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Performance of Polyphenylsulfone-based Solvent Resistant Nanofiltration Membranes in Removing Dyes from Methanol Solution

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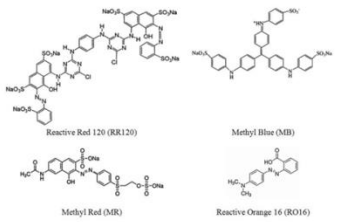
Graphical abstract



Abstract

In this study, polyphenylsulfone (PPSU) which is a third member of the polysulfone (PSF) family, with even better properties than PSF and polyethersulfone (PES) was used to prepare flat sheet solvent resistant nanofiltration (SRNF) membranes. The SRNF membranes were prepared from different PPSU concentrations (i.e. 17, 21 and 25 wt%) via phase inversion method. The performance of membranes was then evaluated by measuring the methanol flux and rejection against dyes of different molecular weight (MW) dissolved in methanol. The study revealed that the membrane with the lowest polymer concentration produced the highest pure methanol flux and required the longest time to achieve steady-state owing to its porous structure. Results also showed that the flux of the membranes tended to decrease with filtration time due to the membrane compaction. With respect to the membrane separation performance, it was found that the membrane dye rejection increased while permeate flux decreased with increasing the MW of dye components from 269 to 1470 g/mol, irrespective of the polymer concentration. Furthermore, the membrane MWCO was found to change with polymer concentration in which an increase in polymer concentration led to a lower membrane MWCO.

Keywords: Polyphenylsulfone; solvent resistant nanofiltration; methanol flux; dye rejection

1.0 INTRODUCTION

Organic solvents are widely used in many fields of industry and in most cases they have to be discarded after use. Solvent lube oil dewaxing processes, deacidification of crude oil, edible oil processing and chemical syntheses are the examples of industrial applications involving the use of organic solvents. Conventional separation processes such as distillation, evaporation and extraction are generally employed in these processes for solvent recovery. However, they are associated with many significant drawbacks such as high energy consumption, loss of neutral oil, need for large amounts of water and chemicals, loss of nutrients, and disposal problem of highly concentrated solutions [1]. Membrane technology especially in NF, experiences increasing attention compared to these separations techniques as it offers many advantages such as less energy consumed, no additives required and low operational cost [2].

Nanofiltration (NF), which is intermediate between reverse osmosis and ultrafiltation, is a pressure driven process used for removing solutes from aqueous system. Recently, much interest has been focused on NF for filtration and concentration of organic solutions. NF of organic solutions, which is also known as solvent resistant nanofiltration (SRNF), is applied to separate compounds dissolved in solvents with molecular weight (MW) ranging from 200 to 1400 Da, with simultaneous passing of the organic solvent through the membrane. SRNF-based technologies allow effective recovery of solvent in lube oil dewaxing processes [3], degumming of vegetable oil [4], reuse of extraction solvent in food industries [5] and purification of pharmaceutically active ingredients [6].

It must be pointed out that the applications of NF membrane in organic solution are not very successful compared to their uses in aqueous solution. The use of polymeric membranes in SRNF has been employed by a growing number of researchers [7-11], however these membranes show severe performance loss due to their chemical instability in organic solvents. Among the problems include infinite [12], flux caused by either the membrane swelling or dissolve [12], zero flux due to membrane collapse poor selectivity or rejection11 and membrane performance deterioration as a function of filtration time [13].

Besides, most of the published studies on the SRNF membrane have been performed using the commercially available membranes which the membranes can become unstable in certain classes of solvents such as chlorinated solvents and aprotic solvents. Moreover, the membranes are proprietary products, without any details known about the materials and the structures. For example, Geens *et al.* [14] have found that commercial membranes, e.g. StarMem 120, StarMem 122 and StarMem 228 dissolved from its support layer and resulting in low rejections against dichloromethane. Tarleton *et*

al. [15] on the other hand observed that selective polydimethylsiloxane layer on polyacrylonitrile support swelled after tested with low polarity solvent systems.

Several solutions have been proposed in literature to overcome the recurrent problems. Aerts *et al.* [16] have prepared plasma modification of PDMS membrane and subjected for the separation of dyes in aprotic solvent. Bitter *et al.* [17] have used halogen-substituted silicon rubber for the separation of solvents from hydrocarbons dissolved in the solvents. However, both approaches were not practical for industrial applications due to the significant flux reduction after a short period of operation.

