Jurnal Teknologi

Full paper

Preparation and Characterization of Polyethersulfone Membrane Containing Zinc Oxide Nanoparticles and Polyvinylpyrrolidone

A. A. Abdulkarim[a,b], A. L. Ahmad[a*], S. Ismail[a], B. S. Ooi[a]

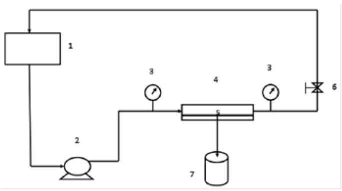
[a]School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300, Nibong Tebal, Penang, Malaysia
[b]Chemical and Petrochemical Research Center, Commission for Research and Industrial Development, Ministry of Industry and Minerals, 10068 Baghdad, Iraq

*Corresponding author: chlatif@eng.usm.my

Article history

Received :21 August 2013
Received in revised form :
30 October 2013
Accepted :15 November 2013

Graphical abstract



Abstract

Flat sheet polyethersulfone (PES) ultrafiltration membranes were fabricated by a dry/wet induced phase inversion process. Various ranges of ZnO concentrations (from 0 –5 wt. %) were utilized in conjunction with 16.5 and 2.5 wt. % of polyethersulfone and polyvinylpyrrolidone (PVP), respectively. The prepared membranes were characterized using scanning electron microscope (SEM), contact angle (CA), and flux/rejection performance. The modified membranes were tested on humic acid removal. The hydrophilicity of PES membrane was improved after addition of zinc oxide nanoparticles in the casting solution. Highest pure water flux was obtained at 5 wt.% ZnO nanoparticles. The modified membranes with 2.5 wt. % of zinc oxide exhibited higher humic acid flux and rejection.

Keywords: Polyethersulfone membrane; zinc oxide nanoparticles; humic acid

■1.0 INTRODUCTION

Polyethersulfone (PES) is considered as one of the most important polymeric materials applied in water treatment membranes.[1] Due to its high Tg (225 ºC) and amorphous characteristics, making it highly preferable for use in preparing asymmetric membranes with different pore sizes and varying surface geometry.[2-4] However, PES-based membranes often cause serious fouling when used in water treatment due to its hydrophobocity. One of the possible ways to improve the membrane fouling resistance is by increasing its hydrophilicity. It is reported that incorporating inorganic materials in the PES membrane matrix could result in improving the hydrophilicity.[5-10] Adding nanoparticles (NPs) to the PES membranes have the potential to enhance the structure and the performance of these membranes. This might be attributable to the stable physical properties such as the high surface area, and thermal/mechanical stability of NPs. The fabrication of membranes with high fouling resistance can be achieved using these particles. Indeed, the improved fouling resistance of such membranes may be ascribed to the functional groups as well as the hydrophilic characteristics of these particles.[11]

Efficiently, ZnO-NPs have acquired a particular attention due to their low cost, superior surface area, photo-catalytic activity and anti-bacterial nature.[12-13] In several reports, ZnO-NPs has been used with different membrane materials and led to an improved performance.[14-19] Wang et.al improved the cellulose acetate membrane by ZnO-NPs (4 wt.%).[14] There was an enhancement of 111.1 % in flux compared to that of pristine membrane. Leo *et al*. improved the hydrophilicity of the polysulfone membrane by incorporation of ZnO-NPs in the range of 1–4 wt. %.[19] There was a 12 times improvement in membrane permeability due to present of ZnO nanoparticles (2 wt. %) in PS membrane. Also, this membrane exhibited highest fouling resistance during oleic acid filtration. Balta *et al*. used high PES concentrations with a wide range of ZnO-NPs concentrations (0.035–4 wt. %) to develop a mixed matrix membrane.[15] They found that there is a significant improvement in water permeability as well as humic acid rejection. However, at a high polymer concentration the composite membrane showed decreases in permeability due to reduction in nanoparticles dispersion rate. While, Shen and co-workers dispersed ZnO-NPs in solvent using low concentration of PES (16 wt. %) and pore forming additive (PEG).[16] The results revealed that the membrane hydrophilicity increase with increasing ZnO concentrations, while the flux exhibiting an improvement of 254 % (obtained at 0.398 wt. % of ZnO-NPs) relative to the pristine PES membrane.

