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Performance of PSf Ultrafiltration Membrane: Effect of Different Nonsolvent on Coagulation Medium

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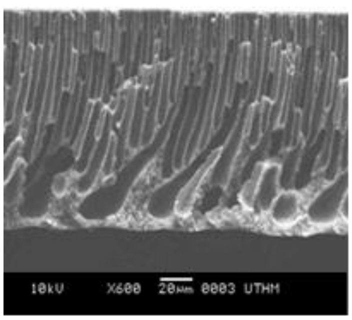
Graphical abstract



Abstract

One of the big challenges in developing a good asymmetric membrane is macrovoid formation that leads to reduction of rejection value. The most common method to reduce or suppress macrovoid formation is by addition of controlled solvent to the coagulation bath. Therefore, the effect of difference coagulants based on dissolved KCl (monovalent) and dissolved Na_2SO_4(divalent) with different concentration onto asymmetric Polysulfone (PSf) ultrafiltration membrane was investigated in this work. The PSf ultrafiltration membranes were prepared by using phase inversion method using these two immerse aqueous solutions. The performances of membranes were evaluated via pure water flux (distilled water) and solute rejection (humic acid). Results on the cross section revealed that the structure of membrane show a straight pattern of bigger finger-like pore structure from top to bottom layer tend to reduce with at the same time the diameter of finger-like pore structure also increased, as salt medium of coagulant increases. These obviously shown by permeation values for both salt mediums were higher compared to without salt coagulant. This reduction of finger-like structure at bottom layer occurred along together with the formation of sponge shape structure. The growth of thick sponge shape is strongly influence by kinetic phase inversion of salt coagulant that also creates resistance to permeation mechanism. However the intense salt coagulant medium can cause the bigger sponge structure that will slightly reduce rejection and increase the permeation. This was proved by the rejection of KCl medium started to increase at 1-3% but slightly reduced at 4%. Based on the result analysis demonstrated that the ideal membrane with highest rejection and good permeation values was membrane immersed into 1% Na_2SO_4 coagulation medium.

Keywords: Polysulfone (PSf); polyethelene glycols (PEG); sodium sulphate (Na_2SO_4); potassium chloride (KCl)

1.0 INTRODUCTION

Phase inversion that also known as "phase separation process" is one of the most established method that used by numerous researchers to produce asymmetric membrane structure. This technique that used Non-solvent Induced Phase Separation (NIPS) to prepare assymetric of microfiltration and ultrafiltration polymeric[1-8] and ceramic membranes[9-11]. In this technique, a thin film of polymer homogenous dope solution is casted with gadner film knife on a suitable substrate such as glass, polyester or polyethylene non-woven fabric, metal, Teflon directly immersed in a non-solvent coagulation bath where exchange polymer precipitation between solvent and non-solvent will take places. The removal of solvent and the entering of water as coagulation medium into membrane substrate produce anisotropic membrane with a dense top layer and porous sub-layer which is related to thermodynamics and kinetic equilibrium during phase inversion process[5,12].

Nonetheless, this conventional technique is not sufficient to produce an excellent membrane morphologies and properties. Thus, modification of basic procedure are commonly required including the addition of certain additive [1-8], introducing of appropriate potential mechanism to make enhancement such as evaporation[13] or annealing [14], and coupling chemical reaction with phase separation[15]. Previous studies revealed that by modification of polysulfone (PSf) ultrafiltration membrane via controlling casting solution or coagulation bath will bring positive result to morphology and membrane properties[16,17].

Controlling the coagulation medium by using inorganic salt is one of the technique that can be used to enhance membrane properties in term of morphology and performance. The presence of inorganic salts as a ionic particles in coagulation bath gives and produce better performance of membrane as reported in previous studies[16,17]. Basically, the addition of inorganic salt to the coagulation bath tend to decrease the activity of the aqueous coagulation bath and suppressing the macrovoid formation[16-18]. This was agreed with other work reported by Yves Termonia that shows a salt poorly soluble in polymer solvent and acting as the most proficient method in preventing macrovoid formation[19]. Theoretically, this mechanism occur due to the presence of inorganics salts will form complexes with carbonyl groups in polar, aprotic solvents such as N-methy-2-pyrrolidone (NMP) via an ion-dipole interaction[20]. This entanglaments formation nature can be analyzed by many methods, such as infrared, H^1- and C^{13}- NMR spectroscopies[20]. The existence of inorganic salt additive in coagulation bath possibly interact strongly to form complexes with solvent utilized for membrane preparation. This behavior slightly attributes to the change of membrane morphology and properties.

