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Preparation and Characterization of PVDF-TiO_2 Composite Membranes Blended with Different M_w of PVP for Oily Wastewater Treatment using Submerged Membrane System

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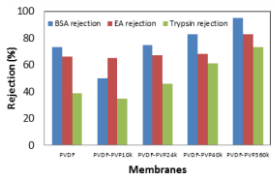
Graphical abstract



Abstract

Polyvinylidene fluoride (PVDF) hollow fiber ultrafiltration (UF) membranes consisted of TiO_2 and different molecular weight (M_w) of polyvinylpyrrolidone (PVP) (i.e. 10, 24, 40 and 360 kDa) were prepared to treat synthesized oily wastewater. The membrane performances were characterized in terms of pure water flux, permeate flux and oil rejection while the membrane morphological properties were studied using SEM and AFM. PVDF-TiO_2 composite membrane prepared from PVP40k was found as the optimum membrane due to its high flux and high rejection during filtration process, recording 45 L/m^2.h and 80% respectively, when tested using 250 ppm oily solution under submerged condition. The experimental results demonstrated that with increasing M_w of PVP, PVDF-TiO_2 membrane had higher protein rejection, smaller porosity and smoother surface layer. With increasing oil concentration from 250 to 1000 ppm, the permeate flux of the PVDF-PVP40k was obviously decreased while the oil rejection was gradually increased due to the additional selective layer formed on the membrane surface. Based on the findings, the PVDF-TiO_2 membrane with PVP40k can be considered as a potential membrane for oily wastewater industry due to the high permeate flux and oil rejection.

Keywords: Polyvinylidene fluoride; polyvinylpyrrolidone; ultrafiltration; oily solution; hydrophilicity

1.0 INTRODUCTION

There has been increasing attention to the efficiency of the oil refinery wastewater treatment because oil refinery wastewater is toxic, harmful and exhibits potential risks to the marine environment. There are many oil separating methods reported so far. These include gravity settling, centrifugation, air flotation and fibrous or packed bed coalescence and membrane-based technologies [1-7]. Of all these methods, ultrafiltration (UF) membrane technology is generally known as a promising technique to substitute the existing conventional treatment methods due to its smaller pore sizes (i.e. in the range of 2-50 nm) which make it capable of removing oil droplets without the use of chemical.

Polyvinylidene fluoride (PVDF) is favored over other polymers due to its excellent membrane forming ability, high mechanical strength and good resistance in severe chemical environment [8]. PVDF blending with titanium dioxide (TiO_2) has been studied intensively due to the high chemical and physical stability, resistance of fouling problem, photocatalytic and superhydrophilicity effects [9-11]. Nevertheless, the performance of PVDF-TiO_2 composite membrane is always hindered by the aggregation of TiO_2 nanoparticles hence resulted in lower flux [10]. Polyvinylpyrrolidone (PVP) has been commonly used in membrane formation due to its pore forming ability. According to Wang *et al.* [12], high permeation flux and good solute rejection could be obtained for the PVDF-TiO_2 membrane prepared using PVP10k. The use of high M_w of PVP however tended to significantly decrease membrane water permeability. Jung *et al.* [13] found that the water flux was improved with addition of PVP but it was decreased when further increasing M_w of PVP from 10 to 360 kDa. Chakrabarty *et al.* [14] reported that increasing M_w of PVP from 24 to 360 kDa could lead to lower flux and higher hydraulic resistance due to the reduction of pore size caused by the swelling of PVP on the membrane surface layer. Furthermore, the finger-like cavities in the sublayer are significantly suppressed upon addition of high M_w of PVP. Zhang *et al.* [15] on the other hand studied the properties PSf membranes made of different M_w of PVP, ranging from 10 to 1300 kDa. Their findings showed that both the porosity and pure water flux of membrane were increased by increasing the M_w of PVP from 10 to 58 kDa and tended to decrease with further increase in the MW of PVP. According to Basri *et al.* [16], the addition of PVP10k, PVP40k

and PVP360k has altered the wettability of membrane to become more hydrophilic but the pore size and porosity were not significantly affected. Lang *et al.* [17] reported that the size and number of membrane pores decreased with increasing M_w of PVP.

