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Influence of Inorganic Additives on the Performance of Polysulfone Ultrafiltration Membrane

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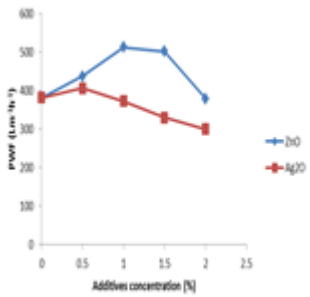
Graphical abstract



Abstract

The influence of zinc oxide and silver (I) oxide in polysulfone ultrafiltration membrane was studied. The membranes were prepared via phase inversion method. The morphology, surface roughness, hydrophillicity and antibacterial properties of membrane were investigated using SEM, AFM and contact angle device consecutively. It was found that membrane with zinc oxide additive has excellent pure water flux as compared to silver (I) oxide. However silver (I) oxide has better humic acid rejection due to the tradeoff effect. SEM-EDX for PSf/silver (I) oxide reveals that the accumulation of silver on top area in cross section of membrane while for zinc oxide seems more concentrated on the bottom. Interestingly, the AFM results support the previous result when PSf/zinc oxide showed better surface roughness on the top of the membrane. Eventhough zinc oxide is known one of antibacterial material, however from qualitative experiment using disc diffusion test (e-coli), there is no inhibition ring for PSf/zinc oxide membrane as compared to membrane with PSf/silver (I) oxide membrane which shows excellence inhibition ring.

Keywords: Zinc oxide; silver (I) oxide; humic acid

1.0 INTRODUCTION

Production of a good membrane necessary for effective filtering process. Membrane must have chemical, mechanical and heat stability to allow various condition of raw water for filtration purposes. Normally, polymer membrane are used as the key ingredient for membrane preparation for the reason that low cost and easy to process. Various type of commercial membrane is available in market such as polysulfone (PSf), polyether sulfone (PES), polyvinildifloride (PVDF) and polyacerilnitrile (PAN). However this polymeric membrane possess hydrophobic in nature which is lead to adsorption of foulant on the surface of membrane [1]. This adsorption will causes pore blocking on membrane surface and reduce separation performance which is known as fouling [2].

Membrane fouling often involves interaction on hydrophobic materials that have a high tendency in the accumulation of foulant, especially in water treatment . Therefore cleaning strategies are needed to reduce the level of impurities adsorbed on the membrane surface. Membrane fouling can be categorized into two types such as reversible and irreversible. The reversible fouling can easily cleaning by water however irreversible fouling will requires a lot of chemical at extreme pH in order to remove the foulant. If the chemical cleaning becomes uneffective, membrane must be replaced. There are several types of foulants such as considered to contribute irreversible fouling in membrane process such as biological (bacteria, viruses and fungi), organic matter (oil and humic acid) and polysaccharide [3, 4].

According to previous research, in order to overcome fouling in hydrophobic membrane, modification of surface is the most economical and effective ways. Hydrophobic polymer surface can be modified via incorporation of hydrophilic additives. Polymeric additives such as polyethylene glycol and polyvinyl pyrrolidone were used to improve hydrophilic of membrane [5]. However due to instability with chemical and foulant, this additives was found to increase fouling. To date this additive is still used but to improve pore size in membrane formulation [6]. The most promising additive that used due to high stability with chemical substance at extreme condition is inorganic additives such as titanium oxide (TiO_2) [7], silica[8-10], silver [11] and zinc oxide [12]. Zinc oxide (ZnO) and silver oxide (Ag_2O) widely used in ceramic, coating and medical due to high temperature resistant, low cost and has antibacterial properties.

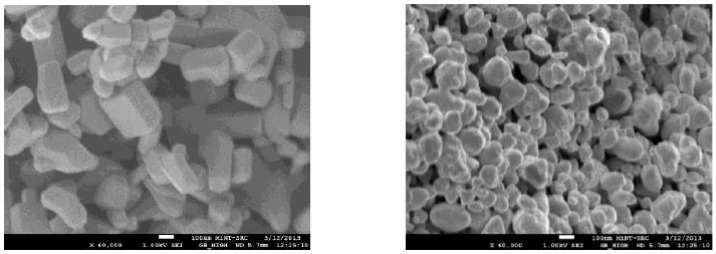
The potential of these type of additives to improve hydrophilicity in polymeric membrane were reported previously [11-14].

