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Effect of Zinc Oxide on Performance of Ultrafiltration Membrane for Humic Acid Separation

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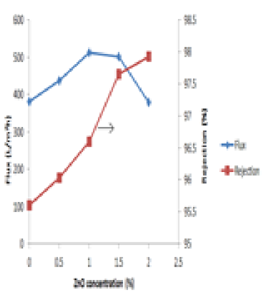
Graphical abstract



Abstract

The effects of different zinc oxide concentration on morphology, contact angle, surface roughness and rejection towards humic acid in polysulfone membrane were investigated. Flatsheet ultrafiltration membrane were prepared by using polysulfone as based polymer, polyethylene glycol as pore forming agent, zinc oxide as manipulated additive and TAP as compatibilizer. In this study, N, methyl-2-pyrrolidone were used as solvent and water as non solvent. The membrane were prepared via phase inversion method. Results showed that pure water flux was enhanced by the presence of zinc oxide up to 1 wt% and tend to decrease beyond this concentration. The increased pure water flux was attributed to the increase in hydrophilicity and surface roughness of membrane according to contact angle and AFM measurement. The rejection test with humic acid as solute revealed that by increasing zinc oxide concentration, rejection increases up to 98% at 2 wt% of zinc oxide. Therefore polysulfone/zinc oxide in this study can provide potential application for river water treatment which consist high humic acid concentration.

Keywords: Zinc oxide; polysulfone membrane; humic acid; polyethylene glycol

■1.0 INTRODUCTION

Preparation high quality of water is necessary nowadays due to an increase in water demand. This water is currently applied in various different fields such as domestic usage, energy production, recreation, industry and agriculture. Thus it can be considered as backbone between industry and human life. There are many technique to improve water quality, however the most promising technique that studied by a lot of researcher is using membrane technology process. This process was found to be the best and suitable for water treatment as compared to others technique such as halogen disinfection, radiation, chlorination and etc. This processes also more favourable as they are cheap and fast, highly selective, and flexible to be integrated with other process. Other than that, membrane process only requires low space and its separation process will not change the water phase [1].

However, membrane fouling is the most unwanted disadvantage in this process which will shorten the life span of membrane and reduce separation process rate. Fouling is defined as adsorption of pollutants on the surface and into membrane pores [2]. Different feed water will contributed different fouling behaviour on membrane. Previous study reported that fouling behaviour of river water which consist a lot of natural organic matter (NOM) contributed several types of fouling such as crystalline fouling, particulate and colloidal fouling, organic fouling and also microbiological fouling. Among all the fouling, organic fouling is most serious problem for membrane process and limits the widespread the use of membrane [3, 4].

Polysulfone (PSf) membranes have been widely used as membranes materials in many industrial fields due to low in cost, superior film forming ability, good mechanical properties, high thermal stabilities and outstanding acidic and alkaline resistance[5]. However the major disadvantage of PSf is hydrophobic characteristic which is easy for pollutant to adsorb on membrane surface and cause serious fouling behaviour. Thus the current investigation to improve PSf surface have been progressively studied such as using low molecular weight hydrophilic polymer, inorganic additives and chemical modification such as grafting and crosslinking [6-13].

Blending inorganic additives such as titanium dioxide (TiO_2), Silica (SiO_2), zinc oxide (ZnO) and silver oxide in PSf membrane was found to improve hydrophilicity and reduce fouling properties of membrane. However, high concentration of inorganic additives will lead to increase surface roughness and reduce water permeability due to pore blockage. Therefore the effect of concentration of these organic additives were investigated and discussed by many researchers [6, 8, 9, 14, 15]. Different opinion and view on behaviour of inorganic additives in membrane behaviour is still open for discussion. It is reported by Hamid *et al*. which using TiO_2 in PVDF membrane that this inorganic additives was found to improve membrane fouling properties [3]. Other paper reported by Yuliwati *et al*. found that similar materials which is TiO_2 at 2 wt% concentration contributed to increase fouling properties of membrane due to increase in surface roughness [16]. Arash *et al*. found that 2 wt% of silver improved water permeability and rejection of membrane eventhough a dense crossection of membrane form [16]. Thus for different materials, the behaviour and characteristic of membrane should be different and unable to predict unless full set experiment were conducted.

Therefore this study investigated the effect of our synthesized ZnO nanoparticle on PSf membrane. The aim of this work to study the concentration effect of this additives on on morphology, contact angle, surface roughness and rejection towards humic acid membrane.