As far as we concerned, the effect of four types of PVP with different M_w (i.e. 10, 24, 40 and 360 kDa) on the morphology and performance of PVDF-TiO_2 membrane has not been reported. With respect of this, an attempt is made to investigate the effect of a wide range of M_w of PVP as additive on the properties of PVDF-TiO_2 composite membrane for oily wastewater treatment under submerged conditions. In the present work, the changes in the morphological structure of PVDF-TiO_2 membranes made of different M_w of PVP are reported, in addition to the membrane performances in terms of water permeation, protein rejection and oil separation efficiency.

■2.0 EXPERIMENTAL

2.1 Materials

PVDF (Kynar®760) pellets purchased from Arkema Inc., Philadelphia, USA were used as the main membrane forming material. N,N-dimethylacetamide (DMAc) (Merck, >99%) was used as solvent to dissolve polymer without further purification. Polyvinylpyrrolidone (PVP) (10, 24, 40 and 360 kDa) purchased from Sigma Aldrich and titanium dioxide (TiO_2) (Degussa P25, average particle size ~21 nm) from Evonik were used as additives to enhance PVDF membrane properties. The cutting oil obtained from RIDGID, Ridge Tool Company was used to synthesize oily solution with different oil concentrations.

2.2 Characterizations

2.2.1 Scanning Electron Microscope (SEM)

The outer surface and cross sectional morphology of membranes was observed by tabletop SEM (Model: TM 3000, Hitachi). Prior to the analysis, the hollow fiber was immersed into liquid nitrogen for few minutes followed by freeze-fracturing to obtain perfect cut structure. The fiber was then placed onto carbon-tape aluminum holder and coated with gold under vacuum.

2.2.2 Atomic Force Microscope (AFM)

The membrane surface roughness and images were investigated by AFM (Model: Seiko SPA-300HV). Small piece of fiber was cut and placed on a square paper card with size of 1 cm^2 using double-sided adhesive tape. The membrane surface was scanned in the size of 5 µm × 5 µm. The surface roughness of the membrane was expressed in terms of mean surface roughness (R_a).

2.2.3 Contact Angle Goniometer

The contact angle of membranes was determined by the sessile drop technique using a contact angle goniometer (Model: OCA 15EC, Dataphysics) with deionized water as the liquid. At least 10 locations were arbitrarily chosen on the membrane surface in order to yield an average value.

2.2.4 Membrane Porosity

The membrane porosity, ε, is defined as the volume of the pores per the total volume of the porous membrane as shown in Equation (1).

$$\varepsilon = \frac{\frac{(w_{wet} - w_{dry})}{\rho_w}}{\frac{(w_{wet} - w_{dry})}{\rho_w} + \frac{w_{dry}}{\rho_p}} \times 100 \quad (1)$$

where ε is the membrane porosity (%), w_{wet} is the weight of wet membrane (g), w_{dry} is the weight of dry membrane (g), ρ_p is the density of the polymer (g/cm^3) and ρ_w is the density of water (g/cm^3).

■3.0 RESULTS AND DISCUSSION

3.1 Effect of Molecular Weight of PVP on Membrane Structural Properties

Figure 1 shows the SEM cross-sectional images and 3D AFM surface images of the hollow fiber membranes prepared with different M_w of PVP. It was clearly observed that membrane with the addition of PVP has larger macrovoids in comparison to the neat PVDF-TiO_2 membrane. However, the size of macrovoids was decreased and the sponge layer became larger with increasing M_w of PVP. The finger-like macrovoids gradually developed at the external and internal surface layer with increasing M_w of PVP. This can be explained by the increases of viscosity of the membrane dope with increasing M_w of PVP (see Table 1).