Thus, in this experiment, the modification of PSf ultrafiltration membranes were prepared by using phase separation method commonly called "phase inversion" with different concentration of KCl and Na_2SO_4 as additive in non-solvent (distilled water) coagulation mediums. The macromolecular additives PEG which is known as pore forming agent to rise the membrane pore size distribution, suppress macrovoid and create hydrophilic property[18-21]. These additives absolutely provide positive influence of membrane performance notably in flux and rejections. The membrane performance testing was evaluated via crossflow filtration method.

■2.0 EXPERIMENTAL

2.1 Materials

Polysulfone (PSf) pellets (UDEL P1700) was used as a matrix polymeric material in membrane fabrication. N-methyl-2-pyrrolidone (NMP) from MERCK was used as solvent and polyethylene glycol (PEG 400 MW) was used as copolymer addive in casting formulation. Distilled water and aqueous solution of potassium chloride (KCl) and sodium sulphate (Na_2SO_4) were used as non-solvent coagulation bath. Humic acids was used as solute rejection evaluation

2.2 Membrane Fabrication

The Polysulfone (PSf) was dried with a control temperature 40˚C in an oven for 1hour before used.Then, the casting formulations were prepared by dissolving the ratio between, PSf and PEG into NMP. firstly, The NMP was stirred by using a mechanical stirrer at temperature 60˚C with a range speed of 400- 500 RPM. Then, The PSf pallet was added into NMP solutions during the stirring process . The stirring process was continued up to 4 hour to get homogenous solution.Next, the PEG 400MW was poured carefully into solutions and the stirring process continued approximately 10 minutes.The solutions were transferred into a dry clean bottle that controlled by an electrostatic machine for release bubbles. Later on, the casting solution was casted using gadner film knife with range thickness 100-120µm and directly immersed into a coagulation bath containing distilled water. Then, the flat sheet membranes were dried for 24 h before testing [1,2,3,6,11]. In this study, the coagulation mediums consist of KCl and Na_2SO_4 at different concentrations with in the range of 1-4 %.

2.3 Characterizations

The cross sectional morphologies of membrane were analyses with a model JEOL JSM6380LA SEM. The membrane were cut into a small area rectangular shape and immersed into liquid nitrogen before immediately broken it. Then, membranes were coated with gold via sputtering to avoid charging effect.

2.4 Membrane Evaluation

The performance of filtration PSf/PEG ultrafiltration membrane was evaluated based on pure water permeation flux (PWP) and solute rejection rates (SR) by UF crossflow filtration method. All the experiment were performed at ambient temperature. The flat sheet membrane was cut into a circle geometry form before it was installed in membrane permeation testing unit .The tested area for membrane permeation test was around 2.0 x 10^{-3} cm² [1-4]. The membrane initially prepressurized at 4 bar with distilled water around 10 minutes before the actual test was performed.The best three membranes with similar thickness and fine surface areas were prepared for each testing to ensure consistent average value. The pure water flux evaluation was calculated as formula (1).

$$PWF = Q/(A \times \Delta t) \tag{1}$$

where J is a permeation flux for distilled water and wastewater ($Lm^{-2}h^{-1}$) , Q is volumetric flow rate of permeation solution and Δt is the permeation time (h). The solute rejection membranes were evaluated by using 200mg/L humic acid. The absorbance was measured by using the spectrophotometer (Shimadzu UV-160) at wavelength of 254 nm against a reagent blank. The calculation of solute rejection is defined as:

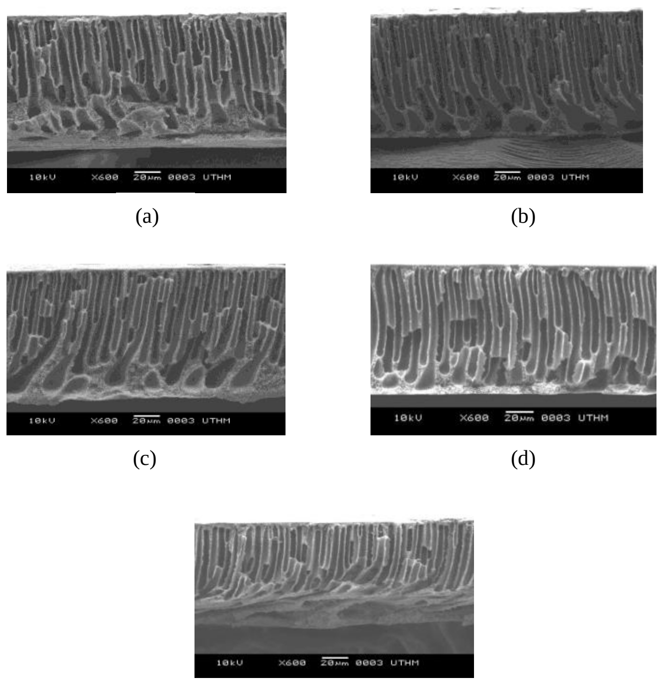
$$SR = \left[1 - \left(\frac{C_p}{C_F}\right)\right] \times 100 \tag{2}$$

where C_p and C_f are humic acid concentration in the feed and permeate solution, respectively.

