Full Paper

EFFECTS OF MEMBRANE FABRICATION CONDITIONS TOWARDS THE PERFORMANCE OF NANOPARTICLES-INCORPORATED MEMBRANES

Ying Tao Chung, Abdul Wahab Mohammad*

Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

*Corresponding author
drawm@ukm.edu.my

Graphical abstract
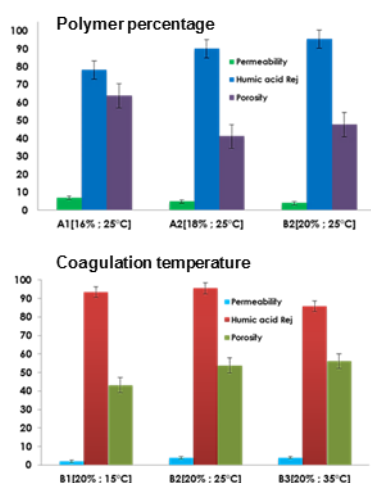
Abstract

The development of nanoparticles-incorporated membranes is one of the recent techniques in improving membrane qualities in terms of fouling propensity. In this study, Zinc oxide (ZnO) has been selected as the nanoparticles to be embedded in membranes due to its excellent antifouling and antimicrobial properties. Several parameters such as polymer percentage and bath temperature were studied during the membrane fabrication process via phase inversion technique. The effects of each parameter towards the membrane structure and performance were significant in producing good membranes. When the polymer percentage increased from 16wt% to 20wt%, the permeability decreased from 6.9 to 3.9 $L.m^{-2}.hr^{-1}.bar^{-1}$ and humic acid rejection increased from 78% to 95%. On the other hand, the coagulation temperature increment will lead to increment of permeability from 2 to 4 $L.m^{-2}.hr^{-1}.bar^{-1}$ but gave rejection from 93% to 96% at 15°C to 25°C, and 86% at temperature of 35°C.In conclusion, the optimum condition for nanoparticles-incorporated membranes fabrication was shown at 20% of PSF at 25°C.

Keywords: ZnO NPs, membrane fabrication, polymer percentage, coagulation temperature, antifouling

1.0 INTRODUCTION

Recent advances of nanoparticles (NPs) in membrane applications are mainly due to their superb properties in terms of photoemission, antimicrobial and fouling commonly reported in membrane fabrication are metal or metal oxides such as, silver (Ag), aluminium (Al), iron (Fe), titanium dioxide (TiO_2), and silica (SiO_2) [1]. Of late, Zinc oxide (ZnO) is selected as a replacement of TiO_2 for the significant improvement of membrane filtration performance in a much economical way [2]. In addition, several studies are investigating the impacts and contribution of ZnO NPs to improve membrane applications such as anti-fouling behaviour, bacteria growth inhibition [3], industrial dye removal [4], photo catalytic activity [5] and so forth. Despite the great

resistance. Membranes embedded with different kinds of NPs have attained great attention possibly due to their ability to increase flux and permeability, fouling propensity, solute retention capability, hydrophilicity, selectivity and physical properties. The NPs which are contribution of ZnO NPs, the membrane fabrication conditions were equally important to develop good membranes. Several factors would give impact on the membrane performance. For instance, the polymer concentration [6],[7], types of solvent, coagulation bath temperature and additives [8], etc. Hence, the main objective of this study is to investigate the influence of polymer concentration and bath temperature towards the performance of PSF-ZnO membranes. The aim of study was to figure out optimum fabrication condition in combination with hydrophilic

ZnO NPs. The membrane performance would be characterized by several techniques such as water permeability, surface wettability, membrane porosity, rejection tendency and morphological study