However based on our knowledge comparison using same formulation of ZnO and Ag_2O to show which superior addtives to blend in membrane were not yet being discover. Thus our alternative to explore and compare the effect of this additive on performance, morphology and antibacterial properties of PSf membrane.

2.0 EXPERIMENTAL

2.1 Materials

Polymer solutions were prepared using polysulfone (UDEL P1700) as polymeric material and N-methyl-2-pyrrolidone (NMP) (MERCK) as solvent. Meanwhile silver (I) oxide (Ag_2O) and zinc oxide (ZnO) was used as additive. The morphology of ZnO and Ag_2O is shown in Figure 1. The figure shows that ZnO used in the hexagonal form, meanwhile Ag_2O in circular shape. Distilled water was used as non-solvent bath for the purposes of phase inversion. All chemical purchased in this study was used without any further purification



(a) (b)

Figure 1 Morphology of inorganic additives a) zinc oxide and b) silver (I) oxide

2.2 Membrane Preparation

Flat sheet membranes were prepared by casting a polymer solution (18 wt % of PSf) with different additives contents on a glass plate. Dope solution was cast on the glass plate with casting knife gap setting at 150 µm at an appropriate casting shear [15, 16]. The cast solution was then immersed in water bath until the membrane thin film peeled off naturally. The procedures were performed at constant temperature and relative humidity (HR) (25 °C; HR 84%).

2.3 Membrane Characterization

SEM-EDS JEOL GSM was used to examine the morphology of membrane. The membrane was immersed in liquid nitrogen and was fractured carefully. Then the fractured samples were gold sputtered before testing.

Surface roughness of membrane were obtained using AFM XE-Series Park System. Small squares of prepared membranes (approximately 1 cm2) were cut and glued on metal plate. Surfaces of prepared membranes were scanned and imaged in a scan size of 5 µm×5 µm.

A contact angle of prepared membrane were measured using contact angle device (KBV, CAM 101) . To minimize the experimental error, the contact angles were measured at five random locations for each sample and the average number was reported.

Antibacterial activity of the prepared membranes was first studied by disc diffusion method against gram-positive gram-negative bacteria, E. coli.. The media used was a microbiology agar purchased from Merck. All types of membrane were cut into circular disks, autoclaved and put on the bacteria media-culture for incubation at 37 °C for 24 h. The inhibition ring formed after 24 h served as an indicator for the antibacterial activity.

The permeation flux and rejection of membrane were measured based on the ultrafiltration experimental set up. The determination of pure water flux by using distilled water as feed was conducted at pressure 200 kPa. The flux was calculated using Equation 1:

$$PWF=Q/(A\times \Delta t) \quad (1)$$

where PWF is the pure water flux (L/m^2h^1), Q is the permeate volume (L), A is the membrane area (m^2), and Δt is the permeate time (h).

Rejection was characterized using 100 mg/L humic acid as feed solution. Membrane was first filtered with distilled water until the flux was steady. The concentration of feed and permeate solution were determined by using UV spectrophotometer (Thermo Scientific, Genesys 10S) and calculated using Equation 2.:

$$\%R =(1- Cp /Cf) \times 100 \quad (2)$$

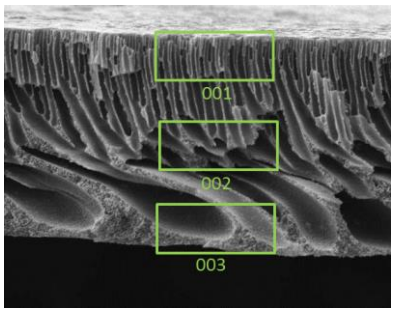
where % R is the rejection percentage, Cp is the permeate concentration and Cf is the feed concentration.