2.0 EXPERIMENTAL

2.1 Experimental

Polymer solutions were prepared using polysulfone (UDEL P1700) as polymeric material and N-methyl-2-pyrrolidone (NMP) (MERCK) as solvent. Meanwhile our synthesized zinc oxide (ZnO) was used as additive. XRD result of synthesized ZnO is shown in Figure 1. The zinc oxide were in the form of hexaganol with a= 3.2489 and c =5.2049.The morphology of ZnO is shown in Figure 2. Polyethylene glycol (Qrec) were used as pore forming agent and 2,4,6-triaminopyrimidine (TAP) were used as compatibilizer. 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

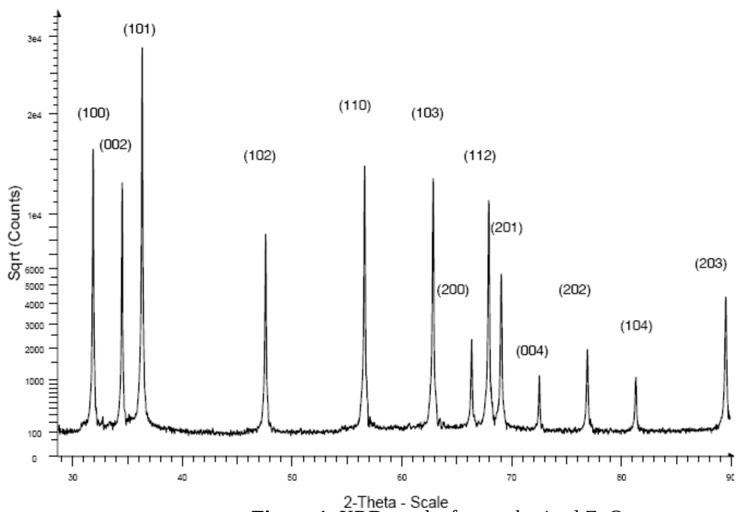


Figure 1 XRD results for synthesized ZnO

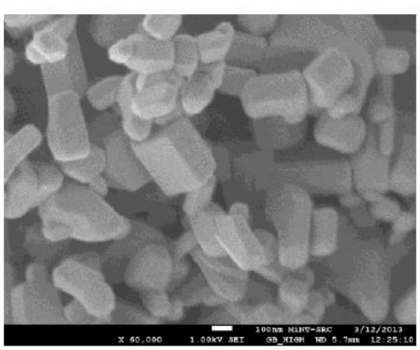


Figure 2 Morphology of synthesized ZnO

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 [10, 11]. The cast solution was then immersed in water bath until the membrane thin film peels off naturally. The procedures were performed at constant temperature and relative humidity (HR) (25 °C; HR 84%).

2.3 Membrane Characterization

SEM 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 cm^2) were cut and glued on metal plate. Surfaces of prepared membranes were scanned and imaged in a scan size of 5 μm×5 μm.Tensile properties were determined by Universal Tensile Machine (Shimadzu). The measurements were carried out at room temperature and a strain rate of 1mm/min was employed. The reported were average of five samples as per standard ASTM D822. 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.

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:

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

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 is steady. The concentration of feed and permeate solution were determined by using UV spectrophotometer (Thermo Scientific, Genesys 10S) and calculated using Equation 2.:

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

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

3.0 RESULTS AND DISCUSSION

The surface morphology of and membrane characteristic at different ZnO concentration is shown in Figure 3 and Table 1. Figure 3 shows that as amount of ZnO increased, accumulation of ZnO on the surface of membrane increased. This might be due to low compatibility between ZnO and PSF matrix. Similar result was found by Hong and He where ZnO is used as additive in polyvinylidene fluoride membrane [17]. This trend also proved by an increased in surface roughness of membrane as shown in Figure 4 and Table 1. Figure 4 shows the valley of membrane which indicate membrane roughness increased as ZnO content increases. The roughness average rose 63% (30.21 nm) at 2.0 wt % of ZnO as compared to PSf membrane without ZnO.

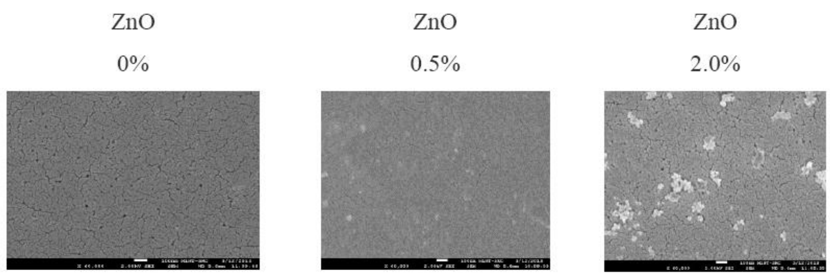


Figure 3 Top surface of PSf/ZnO at different concentration of ZnO

Table 1 Characteristic of PSf/ZnO membrane at different concentration of ZnO

Sample		Contact angle (°)	Roughness Average (nm)	Mean Pore Radius (nm)	Tensile Strength (MPa)
ZnO	0.0	72.84	18.56	75.4	2.80
	0.5	71.01	24.91	76.0	3.84
	1.0	68.98	26.66	77.4	3.76
	1.5	65.23	28.77	81.8	3.74
	2.0	62.45	30.21	85.3	3.68

