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Research paper

Effect of Polymer Concentration on Salt Rejection of Polysulfone Membrane

Azman Ismail[1], Ramlah Mohd Tajuddin[2*]

[1]Faculty of Civil Engineering, UiTM Shah Alam, Malaysia.
[2]Faculty of Civil Engineering, UiTM Shah Alam, Malaysia.
**Corresponding author E-mail: ramlah160@salam.uitm.edu.my*

Abstract

A newly fabricated microfiltration membrane was used to evaluate the effect of polysulfone concentration on salt rejection for seawater. The material chosen in this study was polysulfone (PSF). The dope formulation was gathered from past researches via literature review. The gathered formulation were 10:89:1, 15:84:1, 20:79:1 and 25:74:1 based on weight to weight percentage (wt%) for PSF:NMP:PVP composition. The formulations were named as PSF1, PSF2, PSF3 and PSF4. The membranes were fabricated by using dry wet phase inversion method with pneumatically control flat sheet systems. The membranes were analyzed using Scanning Electron Microscope (SEM) to understand the morphology and surface pore size. 25 liters of seawater was collected from Port Dickson beach in Malaysia to evaluate water flux and salt rejection for each membrane sample. SEM images result shows that membrane pore size decreases by PSF1 > PSF2 > PSF4 > PSF3. PSF1 have the highest pore size ranging from 1.83 µm to 2.57 µm. Meanwhile, PSF3 have the lowest pore size among all samples used, which is 273 nm – 542 nm. Cross sectional structure shows fingerlike structure and skin layers developing on the membrane. Water flux test shows a decrement from PSF1 > PSF2 > PSF3 > PSF4. The highest water flux was recorded at 12.5 l/m^2.hr, and the lowest was at 1.1 l/m^2.hr. For salt rejection, PSF4 recorded the highest rejection of 62% while PSF1 recorded the lowest rejection, which is 10.5%. This shows that the increment of polysulfone concentration in membrane solution would decrease water flux while increasing water rejection at the same time. The best membrane formulation in this research is PSF2 with PSF:NMP:PVP at 15:84:1.

Keywords: *Desalination; dry wet phase inversion; microfiltration;, polysulfone (PSF); polyvinylpyrrolidone (PVP).*

1. Introduction

Water is the most precious and renewable resources on this planet. There are 3% of the world's water budget consists of fresh water, while 97% consists of seawater [1]. It is estimate that the consumption of water by human being will be increase until 50% within the next 50 years. With the growth of population, coupled with industrialization and urbanization eventually increase fresh water demand [2]. Numerous research and finding been made in order to produce the balance between water supply and demand.

Membrane is a technology that offers a wide range of applications which are applicable in food industries, paper and pulp industries, also wastewater reclamation projects. Water treatment plants are widely used for seawater desalination process, for which membrane is one of the popular methods for this purpose. Membrane technology has a high potential to be employed for the treatment of lake water, mine water and tube well. Teow et al. studied the potential of membrane application in treating lake water. Result showed that permeate water filtered by NF270 membrane were able to meet the Class 3 NWQS eventually leading to recycle for livestock drinking and irrigation purposes [3]. Membrane technology also widely use in desalination plant. Desalination can be defined as the process of turning the sea-water into drinkable water. Desalination process divided into two main types, which is thermal desalination and membrane desalination. Between both two processes, membrane desalination provide hope for the future [4].

Significant progress have been made in membrane materials, dope preparation, fabrication technique and fundamental understanding of membrane formation. Choosing appropriate membrane materials is one of the key factors to the success of membrane performance. This paper attempts to study the effect of polysulfone concentration to membrane morphology and their effects to water flux and salt rejection, hence choosing the best polysulfone concentration for seawater desalination.