3.0 RESULTS AND DISCUSSION.

Morphology and EDS results for crossection of membrane for PSf/ZnO and PSf/Ag_2O is shown in Figure 2. The figure shows ther is no significance different for both membrane. However, EDS results the distribution for inorganic particle trough the membrane is dissimilar. EDS results in Figure 2a revealed that Ag tend to distribute on the surface of membrane meanwhile Zn particle (Figure 2b) in the bottom. The inorganic materials is found to distribute to all over the membrane eventhough not evenly. In the case of ZnO, the gravity during phase inversion might be the reason for high concentration in the bottom of membrane. Meanwhile, for Ag_2O, this behavior probably during phase inversion Ag_2O try to leachout from membrane [11]. However, fast polymer solidification was prevent Ag_2O from

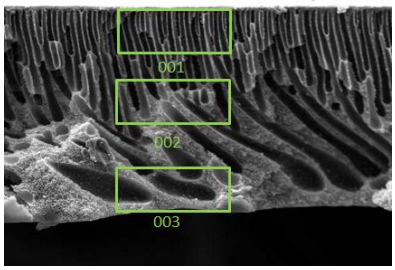
leachout and trap Ag_2O in the upper part of polymer membrane matrix.

(a)



EDS	Mass %			
	C	O	S	Ag
001	72.75	20.98	2.307	2.83
002	73.18	17.25	6.91	2.66
003	74.01	16.95	6.21	1.3

(b)



EDS	Mass %			
	C	O	S	Zn
001	75.23	16.36	7.37	1.04
002	73.41	18.24	6.34	2.01
003	71.23	21.03	4.90	2.84

Figure 2 SEM images and EDS result for cross section of membrane, a) PSf/Ag_2O and b) PSf/ZnO

Surface roughness of PSf/ZnO and PSf/Ag_2O membrane is shown in Figure 3. The figure shows that the roughness of both composite membrane increase as additives concentration increases. This might be due to fine distribution of inorganic particle on the surface of membrane . The figure also shows that the roughness average of PSf/ZnO is higher as compare to PSf/Ag_2O. This behaviour might be due to different shape and size of inorganic particle. Ag_2O was found to hace circular shape (Figure 1), meanwhile ZnO have hexagonal shape which more tend to disrupt the surface of membrane.

Contact angle for both membrane at different concentration of additives is shown in Figure 4. As shown in the figure, water contact angle with membrane reduces as additives concentration increases. As could be understood from the result, as contact angle decreases, more hydrophilic surface produced. This could result in better water permeability behavior of membrane.

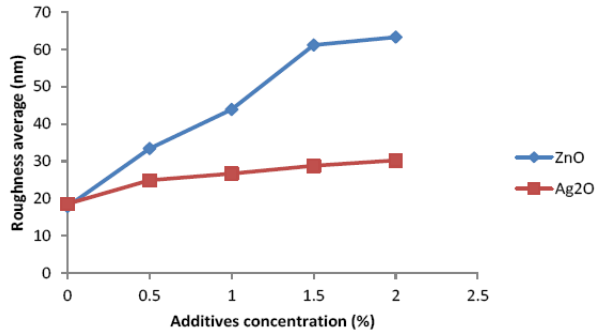


Figure 3 Surface roughness of membrane

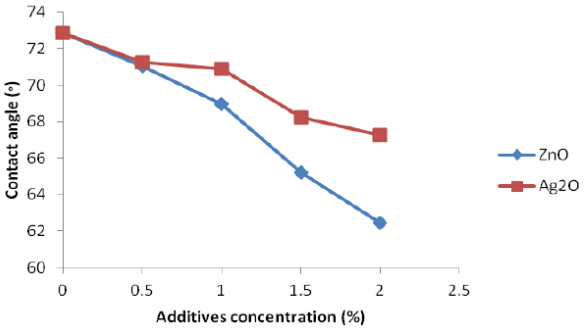


Figure 4 Membrane contact angle at different additive concentration

Figure 5 shows the PWF results of PSf/ZnO and PSf/Ag_2O membrane at different concentration of inorganic additives. The figure shows that the flux of both membrane increase up to 1.0% for PSf/ZnO and 0.5% for PSf/Ag_2O membrane. The similar behavior also reported elsewhere where the presence of inorganic particle improve membrane PWF [7, 13]. The figure also shows that PSf/ZnO has better flux as compared to PSf/Ag_2O. This might be due to the difference of surface roughness of both membrane. An increase of surface roughness will increase membrane surface area and improve PWF of membrane. This study found that surface roughness of PSf/ZnO is higher as compared to PSf/Ag_2O leading to better performance of PWF as evidenced in PSf/ZnO.