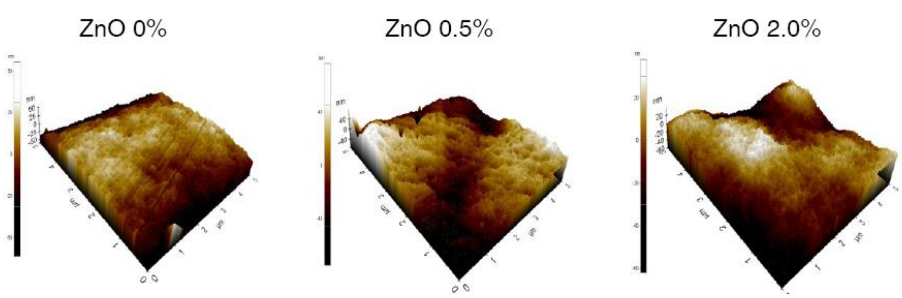


Figure 4 AFM results for PSf/ZnO at different concentration of ZnO

The hydrophilicity of membrane is presented in Table 1. It can be observed that the hydrophilicty of membrane increased as ZnO content increases. This indicate that the presence of ZnO can improve hydrohpilicity of membrane. Membrane with hdyrophillic characteristic will improve water permeability and reduce fouling properties of membrane.

The table also shows that the mechanical or tensile strength is increased by addition of zinc oxide from 0% to 1% (2.80MPa to 3.76 MPa). However the strength was reduces at concentration more than 1.5 % and above. This trend might be due to zinc oxide being able to provide stress transfer to PSF matrix during tensile test at low concentration. However due to low interaction between zinc oxide and PSF membrane at high concentration, the strength of membrane reduces.Similar trend was reported by Aihua *et al*. [18]. They found that the zinc oxide can improve strength of membrane but high concentrations of zinc oxide were cause decreasing in tensile strength, elasticity and elongation at break value.

Figure 5 shows the effect of zinc oxide on the performance of PSF membrane. From the figure, pure water flux increase as zinc oxide increases up to 1.0 wt. %, then the flux reduces at concentration 1.5 wt% and 2.0 wt%. The increase of PWF can be attribute to an increase in hydrophilicity and surface roughness of membrane. The hydrophilicity of membrane can give better interaction between water and membrane. Water tend to diffuse inside hydrophilic membrane instead hydrophobic membrane. In case of surface profile, as surface roughness increases, area for water to diffuse is enhanced. This will allowed more water to permeate through membrane and increase PWF.

However, beyond 1.0 wt. % of ZnO, PWF of membrane is decreased.This trend is due to pore size of membrane is decreased as shown Table 1. This might be due to pore blocking of ZnO in PSf matrix which prevent water to penetrate inside membrane. This PWF result can be verified with mean pore radius results which is depicted in Table 1.The relationship between pure water flux and porosity happen might be cause by zinc oxide able to disturb miscibility at low concentration hence enhance flux and pore size. However an increase amount of zinc oxide, pore were blocked inside PSF matrix and reduce the performance of membrane. This trend can be observed from result investigated by other researcher which found that addition of inorganic additives in the membrane will increase of water flux at first and then decreased by addition at high concentration of additives [17].

Figure 5 also shows that, humic acid rejection is increased as ZnO concentration increases. The highest rejection was found at 2 wt% of zinc oxide which is 97.93%. Membrane function as filter that allowed smaller particle then its pore size to pass trough. Therefore as the pore size decreases, the rejection of membrane increases. This trend was discovered by a lot of researcher in this field [3,6, 8, 15].

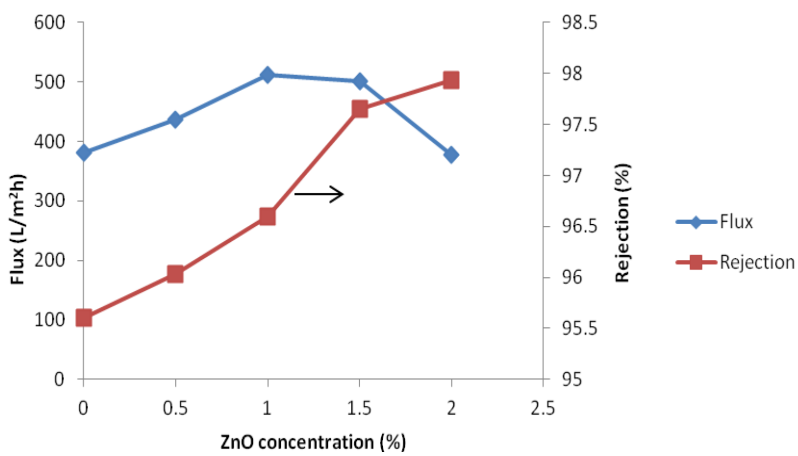


Figure 5 Flux and rejection of PSf/ZnO at different concentration of ZnO

4.0 CONCLUSION

The study reveals the effect of zinc oxide on the performance of PSf membranes. In this study, PSf/ZnO membranes were prepared by incorporating ZnO from 0 wt% to 2 wt%. These composite membranes were characterized with SEM, AFM, contact angle and mechanical properties. The hyrophilicity, surface roughness, and mechanical properties of membrane increased as ZnO particle increases.The performance result showed that pure water flux increased as ZnO increases up to 1 wt% then it decreased. The humic acid rejection of membrane increased as ZnO content increases up to 98% at 2 wt% of ZnO concentration. Therefore polysulfone/zinc oxide membrane in this study can provide potential application for river water treatment which consist high humic acid concentration.

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