Therefore, the aim of this study is to provide valuable information about the third member of the polysulfone family, polyphenylsulfone (PPSU) for organic solvent NF application. In this work, the properties of the PPSU membranes were evaluated by varying the polymer concentration during dope solution preparation. The performance of the PPSU membranes were then characterised with respect to methanol flux and dye rejection. Different MWs of dyes in the range of 269–1470 g/mol were used to investigate the separation behavior of the PPSU membrane.

2.0 EXPERIMENTAL

2.1 Materials

PPSU (MW of 11044 g/mol) purchased from Sigma-Aldrich, Malaysia was used as a membrane forming material for SRNF preparation. N-methyl-2-pyrrolidinone (NMP) obtained from Merck, Malaysia was used as solvent to dissolve PPSU polymer. Methanol (≥99% purity) was used in this study is the common solvent used in pharmaceutical industry. Methyl red (MR), reactive orange 16 (RO16), methyl blue (MB) and reactive red 120 (RR120) purchased from Sigma-Aldrich, Malaysia were selected as a marker in this study to check the rejection of the membranes. The MWs of dyes and their maximum absorption wavelengths are shown in Table 1; the structures of the dyes are shown in Figure 1.

Table 1 Dye properties

Dye	Molecular weight (g/mol)	Maximum absorption wavelength (nm)
Reactive Red 120 (RR120)	1470	335
Methyl Blue (MB)	800	315
Reactive Orange 16 (RO16)	616	295
Methyl Red (MR)	269	495

2.2 Preparation of Membranes

PPSU membranes were prepared from polymeric dope solutions containing various PPSU concentrations, i.e., 17, 21 and 25 wt%. PPSU membranes were prepared by dissolved pre-weighed quantity of the polymer pellets in NMP at room temperature and stirred overnight to ensure complete polymer dissolution. The solutions were left at least 24 h to remove air bubbles before it were used for membrane casting. The polymer solution was cast on a glass plate without any non-woven support using a casting knife at room temperature. It was subsequently immersed in a non-solvent bath of tap water and kept for 24 h. The membranes were subjected to air drying process at room temperature for at least 24 h prior to use. The morphology of prepared membrane was observed by scanning electron microscope (SEM) (TM3000, Hitachi, Japan). Samples of SEM analysis were prepared by fracturing the membrane in liquid nitrogen.

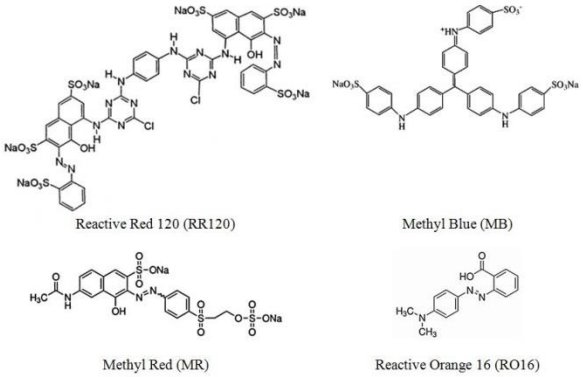


Figure 1 Molecular structure of dyes used in this study

2.3 Experimental Procedure

The separation performances of the membranes were carried out using dead-end stirred cell (Sterlitech HP4750, Sterlitech Corporation, USA) with maximum capacity of 300 mL. The active membrane area was approximately 14.6 cm^2. A nitrogen cylinder equipped with a two-stage pressure regulator was connected to the top of the stirred cells to supply the desired pressure for filtration experiments. In order to minimize concentration polarization during the experiments, a Teflon-coated magnetic stirring bar was used and was controlled at 700 rpm on top of the active side of membrane. Prior to the experiment, the membrane was soaked in the methanol for about 1 min. The experiment was then performed at 5 bar using pure solvent and 6 bar for solvent-dye mixtures experiment. The membrane flux was collected after 30 min of experiment when flux had achieved steady-state and measured every 10 min for up to 3 h. The flux (J) ($L/m^2 \cdot h$) was calculated by the following equation where V, A and t are permeate volume, membrane area and time, respectively. Three flux measurements were made and the average value was reported.

$$J = \frac{\Delta V}{A \cdot \Delta t} \quad (1)$$

With respect to dye rejection determination, the experiment was carried out by filtering methanol containing different MW of dyes (see Table 1) at initial concentration of 10 mg/L. The rejection rate, R (%) of the dyes by the membranes was calculated using the following equation:

$$R\,(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where is the dye concentration (mg/L) of permeates and is the initial concentration (mg/L). The dye concentrations in the permeate and feed stream were measured using UV-vis spectrophotometer (DR5000, Hach Company, USA). A blank wavelength scan with pure solvent was performed first followed by the permeate sample. The properties and wavelength of

maximum absorbance (λ_{max}) for each dye used in the experiment are presented in Table 1.