■3.0 RESULTS AND DISCUSSION

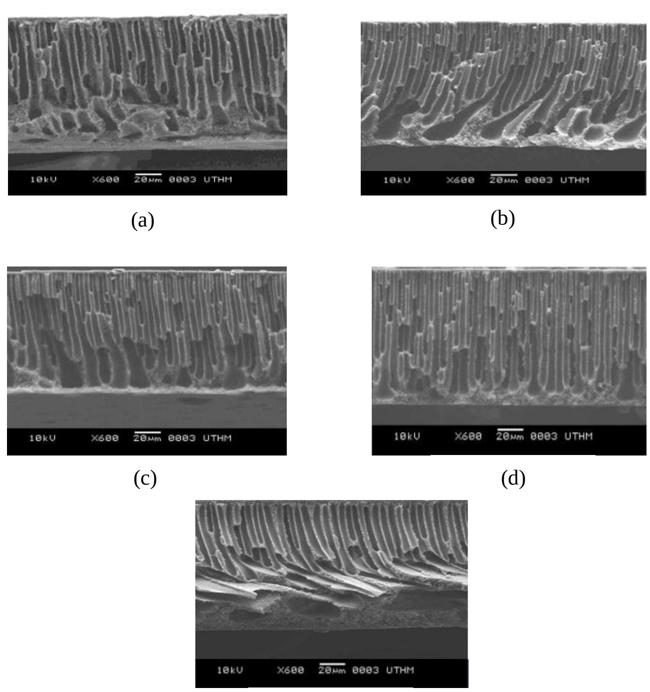
3.1 Membrane Morphology

The SEM cross sectional membrane structure are presented in Figure 1 and 2, these SEM results demonstrate the effect of membrane immersed in aqueous solution of KCl and Na_2SO_4. Overall observation on the membrane images revealed that the membrane produce an anisotropic structure with dense at top layer and followed by porous and sponge structure at sublayer and bottom layer that provide a mechanical strength [21]. Detail observation on images cross section also indicates that as the KCl and Na_2SO_4 increased, finger-like cavities become shorter. Inherently, the changes of membrane structure not only due to salt effect in coagulation bath as mentioned by others researcher but also the influence of PEG in dope solution as pore forming agent. It is well-known that PEG is hydrophilic substance. Thus, the hydrophilicity of PEG in membrane casting solution will influence the exchange rate of solvent and non-solvent during phase inversion process and definitely affect the precipitation kinetics. This circumstance lead the formation of different membrane morphology and structure [21]. The image also display that the suppression of macrovoids appear at membrane drain out layer when increase of KCl and Na_2SO_4 concentration compared to membrane immersed in distilled water. According to A. Conesa *et al.*, this macrovoid structure is a strong effect due to delay in demixing polymer precipitation rate that arises from a high miscibility between solvent /non-solvent [22]. This result is agree well with others previous studies that used different salt coagulation mediums[16-18]. Besides that, this transformation also strongly influence the membrane morphology that resulted from interactions of components in the casting solution and phase inversion kinetics [16-18]. Basically, the addition of inorganic salts decrease the chemical potential (µ) of water and result in delayed of phase transition due to restrained of water inflow and solvent outflow mechanisms[16]. On the other hand the addition of inorganic salt also reduce temperature of water in phase inversion that also produce better membrane performance and properties as shown in the following section figures. Therefore the effect Na_2SO_4 (divalent ion) as show better structure membrane in terms of suppression macrovoids compared to monovalent ion (KCl).



(e)

Figure 1 SEM pictures of the cross-sections of membrane prepared different concentration of KCl, (a) control, (b) 1% of KCl, (c) 2% of KCl, (d) 3% of KCl and (e) 4% of KCl



(e)

Figure 2 SEM pictures of the cross-sections of membrane prepared different concentration of Na_2SO_4, (a) control, (b) 1% of Na_2SO_4, (c) 2% of Na_2SO_4, (d) 3% of Na_2SO_4 and (e) 4% of Na_2SO_4

3.2 Permeation Properties

The effect of aqueous solution KCl and Na_2SO_4 as a non-solvent coagulation bath on the membrane performance was studied. The concentration of KCl and Na_2SO_2 varies from 1%-4% and the dope solution composition was keep constant.