The novel approach attained in this work has led us to the preparation of PES/PVP/ ZnO composite membranes by a phase-inversion method. The nanoparticles effects on membrane permeability as well as humic acid rejection rate were also investigated. The herein modified membranes were characterized using scanning electron microscopy (SEM), contact-angle goniometry, membrane filtration experiments.

■2.0 EXPERIMENTAL

2.1 Materials

Polyethersulfone (PES Ultrason E6020P with Mw=58,000 g/mol) was supplied from BASF. Polyvinylpyrrolidone (PVP) (with Mw=40,000 g/mol), sodium hydroxide, humic acid (HA) with molecular weight ranging from 20000−50000 g/mol, and N,N-dimethylacetamide (DMAc) as solvent were supplied from Sigma Aldrich, USA. A commercial form of zinc oxide nanoparticles, ZnO (particles range 10-30 nm) nanopowder (purity >99%) was supplied from US research nanomaterials, Inc. 3302 Twig Leaf Lane.

2.2 Preparation of PES/ZnO Composite Membrane

The flat sheet membranes were prepared by phase inversion via immersion precipitation technique. The membrane solutions were prepared by dispersing of different amounts of nanoparticles (0, 2.5 and 5 wt. %) in the corresponding volume of DMAc for 3 h by mechanical stirring at 600 RPM and room temperature. Then, the solution was ultrasonicated for 10 min and stirred for 3 h. Subsequently, 2.5 wt.% of PVP was added under rapid stirring for 5 h. The PES polymer (16.5 wt.%) was added and the mixture solution kept at around 60 °C under mechanical stirrer at 500 RPM for 24 h. The compositions of casting solution are shown in Table 1. The homogeneous polymer solution was put in an ultrasonic bath for five hours for the removal of bubbles. The solution was cast using a casting knife with 200 µm thickness using a filmograph (K4340 automatic Film Applicator, Elcometer) in an atmosphere at temperature below 20 °C. Then, the membrane kept in air for 60 s and moved to the non-solvent bath containing distilled water at 15 °C for precipitation for one day. The prepared membranes were washed thoroughly and stored at 25 °C in distilled water for 1 day to completely leach out the residual of solvent, and stored wet. For each polymer solution composition, three identical membranes were prepared and tested to get an average value of fluxes.

Table 1 The composition of casting solutions (wt.%)

Membrane ID	PES	ZnO	PVP	DMAC
MS-1	16.5	0	2.5	81
MS-2	16.5	2.5	2.5	78.5
MS-3	16.5	5	2.5	76

2.3 Characterizations

2.3.1 Scanning Electron Microscope (SEM) Analysis

The surface morphologies and the cross sectional area of the prepared PES/ZnO membranes were studied by scanning electron microscopy (SEM) using a HITACHI Tabletop Microscope instrument (TM-3000-Japan) operated at 20 kV. Membranes samples were cut into small size and mounted on a double-sided carbon adhesive foil as the sample holder. Prior to the SEM test, sputtered coating was used (Quorum -SC7620) to coat the membrane surface and cross sectional area with a thin layer of gold under vacuum to avoid the effect of electrostatic charging.

2.3.2 Contact Angle Measurements

For the evaluation of the membrane's surface hydrophilicity, the contact angle between the water and the membrane surface was directly measured using contact angle measuring system (Rame-Hart 250-F1, USA). A water droplet (0.2 µL) was placed on a dry flat membrane surface and the contact angle was calculated for such contact. To decrease the experimental errors, the average value of a series of seven measurements for each membrane sample was considered.