3.0 RESULTS AND DISCUSSION

3.1 Flux behaviour of PPSU Membrane as a Function of Time

Figure 2 (a-c) shows the flux stability of the PPSU membrane at different polymer concentration (i.e. 17, 21 and 25 wt%) as a function of time for pure methanol solvent at 5 bar. The experiment was carried out for the period of 180 min. The PPSU membrane prepared with 17 wt% polymer concentration has the highest flux and 25 wt% polymer concentration shows the lowest flux. The flux increased as the polymer concentration increased from 17 to 25 wt%, owing to the increase in the entire membrane resistance which mainly resulted from reduces surface pore size and suppression of finger-like pores as confirmed by the inserted SEM images in the Figure 2. Compared to the 17 and 21 wt% PPSU membrane, in which the cross sectional structure was dominated by finger-like microvoids, the development of sponge-like morphology as shown in the 25 wt% PPSU membrane has played a role in increasing solvent transport resistance and reducing methanol productivity.

Results for all of the membrane show that the flux was at its highest at the initial period and declined as the test progressed. For 17 wt% of PPSU membrane, the flux decreased from 57.5 to 36.2 L/m^2.h with a reduction of 37.1%. The 21 wt% of PPSU membrane displays a relative stable flux compared to 17wt% of membrane and the flux changes from 22.1 to 10.6 L/m^2.h with a reduction of 52%. The flux of methanol for 25 wt% of PPSU membrane shows reduction for about 68.1% from 2.5 to 0.5 L/m^2.h. This behavior suggests that the membranes were compacted during the test. The membrane pores were shrunk because of the membrane compaction, hence the pore size became smaller, leading to reduction in the permeate flux. Whu *et al.* [18] and Yang *et al.* [19] also observed this inclination when filtering methanol through commercial membrane (MPF membrane series), and suggested that this were caused by membrane compaction. The results also show that the 17 wt% of PPSU membrane took the longest time to reach steady state which about after 140 min, while the 25 wt% of PPSU membrane achieved steady-state only after 80 min. The factor that contributes to this phenomenon is a macrovoid structure of the membrane. The microvoids structure of 17wt% of PPSU membrane causes the membrane required longer time (compaction process) to achieve steady-state compared with sponge-like structure of 25wt% of PPSU membrane. This result shows good agreement with Persson *et al*. [20] in which the macrovoid structure is more affected by compaction than a sponge-like structure. Jonsson [21] also reported that the compaction preferentially occurs in the bulk layer where most of the pore volume, i.e. large pores and macrovoids are situated. Compaction also reduced the membrane thickness which would lead to increased permeate flux. However, the effect of a smaller pore size on the permeate flux reduction seem to be predominant.

3.2 Performance of PPSU Membrane in Dye Removal

In this study, four different dyes with increasing molecular weight (MW) from 269 to 1470 g/mol were used to determine the performance and molecular weight cut off (MWCO) of PPSU membranes. The MWCO was determined by plotting rejection of solutes against solute MW and interpolated to determine the MW at 90% rejection. Figure 3 illustrates the rejection of four different dyes as a function of MW at an operating pressure of 5 bar. Rejections of dyes were reported by varying the polymer concentration of PPSU membrane. From Figure 3, it is obvious that the dye rejection increased with increasing MW of dye components from 269 to 1470 g/mol, irrespective of polymer concentration. As the MW of the dye gets larger, the sieving effect due to steric hindrance increases and the higher MW of solute is rejected by the membrane better than the lower MW of solute. With respect to the MWCO of the membranes, an increase in polymer concentration was observed to give a lower MWCO. The membrane MWCO was reported to shift approximately 660 to 580 g/mol, by changing the polymer concentration from 17 to 25 wt%, recording close to a 12% decrease in membrane pore size.