2. Experimental

2.1. Material selection

Polysulfone (PSF) have been chosen as the main polymer in this research. Polysulfone in this research is provided by Sigma-Aldrich Company with an average molecular weight of 35 000 g/mol. According to Song et al. [5], polysulfone have excellent characteristics in chemical, thermal and mechanical properties. Solvent that have been used for membrane dope solution was N-Methyl 2-Pyrolidone

(NMP). NMP was used as it was found that NMP can dissolve in several type of polymer, including polysulfone and polyvinylpyrolidone. NMP is supplied by Merck Company. Polyvinylpyrolidone (PVP) used in this research is supplied by Sigma-Aldrich Co. with a molecular weight of 40000 g/mol and 99% purity.

2.2. Preparation of casting solution

Polysulfone (PSF) was used as polymer whereas Polyvinylpyrolidone (PVP) and N-methyl 2-Pyrolydone (NMP) were used as its additives and solvent. The wt% of PVP was maintained at 1% for every dope solution, while the wt% of PSF and NMP was determined by referring to past research conducted by Ismail et al. [6]. The formulation of each membrane sample is displayed in Table 1 and apparatus for preparing the casting solution is shown in Figure 1.

Table 1: The composition of membrane formulation

Membrane	Polysulfone	PVP	NMP
PSF 1	10	1	89
PSF 2	15	1	84
PSF 3	20	1	79
PSF 4	25	1	74

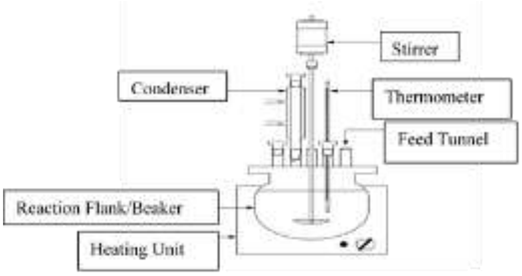


Fig. 1: Apparatus for solution casting

First, the PSF and PVP are mixed into the beaker using a spatula. The mixture then added with the solvent, NMP, until all required amount is achieved. The solution is then stirred using a magnetic stirrer at 300 rpm with a temperature of 60°C. The solution is then continuously stirred for 6 hours in order to get a homogeneous mixture. The dope solution is then poured into a storage bottle and kept in fume cabinet for 24 hours to remove any traces of micro bubbles present in the solution.

2.3 Membrane casting

Asymmetric membrane was prepared using dry wet phase separation method. Flat sheet membranes were fabricated using pneumatically controlled casting machine. The membrane fabrication process was conducted under room temperature (30°C), using casting knife gap of 150µm. The dope solution was first poured on glass plate place on the membrane casting system. The membrane is then immersed into coagulation bath (tap water) for solidification process. Membrane was then transferred into water bath for 24 hours before being dried for 48 hours to remove any residual organic compound which might have been formed in previous stages.

2.4 Membrane characterization methods

2.4.1 Scanning electron microscope (SEM)

SEM model Hitachi TM-3000 with an acceleration of 15 kV and a distance of 6-10 mm was used to examine the morphology of membrane. Small piece of membrane samples was cut by 1cm x 1cm size and mounted on sample stubs. The membranes are then coated with gold layer using sputter coater.

2.4.2 Water permeation test (flux test)

Permeation test was conducted using cross flow filtration process located at the Membrane Laboratory. The membranes used in this research were fractured into small sizes to fix with the system. Seawater was used as feed solution, being pumped into the system using 3 bar feed pressure. The volume of permeate and collection time were then measured. The calculation of flux was based on the formulae provided by Minhas et al. [7]. The formulae to calculate water flux is shown in Equation 1, where J is the water flux, V is the permeate volume (litre), A is the membrane contact area (meter^2) and t is equal to time(hour).

$$J = \frac{V}{A \times t} \tag{1}$$

2.4.3 Salt Rejection Test

Permeate for each filtration process were collected and tested to measure the Total Salt Concentration found in the permeate. This process was conducted in Environmental Laboratory, UiTM using conductivity meter model HACH, Sens ION7. In order to calculate membrane salt rejection (R), Equation 2 were applied to the study. The equation is based on the research done by Minhas et al. [7], where R is the salt rejection, Cp is the permeate concentration and Cf is equal to feed concentration.