2.3.3 Filtration Experiments

Membrane flux and the separation performance measurements of the prepared membranes were performed in a cross-flow filtration setup as shown in Figure 1. All experiments were performed at ambient laboratory temperature of 22 ±1 °C. Typically, the experiments were conducted through a cross-flow cell with an effective membrane area of 42 cm^2 and constant cross flow velocity of 1000 ml/min using a Flex-Pro-A4V Peristaltic Metering Pump (Blue-White, USA). Initially, each of the tested membranes was compressed with pure water at 150 kPa for 1 h. The pure water flux was performed at 100 kPa and measured after 60 min of water filtration. A 5 L feed solution containing (10 mg/L, pH=7.7) of the humic acid solution was prepared and re-circulated at 100 kPa through the aforementioned cell. The HA solution was used to investigate the membrane rejection and fouling evaluation. The HA concentration in permeate was recorded after 60 min of the filtration experiment in full recycling of both permeate and retentate except the flux sampling.

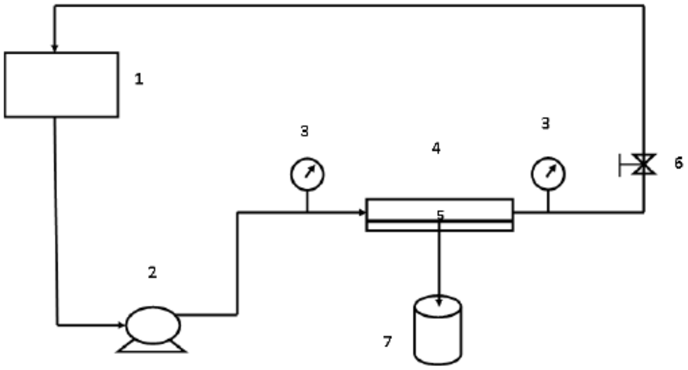


Figure 1 Schematic diagram of cross-flow unit: 1–Feed Tank, 2–Peristaltic pump, 3–Pressure gauge, 4– Cross-flow cell, 5–Membrane, 6– Control Valve, 7– Permeate

The pure water flux (J_{WF}) was computed according to Equation (1):

$$J_{WF} = \frac{V}{A * t} \tag{1}$$

where J_{WF} is the pure water flux (L/m^2 h), V refers the permeate volume (L), A is the effective membrane surface area (m2), and t is the measurement time (h).

The HA concentration in the feed and permeate flux was determined using UV-visible spectrophotometer (Pharo 300, Merck-Germany) at 254 nm wave length. As such, the membrane rejection was calculated according to Equation (2)

$$Rejection = \left(1 - \frac{C_p}{C_f}\right) X100\ \% \qquad (2)$$

in which C_p (mg/L) and C_f (mg/L) represent the solute concentrations in permeate and feed, respectively.

■3.0 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscope (SEM) Analysis

Figure 2 shows the surface and cross-sectional images of pristine and modified membranes. Inspection of the surface images indicated the formation of pore-like structures on the membranes surfaces. The size of these pores were decreased in all ZnO/PES membranes. It is generally accepted that the addition of ZnO nanoparticles into membrane solution can increase solution viscosity as well as the water solvent exchange rate during the phase separation. The ZnO nanoparticles concentration used in this study was relatively high, this resulted in a high difference between viscosities of pristine and modified membranes. It can be observed that the ZnO nanoparticles aggregate on membrane surface and the degree of aggregation was increased with increasing of ZnO amount. These aggregations of nanoparticles on membrane surface increase the chance of pore plugging especially for MS-3 membrane.