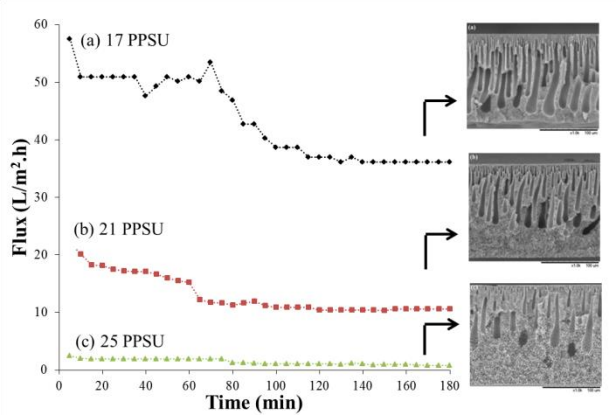


Figure 2 Pure methanol flux of PPSU membranes as a function of time together with membrane cross-sectional images

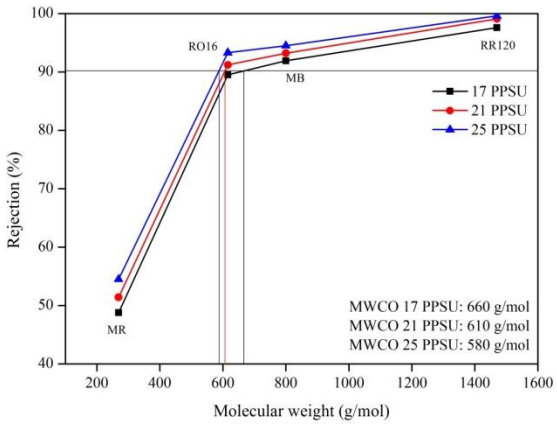


Figure 3 Effect of polymer concentration on rejection of different MW of dyes

With respect to the permeate flux of the PPSU membrane, the flux for different polymer concentration is inversely proportional to the rejection trend of dyes. From Figure 4, it can be seen that the flux decreased with increasing MW of dye components from 269 to 1470 g/mol, irrespective of polymer concentration. The flux of the larger MW of the dye component was obviously lower than that of smaller MW for all three types of PPSU membranes. The decrease in solvent flux can be explained by the fact that the large MW of the dye component tends to form additional selective layers on top of the membrane

(resulting from almost complete solute rejection), leading to an increase in solvent transport resistance and decrease in solvent permeability.

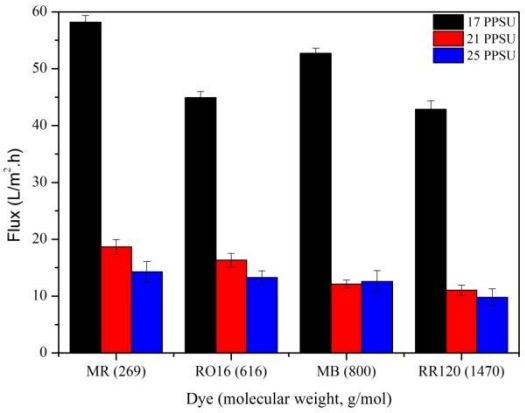


Figure 4 Effect of polymer concentration on permeate flux of different MW of dyes

4.0 CONCLUSION

In the present study, PPSU membrane with different polymer concentrations (i.e. 17, 21 and 25 wt%) were successfully prepared using the phase inversion method. The performance of PPSU membranes with different polymer concentration in pure methanol solvent exhibited slightly decrease in time. The highest polymer concentration required longer time to achieve steady-state (compaction process) compared to the lowest polymer concentration. This behavior can be related to microvoids structure of membrane and compaction process. With respect to the membrane performances using dye-solvent mixtures, increasing the MW of dye components leads to increase in the membrane rejections and lower the permeate fluxes. It was also found that the membrane MWCO decreased from approximately 660 to 580 g/mol by increasing the polymer concentration from 17 to 25 wt%.

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References

[1] Subramanian, R., Nakajima, M., Raghavarao, K. S. M. S. and Kimura, T. 2004. Processing Vegetable oils using Nonporous Denser Polymeric Composite Membranes. *J. Am. Oil Chem. Soc.* 81(4): 31–322.

[2] Dobrak, A., Verrecht, B., Van den Dungen, H., Buekenhoudt, A., Vankelecom, I. F. J. and Van der Bruggen, B. 2010. Solvent Flux Behavior and Rejection Characteristics of Hydrophilic and Hydrophobic Mesoporous and Microporous TiO_2 and ZrO_2 Membranes. *J. Membr. Sci.* 346(2): 344–352.

[3] White, L. S. and Nitsch, A. R. 2000. Solvent Recovery from Lube Oil Filtrates with a Polyimide Membrane. *J. Membr. Sci.* 179: 267–274.

