2 adsorption/desorption analysis, thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscope in order to confirm the formation of Cu-BTC.

(vii) Preparing the PPSU/Cu-BTC membranes by varying the Cu-BTC concentration (0.5, 0.8, 1 and 3 wt%) in the dope containing 17 wt% PPSU.

(viii) Characterizing membrane morphology structure and Cu-BTC dispersion in the PPSU membrane using scanning electron microscope (SEM), energy dispersive X-ray (EDX) spectroscope, atomic force microscope (AFM) and Fourier transform infrared (FTIR) spectroscope.

(ix) Determining physicochemical properties of the PPSU/Cu-BTC membranes in terms of contact angle, tensile strength, elongation at break and thermal decomposition behaviours.

(x) Identifying the optimum Cu-BTC loadings for the PPSU/Cu-BTC membrane based on separation performance using methanol and dye/methanol solutions.

(xi) Investigating the effect of solvent (methanol, ethanol, isopropanol, acetonitrile, ethyl acetate, *n*-hexane and *n*-heptane) exposures, various operating conditions, such as dye concentrations and operating pressures on the performance of selected PPSU/Cu-BTC and PPSU membranes.

(xii) Investigating the potential of the PPSU/Cu-BTC membrane for pharmaceutical application by separating erythromycin from methanol solution.

1.6 Rational and significance of the study

The lack of SRNF membranes with high performance, chemical and mechanical stability has been the major problem for SRNF development. Currently, the membrane materials used for commercial SRNF are primarily cross-linked polyimides (PI) and polydimethylsiloxane (PDMS). The typically high price of PI and the serious swelling of PDMS have limited the practical applications of these membranes in non-aqueous medium. Therefore, in this study, the development of new types of MMMs which consist of PPSU and Cu-BTC particles has been explored. The impact of this study will be significant since the incorporation of Cu-BTC in PPSU-based membrane could enhance the chemical and mechanical properties of PPSU membrane. Besides, the MMMs could provide high rejection of dyes and solvent flux. PPSU is a remarkable candidate for synthesis of SRNF membranes due to its high resistance to degradation, good chemical stability, lower cost than PI and ease of manufacturing (Darvishmanesh *et al.*, 2011a; Díez-Pascual and Díez-Vicente, 2014). The addition of Cu-BTC as the inorganic filler has further made this membrane mechanically stable owing to its good affinity with PPSU matrix. Besides, its high porosity could enhance the performance of PPSU membrane by allowing transport of most solvents whilst rejecting solute of a certain size. With a rapid synthesis at room temperature, nanoparticle Cu-BTC can be easily obtained instead of conventional methods which require long reaction times with high temperature (Seo *et al.*, 2009; Decoste *et al.*, 2012). Therefore, combining both of PPSU and Cu-BTC advantages could offer opportunities to expand application area of MMMs, particularly in pharmaceutical industry.

1.7 Organization of the thesis

The thesis consists of 8 chapters. Chapter 1 outlines brief information on membrane separation processes and the introduction of SRNF. Then, the details of the problem statements, objectives and scopes of this study have also been stated in detail. Chapter 2 provides the background information of SRNF development and a brief review regarding SRNF polymeric membranes. The limitation of polymeric membranes in SRNF applications and strategies to overcome the limitation using MMM is also described in detail. Additionally, the interaction between solvent-solute-membrane during membrane performance is also discussed. Chapter 3 covers the experimental part of the research whereby the membrane synthesis, characterization and performance were discussed.

Chapter 4 describes in detail the preparation of PPSU membrane made of different polymer weight concentration (17, 21 and 25 wt%) *via* phase inversion method. The chapter highlights the influence of polymer concentration on membrane formation, properties and performance. The effect of solvent properties on membrane performance was further investigated using selected PPSU membrane. Chapter 5 focuses on the influence of membrane pretreatment period on membrane properties and performance. This study was carried out using 17 wt% PPSU with good balance of flux and selectivity. Chapter 6 presents the development of PPSU/Cu-BTC membranes made of Cu-BTC loadings and their separation performance in methanol-dye solutions. This chapter also describes in detail the properties of synthesized Cu-

BTC. The best performing PPSU/Cu-BTC membrane was then tested under various operating condition and the results were compared with control PPSU membrane (Chapter 7). The effect of solvent exposures, dye concentration in feed solution and operating pressure thoroughly investigated in this chapter. The operational stability test and its industrial potential are also studied using the best performing PPSU/Cu-BTC membrane. General conclusion of this research is drawn in Chapter 8. Some recommendations for future research are also included in the chapter.

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