The SEM cross-sectional images indicated that the prepared membranes possessed a finger-like structure. The macro-void volume of all the PES/ZnO membranes is lower than that in the pristine PES membrane (Figure 2:b1-b3). Commonly, the addition of nanoparticles in certain amount in the membrane casting solution can slower the exchange between solvent and non-solvent (water) because of a kinetic effect (solution viscosity) during the phase-inversion process. This result is in contrast with other similar work that believed that the addition of the nanoparticles enhance the macro-voids formation [15]. In addition, skin layer thickness was found to vary with the addition of ZnO nanoparticles in which was found to be decreased at 5 wt.% of ZnO nanoparicles as shown in Figure 2:b1-b3. The finger-like structure was found to be more extended at 5 wt.% of ZnO (Figure 2:b2)

3.2 Contact Angle

In order to assess the effect of ZnO-NPs on the membrane hydrophilicity, the angle between a small droplet (2 µl) of water and the membrane surface was measured by the contact angle instrument. The obtained results are shown in Figure 3 which indicates that the addition of ZnO-NPs assist to improve the membrane hydrophilicity (decrease the contact angle) by about 5.76 and 19.23 % for MS-2 and MS-3 membranes, respectively. As shown in Figure 3, all of the PES/ZnO membrane samples poses lower contact angle than the pristine PES membrane. Logically, this disparity in the contact angle values between the pristine and the modified membranes could be attributed to the effect of the added ZnO-NPs. Physically, this phenomenon is manifested in the modified membranes due the hydrophilicity of the added ZnO-NPs, which was interrupted within the membrane structure and possibly resulted in a membrane material with higher attraction toward the water molecules.

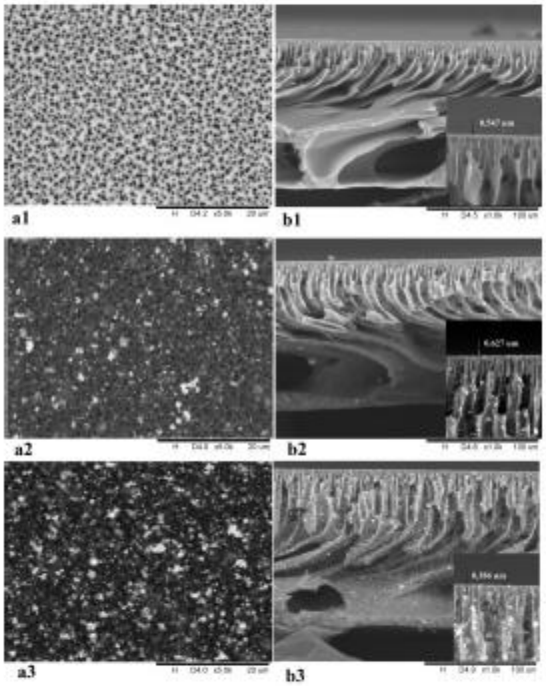


Figure 2 SEM surface images of the membranes with different ZnO nanoparticles content: (a1) MS-1, (a2) MS-2, and (a3) MS-3; and SEM cross-sectional membranes images: (b1) MS-1, (b2) MS-2, and (b3) MS-3

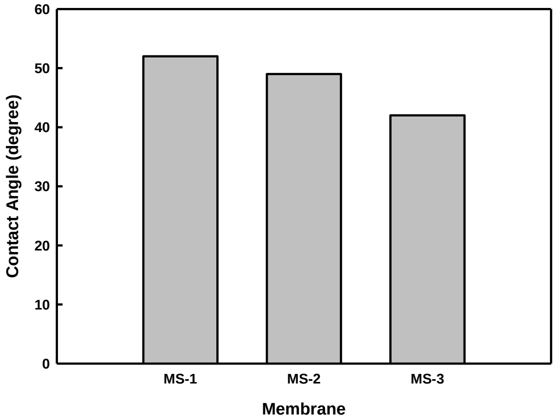


Figure 3 Water contact angles of MS-1, MS-2, and MS-3 membranes

3.3 Filtration Performance

Figure 4 summarizes the average pure water and humic acid fluxes (measured for three membrane samples). It can be clearly seen that the highest pure water flux was obtained at a ZnO concentration of 5 wt.% (MS-3 membrane). Over MS-3 membrane, the recorded water flux was 295.55 L/m2 h, which pose an improvement of 69.33 % as much as that of pristine membrane (MS-1). This enhancement in membrane flux is due to the improved membrane hydrophilicity (Figure 3). However, other researchers believe that the pore size plays the major role in flux improvement [20-21]. The water flux was observed to increase with the addition of ZnO nanoparticles. At 5 wt.% ZnO due to low dispersion rate of nanoparticles, there was a high possibility to form a clusters of nanoparticles that increase the membrane pore size and resulted in an increase in water flux as well as HA flux.