2.0 METHODOLOGY

Polysulfone (PSF) pellets and 1-methyl-2-pyrrolidone (NMP) were analytical grade and purchased from Merck. All chemicals were used for the synthesis process without any further purification. ZnO NPs was synthesized through sol-gel method with average size of 20 nm. The synthesized ZnO NPs were applied in membrane fabrication via wet phase inversion technique. ZnO NPs were incorporated during the preparation of PSF casting solution. The casting solution was prepared by dissolving certain amount (16%, 18%, 20%) of PSF pellets into NMP with average temperature of 65°C under continuous stirring for 5 hr. ZnO NPs were sonicated for better dispersion before mixing in the homogeneous PSF casting solution. The membranes were casted by using Filmographe Doctor Blade 360099003 (Braive Instrument, Germany) with thickness of 0.2mm. The phase inversion process occurred in a water bath with various temperatures, i.e. 15°C, 25°C and 35°C. The fabricated membranes were then kept with UP water for storage.

2.1 Surface Hydrophilicity Study

Hydrophilicity analysis was performed by contact angle meter (Model Kruss GmbH, Germany) with Drop Shape Analysis software.

2.2 Membrane Permeability

Membrane permeability was measured by using stirred cell (Sterlitech HP4750). The pure water flux was calculated by using the following equation:

$$J = V / S\,t \qquad (1)$$

where J is the water flux ($L.m^{-2}.hr^{-1}$); V is the permeate volume (L); S is the effective membrane area (m^2); t is the operation time (hr^{-1}). Permeability was determined based on the gradient of the linear line from the water fluxes against pressures graph.

2.3 Membrane Porosity

The overall porosity (ε) was evaluated by using gravimetric method, as defined in the following equation:

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times t \times d_w} \qquad (2)$$

where ω_1 is the wet membrane weight and ω_2 is the dried membrane weight; $A(m^2)$ is the area of the membrane; t is the thickness and d_w is the water density (998 kg/m^3).

2.4 Rejection Study

Humic acid solution of 10 ppm was used to check the membrane rejection tendency. The rejection was determined by using the following equation:

$$R = 1 - C_p/C_f \qquad (3)$$

where C_p is the permeate concentration and C_f is the feed concentration.

2.5 Morphological Study

The membrane surfaces and cross-sectional structures were obtained by using scanning electron microscope (SEM, Gemini SUPRA 55VP-ZEISS).

3.0 RESULTS AND DISCUSSION

In this case, membranes were developed based on the influence of polymer percentage and bath temperature on the structural performance of membranes. Several performance testing were carried out to characterize the fabricated membranes. The characterization approaches consisted of surface wettability, water permeability analysis, rejection study, and membrane porosity. The fabricated membranes embedded with constant amount of ZnO NPs were investigated and confirmed by applying several characterization methods. ZnO NPs which would enhance the membrane performance due to its excellent antifouling and antimicrobial properties and were uniformly dispersed in the PSF membranes structure. The basic performance findings for both parameters were visualized in Figure 1 and 2.

In general, surface wettability study of the membranes was one of the significant characterization methods to indicate membrane hydrophilicity. This could be performed by measuring the contact angle of membranes. The contact angle results obtained exhibited that the overall performance of each fabricated membranes based on different parameters was similar. The contact angle value fluctuated in the range of 45±5°. It was a good enhancement of ZnO NPs as an hydrophilic additive as compared to pure PSF which yield contact angle of 69° [9]. The main reason was ZnO NPs had greater water affinity which improved the surface hydrophilicity [10]. Besides, the results also indicated that the constant amount of ZnO NPs did not show any significant effects on the membrane surface wettability. There was only a slight difference of contact angle for all sets of membrane and hydrophilicity yield insignificant role for this study as per reported elsewhere [7]. Hence, it was concluded that hydrophilicity study was independent from the variation of polymer quantity and bath temperature.