[4] Rama, L. P., Cheryan, M. and Rajagopalan, N. 1996. Solvent Recovery and Partial Deacidification of Vegetable Oils by Membrane Technology. *Lipid/Fett.* 98(1): 10–14.

[5] Tylkowski, B., Tsibranska, I., Kochanov, R., Peev, G. and Giamberini, M. 2011. Concentration of Biologically Active Compounds Extracted from Sideritis ssp. L. by Nanofiltration. *Food Bioprod. Process.* 89(4): 307–314.

[6] Geens, J., De Witte, B., and Van der Bruggen, B. 2007. Removal of API's (Active Pharmaceutical Ingredients) from Organic Solvents by Nanofiltration. *Sep. Sci. Tech*. 42: 2435–2449.

[7] Machado, D. R., Hasson, D. and Semiat, R. 1999. Effect of Solvent Properties on Permeate Flow through Membranes. Part I: Investigation of Parameters Affecting Solvent Flux. *J. Membr. Sci.* 163: 93–102.

[8] Van der Bruggen, B., Geens, J. and Vandecasteele, C. 2002. Fluxes and Rejections for Nanofiltration with Solvent Stable Polymeric Membranes in Water, Ethanol and n-hexane. *Chem. Eng. Sci.* 57(13): 2511–2518.

[9] Van der Bruggen, B., Geens, J. and Vandecasteele, C. 2002. Influence of Organic Solvents on the Performance of Polymeric Nanofiltration Membranes. *Sep. Sci. Tech*. 37(4): 783–797.

[10] Soroko, I., Lopes, M. P. and Livingston, A. 2011. The Effect of Membrane Formation Parameters on Performance of Polyimide Membranes for Organic Solvent Nanofiltration (OSN): Part A. Effect of Polymer/Solvent/Non-Solvent System Choice. *J. Membr. Sci.* 381(1–2): 152–162.

[11] S. Tsarkov, V. Khotimski, P. M. Budd, Volkov, V., Kukushkina, J., Volkov. A. 2012. Solvent Nanofiltration through High Permeability Glassy Polymers: Effect of Polymer and Solute Nature. *J. Membr. Sci.* 423: 65–72.

[12] Raman, L., Cheryan, M., and Rajagopalan, N. 1996. Deacidification of Soybean Oil by Membrane Technology. *J. Am. Oil Chem. Soc.* 73(2): 219–224.

[13] Subramanian, R., Nakajima, M. and Kawakatsu, T. 1998. Processing of Vegetable Oils using Polymeric Composite Membranes. *J. Food Eng.* 38: 41–56.

[14] Geens, J., De Witte, B., and Van der Bruggen, B. 2007. Removal of API's (Active Pharmaceutical Ingredients) from Organic Solvents by Nanofiltration. *Sep. Sci. Tech.* 42: 2435–2449.

[15] Tarleton, E. S., Robinson, J. P. and Low, J. S. 2009. Nanofiltration: a Technology for Selective Solute Removal from Fuels and Solvents. *Chem. Eng. Res. Des.* 87(3): 271–279.

[16] Aerts, S., Vanhulsel, A., Buekenhoudt, A., Weyten, H., Kuypers, S., Chen, H., Bryjak M., Gevers L. E. M., Vankelecom I. F. J. and Jacobs P. A. 2006. Plasma-Treated PDMS-Membranes in Solvent Resistant Nanofiltration: Characterization and Study of Transport Mechanism. *J. Membr. Sci.* 275(1–2): 212–219.

[17] Bitter J. G. A., Haan, J. P. and Rijkens H. C. 1988. Process for the Separation of Solvents from Hydrocarbons Dissolved in the Solvents, US Patent, 4748288.

[18] Whu, J. A., Baltzis, B. C. and Sirkar, K. K. 2000. Nanofiltration Studies of Larger Organic Microsolutes in Methanol Solutions. *J. Membr. Sci.* 170(2): 159–172.

[19] Yang, X. J., Livingston, A. G. and Freitas dos Santos, L. 2001. Experimental Observations of Nanofiltration with Organic Solvents. *J. Membr. Sci*. 190(1):45–55.

[20] Persson, K. M., Gekas, V., Trägårdh. G. 1995. Study of Membrane Compaction and its Influence on Ultrafiltration Water Permeability. *J. Membr. Sci.* 100(2): 155–162.

[21] Jonsson, G. 1978. The Influence of the Porous Sublayer on the Salt Rejection and Reflection Coefficient of Asymmetric Cellulose Acetate Membranes. *Desalination*. 34(1–2): 141–157.