Figure 5 presents the rejection rates of PES pristine and PES/ZnO membranes in filtering HA solution. As seen from the figure, MS-1 and MS-2 membranes exhibited highest rejection compared to MS-3 membrane. As seen from the figure, MS-1 and MS-2 membranes exhibited higher rejection compared to MS-3 membrane. When the composition of ZnO-NPs in the dope solution increases to higher than 0.4 wt.%, the interaction between ZnO-NPs and solvent increases and a dope solution with higher viscosity is formed[16]. The higher dope viscosity results in a membrane with lower pore size. However, when the ZnO-NPs concentration in the casting solution is high (5 wt.%), the aggregation of these particles cannot be avoided. As indicated in the SEM figure (Figure 2), the strong aggregation of the ZnO-NPs during the polymer de-mixing and especially at low PES concentrations (16.5 wt.%) has led to an increase in the pore size and decrease in the contact angle as illustrated in Figure 3.

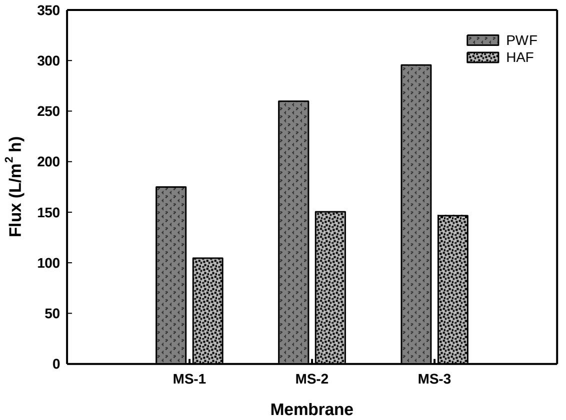


Figure 4 Pure water and humic acid fluxes of MS-1, MS-2, and MS-3 membranes

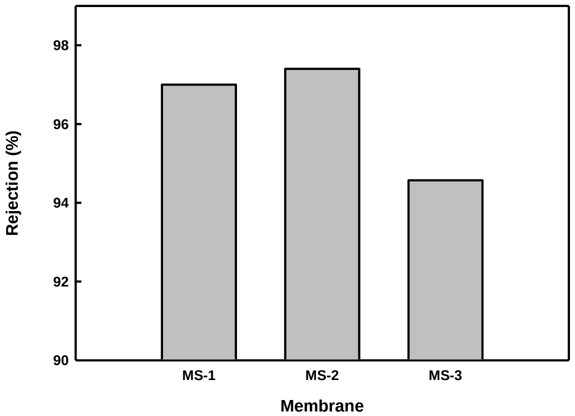


Figure 5 Humic acid rejection rates of MS-1, MS-2, and MS-3 membranes

■4.0 CONCLUSION

Dry /wet phase inversion induced by immersion precipitation technique was used for membrane formation. Due to low PES concentration and high ZnO amount used, the dope viscosity increased with the addition of ZnO nanoparticles. Membrane morphology indicated that the skin layer thickness has been decreased at 5 wt.% ZnO nanoparticles which affect the rejection of HA solution. It was observed that the addition of 2.5 and 5 wt.% ZnO-NPs have resulted in decreasing the contact angle. Membrane performance analysis proved that the pure water flux attained its ultimate value at the optimum level of 5 wt.% ZnO nanoparticles, however the rejection of HA was shown to decrease at this level of nanoparticles. The humic acid rejection rates were found to increase slightly at 2.5 wt. % ZnO nanoparticles. The present of ZnO nanoparticles in PES membrane matrix improved the hydrophilicity as well as the pure water and humic acid fluxes.