3.1 Membrane Characterization Based On Effects of Polymer Quantity

The effects of polymer quantity were investigated by performing permeability analysis, rejection study and porosity study. The above performance testing correlated among each other. Figure 1 demonstrated the findings of membrane performance with various percentages of PSF, i.e. 16%, 18% and 20% at constant bath temperature of 25^oC. Water permeability correlated proportionately to hydrophilicity of membrane. Despite the slight difference of contact angle for each membrane [A1-A3], the membrane permeability decreased from 6.9 to 3.9 $L.m^{-2}.hr^{-1}.bar^{-1}$ when percentage of polymer was increased. This was closely related to the viscosity of the casting solution with different concentration.

Due to the higher amount of polymer, the casting solution was highly viscous and led to higher hydraulic resistance [11]. The occurrence of phase inversion process was slower due to the delay of exchange rate between solvent and polymer during mass transfer. As a result, casting solution with higher viscosity would led to the formation of less porous membranes [12]. This was proven from the porosity findings as presented in Figure 1. The polymer concentration would affect the bulk porosity and inner structure of membrane [6]. The formation of denser membrane with higher polymer concentration was caused by the longer period for the membrane solidification process [13]. The rejection capability was tested by using humic acid solution. From the result, the rejection percentage increased from 78% to 95% when the polymer percentage increased. It correlated with the denser membrane structure which could reject more organic matter. The denser the membrane structure, the higher its retention capability. In addition, ZnO NPs also contributed in the enhancement of humic acid rejection due to its fouling-resistant properties which would reduce the adsorption of organic pollutants within membrane structure [2]. Therefore, the polymer percentage played a vital role in the development of membrane which would determine the formation of membrane structure and morphology.
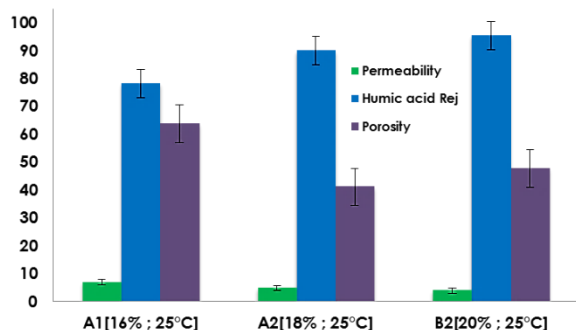
3.2 Membrane Characterization Based On Effects of Bath Temperature

On the other hand, the effects of bath temperature during the phase inversion process were analyzed based on the above characterization methods, too. Figure 2 exhibited the findings of membrane performance with various bath temperatures, i.e. 15^oC, 25^oC and 35^oC at constant amount of PSF polymer. The permeability and porosity findings indicated the proportionate increment when the elevation in bath temperature. This could be explained that the liquid-liquid de-mixing stage was delayed at lower temperature, resulting in membranes with lower porosity as per reported by Wang and colleagues [14]. According to Xu *et al.*, the porous structure was formed by instantaneous de-mixing while the slower de-mixing rate would result in a denser membrane structure [15]. This was further supported by the porosity findings in Figure 2. Thus, it could be confirmed that the increase of bath temperature would enhance the membrane porosity [6]. Owing to the formation of porous membrane structure at higher temperature, the permeation rate of water also increased due to the formation of macrovoids. It would further enhance the water permeability which was presented in Figure 2, whereby the permeability increased from 2 to 4 $L.m^{-2}.hr^{-1}.bar^{-1}$ when temperature was increasing. The rejection capability was closely related to the porous structure of membrane. Despite the higher membrane porosity, it would give adverse effects towards humic acid rejection. The rejection percentage increased from 93% to 96% at 15^oC to 25^oC, but decreased to 86% at bath temperature of 35^oC. As per discussed previously, the retention tendency was dependent on the porosity of membranes. Summarizing the effects of bath temperature, the best membrane performance occurred at set B2, with bath temperature of 25^oC. This set of membrane presented an optimum condition for the fabrication process due to its enhanced rejection ability towards organic matter and improved water permeability rate.
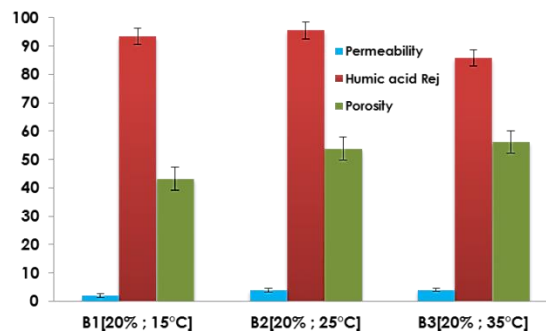
Figure 2 Effects of bath temperature