Figure 3 illustrates the performance of PSf/PEG ultrafiltration membrane in Pure water flux permeation upon immersion into different aqueous solution of KCl and Na_2SO_4.Result from the graph demonstrated that the PSf/PEG membrane immersed into aqueous solution of KCl and Na_2SO_4 shows an increase of pure water flux compared to pristine membrane that immersed in distilled water. In fact, the plot shows the increase of pure water flux when concentration of KCl was added from 1% to 4%. However, the results shows reverse tendency with addition of Na_2SO_4. The highest pure water flux is given by the membrane at 4% KCl with 281.14 LMH and the lowest flux from pristine membrane with 102.69 LMH.

According to the Figure 4, the graph demonstrates the percentage of rejection humic acid by membrane immersed into distilled water, aqueous solution of KCl and aqueous solution of Na_2SO_4 as non-solvent coagulation bath. As clearly shown in the graph, membrane immersed into aqueous solution of Na_2SO_4 shows the highest humic acid percentage rejection approximately 99% compared to membrane immersed into aqueous solution of KCl and distilled water. The highest rejection value is given by membrane immersed in 1wt% Na_2SO_4, whilst the lowest rejection produce is shown by membrane immersed in distilled water. This revealed that the influence of Na_2SO_4 and KCl as additives in non-solvent coagulation bath not only improve permeation flux but also enhance solute rejection. It was observed that in co-operation Na_2SO_4 and KCl as additive in coagulation bath enhance hydrophilicity membrane nature. This was demonstrate by several previous studies[6,16,17] that showed membrane with more hydrophilic property tend to reduce the interaction between the hydrophobic contaminants and inherently increasing the rejection property.

Theoritically, the existence inorganic salts into coagulant bath will minimize the chemical potential that attributes to the reduction of driving force for film precipitation. This phenomena indirectly slightly reduced the flux permeation and rejection of membrane. In general, the higher salt concentration is, the more reduction of permeability is[17]. However this works reflect reverse tendency and have coincidence with M. Wang *et al*.[16] that clearly shown that the increase of flux permeation in the present study has attributed to the interaction between PSf/PEG/NMP in dope formulation and salt coagulation medium. The existence of PEG as pore forming agent give better perfomance of membrane with the increase of flux permeation. The similar result was prefered by M. Wang *et al.* where the interaction occur between aqueous solution of inorganic salts as coagulation bath with additive in polymer dope solution ameliorated the membrane permeability.