$$R\% = \left(1 - \frac{Cp}{Cf}\right) \times 100 \tag{2}$$

3. Result and discussion

3.1 Effect of polysulfone concentration on membrane morphologies

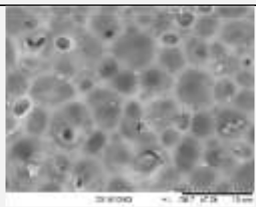
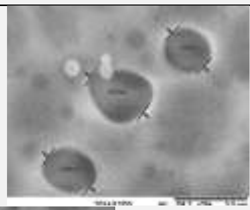
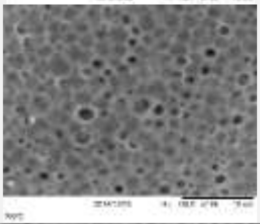
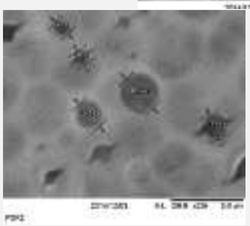
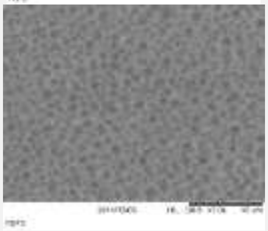
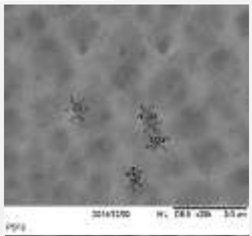
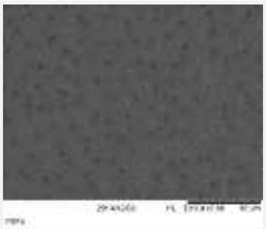
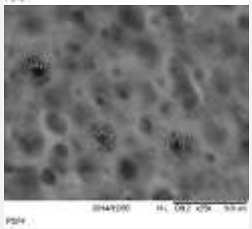
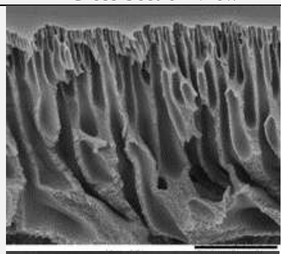
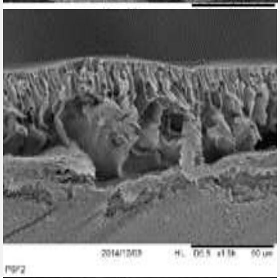
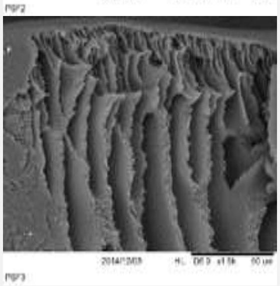
Membrane	Surface View	
PSF 1 Pore size: 1.83µm to 2.57µm		
PSF 2 Pore size: 581nm to 1.62µm		
PSF 3 Pore size: 273 nm to 542 nm		
PSF 4 Pore size: 531 nm to 598 nm		

Fig. 2: Plan view of membrane using Scanning Electron microscope.

Membrane	Cross Section View
PSF 1	
PSF 2	
PSF 3	
PSF 4	

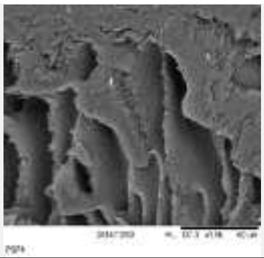


Fig. 3: Cross section view of membrane using Scanning Electron Microscope.

Figure 2 outlines the Scanning Electron Microscope (SEM) images of flat sheet membranes fabricated in this study. From the figures, it was found that the pore size of PSF1 is in the range of 1.83µm to 2.57µm. Figure 3 shows the cross-sectional structure of the membrane. The cross-sectional structure on PSF1 consists of finger like structure from top view of the membrane, hence showing that smooth skin layers are developed on the surface of the membrane with regular thickness.