Figure 1 Effects of polymer quantity

3.3 Morphological Study

In addition, the membrane performance testing could be further supported by morphological study which was the FESEM analysis. Figure 3 displayed the cross sections of membrane structures for the effects of polymer percentage [A1-A3] and effects of bath temperature [B1-B3]. The rapid precipitation rate during phase inversion process would lead to macrovoids formation in membrane [16].

The formation of macrovoids could reduce the water permeation resistance [15]. Besides, all the membrane structure showed typical finger-like pores linked by sponge walls as per reported elsewhere [17]. There were no significant alterations on all the membranes. However, the B3 membrane revealed some imperfections of membrane structures due to the high exchange rate in phase inversion which led to incomplete formation of pores structures. Therefore, it could be assumed that the effects of polymer quantity and bath temperature did not impose remarkable adjustment on PSF membrane with ZnO NPs.

In brief, the membranes fabrication with embedded ZnO NPs was greatly affected by the PSF percentage and also the coagulation bath temperature. It was an important study to figure out the favorable condition for the production of good quality of membrane in terms of permeability, rejection capability and porosity. The improvement of membrane performance was attributed to many factors such as great hydrophilicity, porosity and fouling resistance. Combining the optimum fabrication effects and the excellent characteristics of ZnO NPs, membranes with magnificent performance could be developed.
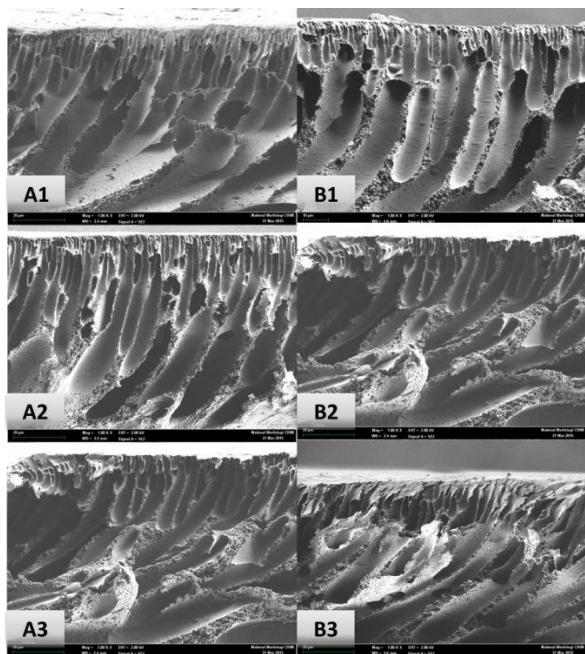

Figure 3 FESEM images: A1-A3 (Polymer %); B1-B3 (Bath T)

4.0 CONCLUSION

The effects of PSF polymer concentration and coagulation bath temperature on membranes were successfully clarified through several performance testing approaches. Based on the findings, the best membrane performance was at 20% of PSF at 25°C, with high water permeability (3.9 L.m^{-2}.hr^{-1}.bar^{-1}) and humic acid rejection (96%). ZnO NPs were excellent alternative nanomaterials for various types of industrial applications. The enhancement of membrane performance was performed with optimum fabrication condition and incorporation of ZnO NPs. Through this study, the influences of membrane fabrication factors were investigated to ensure the great development in nanoparticles-incorporated membrane. Hence, the best condition of fabrication with the combination of hydrophilic ZnO NPs would contribute to the improvement of membrane performance in terms of permeability, porosity and fouling propensity.

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