The graph shows that beyond the maximum point of PWF, as additives concentration increase PWF decreases. This might be due pore blocking of inorganic additive in membrane which leads to decrease of flux. The pore blocking of membrane more critical on the surface or top are of crossection of membrane since the diameter of pore in this area is smaller as compared to other area. This result in line with hamid *et al.* where pore bolcing will reduce PWF [7]. As shown in Figure 1, the Ag in PSf/Ag_2O membrane was distributed more in the top crossection of membrane. This behavior is decreased PWF of membrane, therefore the decrease of PSf/Ag_2O membrane is found dramatically reduce as compared to PSf/ZnO.

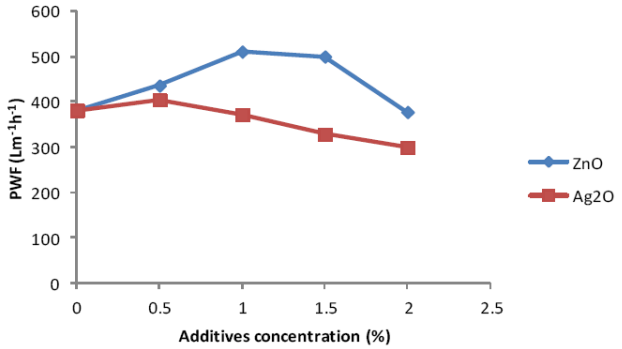


Figure 5 Pure water flux of prepared membrane at various concentration of additives

Figure 6 depicts the humic acid rejection for composite membrane with various concentration of additives. As shown in the figure, humic acid rejection increase as additives concentration increases. The overall results shows that PSf/Ag_2O has better rejection as compared to PSf/ZnO. This might due to tradeoff effect which membrane with higher flux has lower rejection and vice versa. The increase rejection of membrane might be also due to pore blocking by inorganic particle. This blocking is prevent humic acid to pass through the membrane. Similar trend were found by Yuliwati at al. using TiO2 as inorganic additive in PVDF membrane [17].

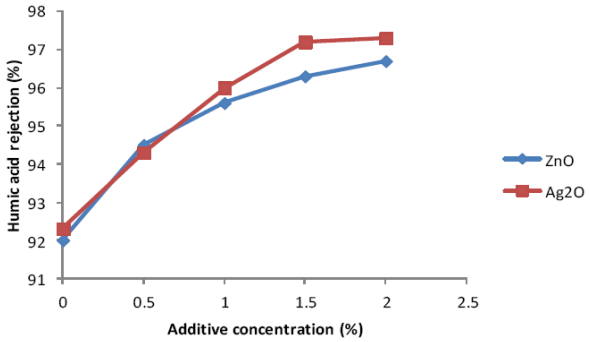


Figure 6 Humic acid rejection of prepared membrane

The inhibition area of e-coli growth is shown in Figure 7. The figure shows inbition area for PSf/Ag_2O membrane, however there is no inhibition for PSf/ZnO membrane. Eventhough both ZnO and Ag_2O toxic to e-coli which can destroy bacteria cell and disrupt bacteria DNA, incorporation of ZnO in PSf is observed unable to produce antibacterial properties. Perhaps at this concentration (2%) the toxicity of ZnO towards e-coli still low to inhibit this bacteria from growth.