In PSF2 (15%), the pore size of membrane is in the range of 581nm to 1.62µm. The cross-sectional images of PSF2 shows thin skin layer on the membrane's surface, finger like structure and micro pores layer at the bottom. In PSF2, the difference between percentages of PSF and PVP play an important role in membrane formations. The difference between these two compositions caused the PVP to change its structure from having totally 100% finger like structure to only 40% finger like structure, while the remaining 60% consists of macro pores.

In PSF3 (20%), the pore size of membrane is in the range of 273 nm up to 542 nm. As compared to the other two samples which were previously mentioned, this membrane sample exhibit smaller pore size. PSF3's pore sizes are in microfiltration range. The high percentage of polysulfone (20%) with PVP (1%) shows that when the polysulfone percentage is high, the membrane tends to create smaller pore size with lowest pore distribution on the membrane surface. From the cross-sectional view of PSF3 we can observe that PSF3 also have finger like structure from top surface to the bottom. The thin selective layer that develops on PSF3 would hence be the most effective way to filter salt composition in seawater.

In PSF4 (25%), the pore size of membrane is in the range of 531 nm up to 598 nm. The cross-sectional view showed that PSF4 have finger like structure with skin layers. When the percentage of polysulfone is higher than 25%, the skin layer of the formed membrane would exhibit a thickness of 20 µm. In water flux analysis, membrane with high thickness is not advisable to be used. This is in line with the research done by Misdan et al. [8], which showed that the composition of polysulfone needs to be in lower than 20% in order to get nanofiltration range with thick skin layer and fingerlike structure. From the result, it is found that the addition of polysulfone into the membrane composition eventually decrease membrane pore size hence producing membrane with smaller pores.

3.2 Effect of polysulfone concentration on water flux

Figure 4 shows water flux versus polysulfone concentration used for each membrane sample. Based on the figure, one can evaluate that the flux for both pure water and seawater decrease when polysulfone's percentage in the solution increases. Water flux decreases by the order of PSF1 > PSF2 > PSF3 > PSF4. Flux for pure water is higher than flux for seawater in all membrane types. This is due to the different compositions found in pure water and seawater. As stated in previous sections, seawater contains 19% of salt, as compared to pure water which do not have any salt composition. The salt composition act as foulant, causing fouling in membrane pore, thus depleting the membrane's performance ie; water flux.

The increase of polysulfone composition also affect the membrane performance in term of fouling. Polysulfone is known as the hydrophobic material which is not suitable for water treatment process. As a result, membrane that have higher polysulfone concentration do have a lowest pure water flux. This is in line with the research done by Ariono et al [9].

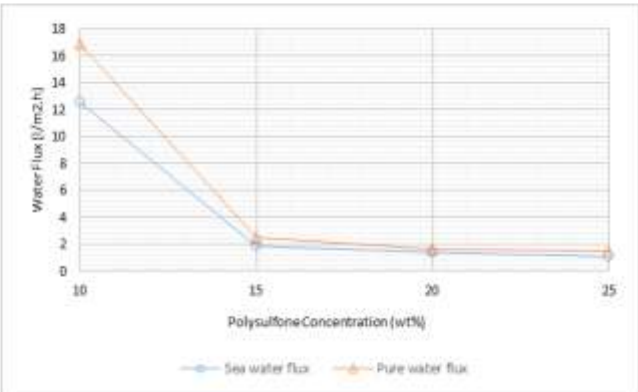


Fig. 4: Pure water flux versus seawater flux for different polysulfone percentage (wt %).