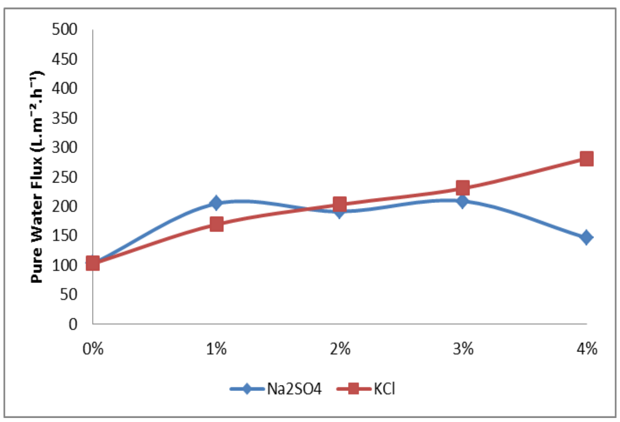


Figure 3 The pure water flux permeation KCl and Na_2SO_4

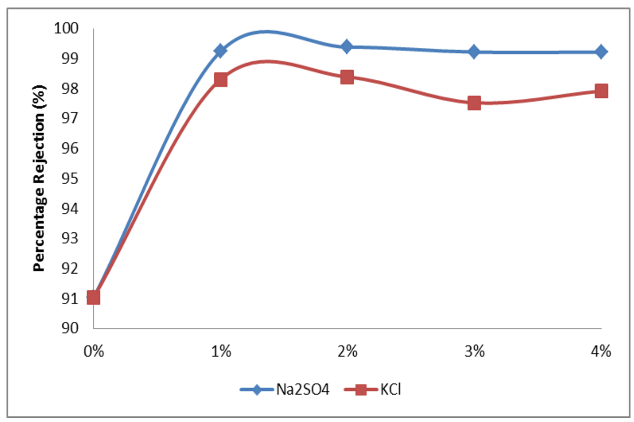


Figure 4 The effect of Humic acid concentration

4.0 CONCLUSION

The PSf/PEG anisotropic flat sheet membrane was fabricated via non-induced phase separation method with direct immersion of preciptation technique utilizing distilled water, aqueous solution of KCl and aqueous solution of Na_2SO_4 as non-solvent coagulation medium. The performance of membranes were analyzed in term of pure water permeation and solute rejection.The cross sectional area morphology were characterized by using Scanning Electron Microscope (SEM). Results obviously show that KCl and Na_2SO_4 as nonsolvent coagulation medium PSf dope formulation in phase inversion method enhanced the performance of membrane permeation and solute rejection rate compared to pristine membrane.The membrane morphology having assymmeric structure with dense top layer and porous sub-layer. The structure also shows suppression macrovoid at the membrane drain out layer when increasing concentration of aqueous solution of KCl and Na_2SO_4. According to the observation,the ideal membrane was membrane immersed in 1% aqueous solution of Na_2SO_4 with forn rejection of humic acid until 99%.

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References

[1] Z. Harun, M. F. Shohur, M. Z. Yunos, M. R. Jamalludin, and A. F. Ismail. 2013 . *Advance Material Research*. 328:798–801.
[2] Z. Harun, M. R. Jamalludin, M. Z. Yunos, M. F. Shohur, and A. F. Ismail. 2013. *Advance. Material. Research*. 701: 319–322.
[3] M. Z. Yunos, Z. Harun, H. Basri. and A. F. Ismail. 2012. *Advance . Material. Research*. 488–489: 46–50.
[4] A. Idris, I. Ahmed, and M. A. Limin, 2010. *Desalination.* 25: 805–809.
[5] A. Rahimpour, S. S. Madaeni, and Y. Mansourpanah. 2010. *Desalination*. 258: 79–86.
[6] M. F. Shohur, Z. Harun, Z. Yunos, S. Hasan, and R. Jamalludin. 2013. *Applied. Mechanic and. Materials.* 372: 3–7.
[7] M. R. Jamalludin, Z. Harun, H. Basri, M. Z. Yunos, and M. F. Shohur. 2013. *Applied Mechanic and Materials*. 372: 8–12.
[8] S. H. Mohamad, M. I. Idris, H. Z. Abdullah, and A. F. Ismail. 2013. *Advance Materials Research*. 795: 318–323.
[9] Kang Li. 2007. *Ceramic Membrane for Separation and Reaction*. John Wiley and Sons, West Sussex,
[10] N. F. Ismail, Z. Harun, N. A. Badarulzaman. 2012 *International. Journal. of Integrated Eng*. 4: 16–21.
[11] Z. Harun, N. F. Ismail, N. A. Badarulzaman. 2012 *Advance Materials Research*. 488–489: 335–33.
[12] T. Mohammadi and E. Saljoughi. 2009. *Desalination*. 243: 1–7.
[13] Drioli, E. and L. 2009. *Membrane Operations.* Wiley.
[14] D. B. Mosqueda-Jimenez, R. M. Narbaitz, T. Matsuura, G. Chowdhury, G. Pleizier, and J. P. Santerre. 2004 *J. Membr. Sci*. 231: 209–224.
[15] J. Bumsuk, Y.J. Ki, K. Bokyung, R. Hee-Woo.2005. *J. Membr. Sci*. 246: 67–76.
[16] M. Wang, L. Wu, and C. Gao.2006. *J. Membr. Sci*. 270: 154–161.
[17] S. Yang and Z. Liu. 2003. *J. Membr. Sci*. 222: 87–98.
[18] J. F. Hester and A. M. Mayes. 2002. *J. Membr. Sci* 202:119–135.
[19] Y. Termonia. 2002. *Polymer*. 50: 1062–1066.
[20] H. Jai, J. Won, H. Lee, and Y. Soo. 2002. *J. Membr. Sci.* 196: 267–277.
[18] G. Arthanareeswaran, D. Mohan, and M. Raajenthiren. 2007. *App. Sur. Sci*. 253: 8705–8712.
[19] J.-H. Kim and K.-H. Lee. 1998. *J. Membr. Sci.* 138: 153–163.
[20] B. Chakrabarty, A. K. Ghoshal, and M. K. Purkait. 2008. *J. Membr. Sci*. 309: 209–221.
[21] Y. Ma, F. Shi, J. Ma, M. Wu, J. Zhang, and C. Gao. 2011. *Desalination*. 272: 51–58.
[22] A. Conesa, T. Gumi, and C. Palet. 2007. *J. Membr. Sci.* 287: 29–40.