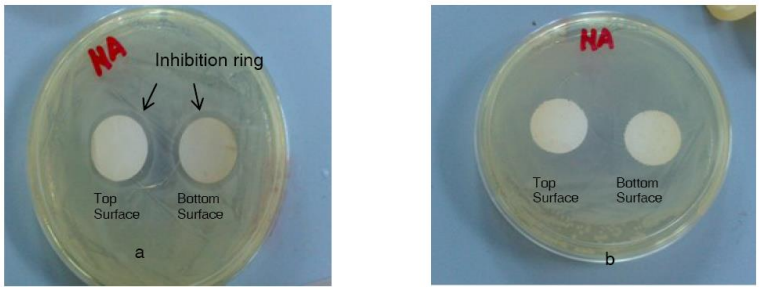


Figure 7 Disc diffusion test for prepared membrane at 2 wt% concentration a) PSf/Ag_2O and b) PSf/ZnO

4.0 CONCLUSION

Investigation on the influence of ZnO and Ag_2O as inorganic addtives has been carried out on the fabrication of PSf membrane. It was observed that distribution of ZnO is concentrated on the bottom of membrane crossection. Meanwhile Ag_2O on top. ZnO and ZnO and Ag_2O also increased PWF value of membrane and ZnO has found to have better PWF as compared to Ag_2O in membrane formulation.The rejection behavior of both membrane was increased as inorganic addtives increases. Eventhough zinc oxide is known one of antibacterial material, however from qualitative experiment using disc diffusion test (e-coli), there is no inhibition ring for PSf/zinc oxide membrane as compared to membrane with PSf/silver (I) oxide membrane which shows excellence inhibition ring.

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References

[1] A. W. Zularisam, A. F. Ismail, M. R. Salim, M. Sakinah, H. Ozaki.2007. *Desalination*. 212: 191–208.
[2] W. Gao, H. Liang, J. Ma, M. Han, Z.-L. Chen, Z.-S. Han, G.-B. Li.2011. *Desalination*. 272: 1–8.
[3] S. K. S. Al-Obeidani, H. Al-Hinai, M. F. A. Goosen, S. Sablani.2008. *Journal of Membrane Science*. 307: 299–308.
[4] Y. Ma, F. Shi, J. Ma, M. Wu, J. Zhang, C. Gao.2011. *Desalination*. 272: 51–58.
[5] J.-F. Li, Z.-L. Xu, H. Yang, C.-P. Feng, J.-H. Shi. 2007.
[6] Y. Ma, F. Shi, J. Ma, M. Wu, J. Zhang, C. Gao. 2011. *Desalination*. 272: 51–58.
[7] N. A. A. Hamid, A. F. Ismail, T. Matsuura, A. W. Zularisam, W. J. Lau, E. Yuliwati, M. S. Abdullah.2011. *Desalination*. 273: 85–92.
[8] Z. Harun, M. R. Jamalludin, M. Z. Yunos, M. F. Shohur, A. F. Ismail.2013. *Advanced Materials Research*. 701: 319–322.
[9] Z. Harun, M. F. Shohur, M. Z. Yunos, M. R. Jamalludin, A. F. Ismail.2013. *Applied Mechanics and Materials*. 328: 798–801.
[10] M. R. Jamalludin, Z. Harun, H. Basri, M. Z. Yunos, M. F. Shohur.2013. *Applied Mechanics and Materials*. 372: 8–12.
[11] H. Basri, A. F. Ismail, M. Aziz.2011. *Desalination*. 273: 72–80.
[12] M. Ali, M. Zafar, T. Jamil, M. T. Z. Butt.2011. *Desalination*. 270: 98–104.
[13] D. Y. Koseoglu-Imer, B. Kose, M. Altinbas, I. Koyuncu. 2012. *Journal of Membrane Science*.
[14] K. Zodrow, L. Brunet, S. Mahendra, D. Li, A. Zhang, Q. Li, P. J. J. Alvarez.2009. *Water Research*. 43: 715–723.
[15] M. Z. Yunos, Z. Harun, H. Basri, A. F. Ismail.2012. *Advanced Materials Research*. 488–489: 46–50.
[16] M. F. Shohur, Z. Harun, Z. Yunos, S. Hasan, R. Jamalludin.2013. *Applied Mechanics and Materials*. 372: 3–7.
[17] E. Yuliwati, A. F. Ismail, T. Matsuura, M. A. Kassim, M. S. Abdullah.2011. *Desalination*. 283: 214–220.