3.3 Effect of polysulfone concentration on salt rejection test

Table 2: Concentration of salt in feed and permeate

Membrane	Pressure	Feed (Cf)	Permeate (Cp)	Rejection (R)
PSF 1	3 bar	19 %	17.0 %	10.5 %
PSF 2	3 bar	19 %	13.6 %	28 %
PSF 3	3 bar	19 %	7.8 %	59 %
PSF 4	3 bar	19 %	7.3 %	62 %

Table 2 displays salt concentration of permeate and retentate for different membrane types. The highest rejection was found in PSF4, with 62%, and the lowest salt rejection is PSF1 with 10.5%. The feed concentrations are same for all membrane types, which is 19% salt concentration in the feed stream. Figure 5 displays the salt rejection percentage with water flux for different polysulfone concentrations. From this figure, salt rejection percentages are in the order of PSF1 < PSF2 < PSF3 < PSF4. PSF1 (10%) have the highest water flux, which is 12.5 l/m^2.hr, but however it has the lowest salt rejection at 10.5%. Meanwhile, PSF4 have the highest salt rejection percentage of 62% but it has the lowest water flux, which is 1.1 l/m^2.hr.

Membrane rejection performance are mainly affected by the pore size of the membrane. The increasing of polymer concentration in PSF4 and PSF3, producing membrane with smaller pore size [10]. That is why membrane with higher polymer concentration have a lower pure water flux but with higher rejection. In order to have good membrane sample for desalination process, the trade-off effect between salt rejection and water flux must be lower. Hence, a conclusion can be made that the best PSF:NMP:PVP membrane composition in this research would be 15:84:1 which is in PSF2. In order for the membrane to have good water flux and salt rejection, polysulfone percentage must be lower than 15% when PVP is 1%, where this can be seen by the interception of water flux and salt percentage line.

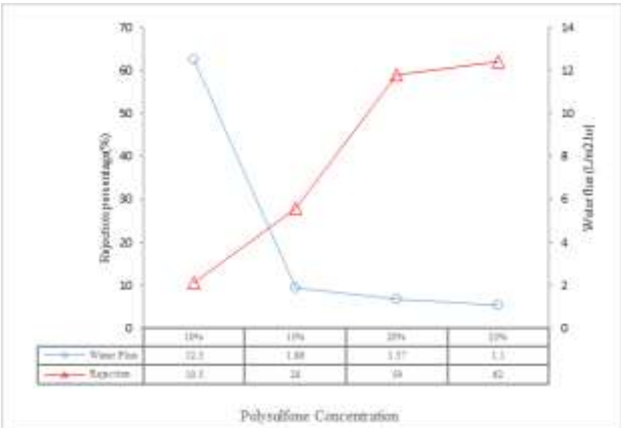


Fig. 5: The effect of polysulfone concentration on water flux and salt rejection.

4. Conclusion

In this paper, Polymer concentration was identified to have significant effect on membrane morphologies thus affecting water flux and salt rejections. From this study, it shows that pore size of membrane was decreased by PSF1 > PSF2 > PSF4 > PSF3. Membrane PSF1, with a composition of PSF:NMP:PVP, of 10:89:1 were identified to have the highest pore size, which is in the range of 1.83 µm to 2.57 µm. On the other hand, membrane PSF3 with the composition of PSF:NMP:PVP at 20:79:1, have the lowest pore size, which is in the range of 273 nm up to 542 nm. Water flux were decreased by PSF1 > PSF2 > PSF3 > PSF4. PSF1 have the highest water flux of 12.5 l/m^{2}hr, while the lowest water flux was made by PSF4 at 1.1 l/m^{2}hr. This was mainly affected by the pore size of membrane. Salt rejection were decreased by PSF4 > PSF3 > PSF2 > PSF1. The highest salt rejection was identified in PSF 4 (R=62%), which has a PSF:NMP:PVP composition of 25:74:1, while the lowest salt rejection percentage was found in PSF 1, which has a composition of PSF:NMP:PVP at 10:89:1, which is 10.5%. The high salt rejection was mainly because the pore size of PSF4 is smaller than PSF1, hence resulting in more salt being filtered in the process. This shows that when PSF concentration is increased, salt rejection would also increase.

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