Acknowledgement

The authors gratefully acknowledge the financial support by the MOSTI Science Fund (Grant no: 305/PJKIMIA/6013386), FRGS (Grant no: 203/PJKIMIA/6071234), and Universiti Sains Malaysia Membrane Cluster Science and Technology.

References

[1] Ahmad, A. L. Abdulkarim, A. A., Ooi, B. S., Ismail S. 2013. *Chem. Eng. J.* 223: 246.
[2] Rahimpour, A., Jahanshahi, M., Khalili, S., Mollahosseini, A., Zirepour, A., Rajaeian, B. 2012. *Desalination*. 286: 99.
[3] Shi, Q., Su, Y., Zhu, S., Li, C., Zhao, Y., Jiang, Z. 2007. *J. Membr. Sci.* 303: 204.
[4] Wang, H., Yang, L., Zhao, X., Yu, T., Du, Q. 2009. *Chin. J. Chem. Eng.* 17: 324.
[5] Idris, A., Ahmed, I., Limin, M. A. 2010. *Desalination*. 250: 805.
[6] Rahimpour, A., Madaeni, S. S., Mansourpanah, Y. 2010. *Desalination*. 258: 79.
[7] Qin, J.-J., Oo, M. H., Li, Y. J. 2005. *Membr. Sci*. 247:119.
[8] Cao, X., Tang, M., Liu, F., Nie, Y., Zhao, C. 2010. *Colloids Surf. B.* 81: 555.
[9] Basri, H., Ismail, A. F., Aziz, M., Nagai, K., Matsuura, T., Abdullah, M. S., Ng, B. C. 2010. *Desalination*. 261: 264.
[10] Basri, H., Ismail, A. F., Aziz, M. 2011. *Desalination*. 273: 72.
[11] Vatanpour, V., Madaeni, S. S., Khataee, A. R., Salehi, E., Zinadini, S., Monfared, H. A. *Desalination*. 292: 19.
[12] Hernández-Sierra, J. F., Ruiz, F., Cruz Pena, D. C., Martínez-Gutiérrez, F., Martínez, A. E., de Jesús Pozos Guillén, A., Tapia-Pérez, H., Martínez Castañón, G. 2008. *Nanomed. Nanotechnol. Biol. Med*. 4: 237.
[13] Dodd, A., McKinley, A., Saunders, M., Tsuzuki, T. 2006. *J. Nanopart. Res.* 8: 43.
[14] Wang, Y., Yang, L., Luo, G., Dai, Y. 2009. *Chem. Eng. J.* 146: 6.
[15] Balta, S., Sotto, A., Luis, P., Benea, L., Van der Bruggen, B., Kim, J. 2012. *J. Membr. Sci.* 389: 155.
[16] Shen, L., Bian, X., Lu, X., Shi, L., Liu, Z., Chen, L., Hou, Z., Fan, K. 2012. *Desalination*. 21: 293
[17] Anitha, S., Brabu, B., Thiruvadigal, D. J., Gopalakrishnan, C., Natarajan, T. S. 2012. *Carbohydr. Polym*. 87: 1065.
[18] Bai, H., Liu, Z., Sun, D. D. 2012. *Colloids Surf.* A. 410: 11.
[19] Leo, C., Cathie Lee, W., Ahmad, A., Mohammad, A. 2012. *Sep. Purif. Technol*. 89: 51.
[20] Li, J.-F., Xu, Z.-L., Yang, H., Yu, L.-Y., Liu, M. 2009. *Appl. Surf. Sci.* 255: 4725.
[21] Razmjou, A., Mansouri, J., Chen, V. 2011. *J. Membr. Sci.* 378: 73.
.