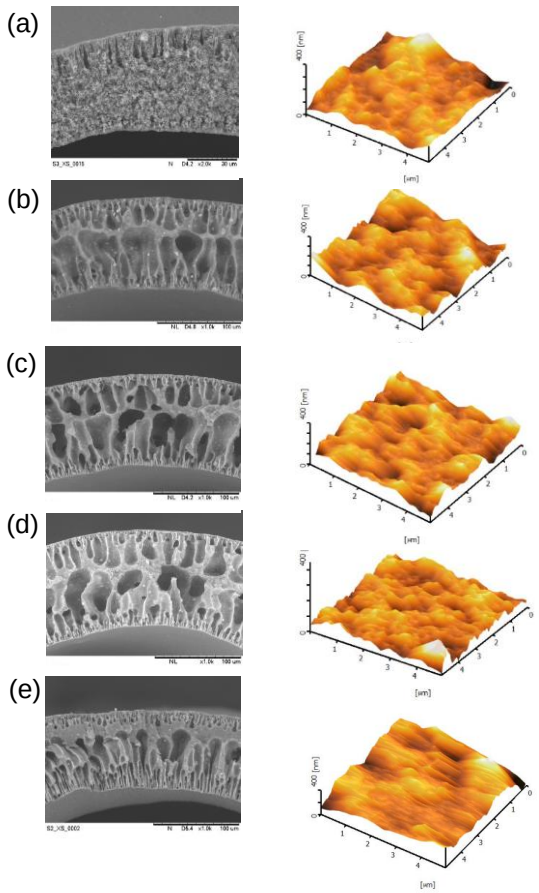


Figure 1 SEM cross-sectional images and 3D AFM images (outer surface) of PVDF-TiO_2 membranes prepared from different molecular weight of PVP (a) 0 (b) 10k (c) 24k (d) 40k and (e) 360k Da

Table 1 Effect of different M_w of PVP on the PVDF-TiO_2 membrane properties with respect to viscosity, contact angle, surface porosity and surface roughness

Membranes	μ (cP)	Contact Angle (θ)	ε (%)	R_a (nm)
PVDF	5375	85.50	81.95	17.58
PVDF-PVP10k	10804	67.95	88.59	26.50
PVDF-PVP24k	11986	69.75	85.15	19.15
PVDF-PVP40k	17118	75.60	85.36	16.37
PVDF-PVP360k	27882	81.55	82.27	15.35

* μ: dope viscosity, ε: surface porosity, R_a: surface roughness

Figure 2 shows the protein rejection of the PVDF-TiO_2 membranes with different M_w of PVP. Compared to the membranes blended with PVP, the neat PVDF-TiO_2 membrane showed moderate protein rejection, for BSA, EA and trypsin rejection which is 73%, 66% and 39%, respectively. It was found that the rejection of BSA was found to be lower than EA and rejection of EA was found to be lower than trypsin for all the membranes, which is due to the differences in the M_w of proteins. The protein rejection of PVDF-PVP10k is the lowest among membranes blended with PVP, indicated largest pore sizes and macrovoids presented in the membrane surface layer as seen in Figure 1(b). In contrast, the high protein rejection of PVDF-PVP360k membrane indicated smaller pore sizes and less macrovoids, which was observed in the Figure 1(e). The increasing protein rejection with increasing M_w of PVP was attributed to the pore blocking effect on the membrane surface caused by smaller pore sizes, this effect was more severe when the M_w of proteins were larger, which made the membrane become more retentive and resulted in high protein rejection.

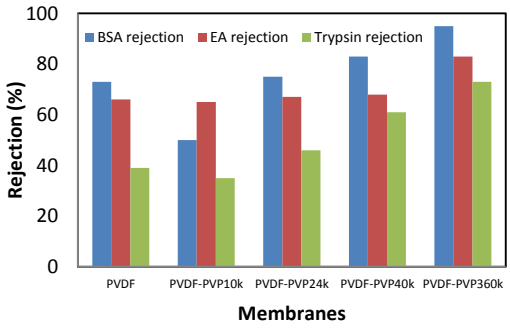


Figure 2 Rejection of BSA, EA and trypsin with different M_w of PVP on the PVDF-TiO_2 membrane (Operating conditions: temperature = 25 °C, concentration of each protein = 1000ppm, pressure = 0.5bar, duration = 1h)

The changes in membrane properties with respect to viscosity, contact angle, surface porosity and surface roughness upon addition of different M_w of PVP are shown in Table 1. As can be seen, the viscosity was increased with increasing addition of PVP. The increase of viscosity restricts the micro phase separation between water and polymer solution, reducing the amounts of macrovoids in the membrane surface layer as evidenced in the cross sectional morphology of SEM images. The contact angle of PVDF-TiO_2 membrane with addition of different Mw of PVP was increased due to the decrease of hydrophilicity in higher M_w of PVP. On the other hand, all the membranes showed reasonably high porosity regardless of the M_w of PVP added. This can be explained by the high viscosity of the membrane dope that caused kinetic hindrance again phase separation, enhanced the diffusion between solvent and non-solvent during phase inversion process, resulted in more porous membranes [14]. The outer surface topology of hollow fibers was measured by AFM technique. The 3D AFM images and the roughness parameters are shown in Figure 1 and Table 1, respectively. It can be seen that the R_a value was significantly decreased as the M_w of PVP increased. Lang *et al.* [17] reported that increases of M_w of PVP could induce the relaxation of the orientated macromolecules hence resulted in lower surface roughness. The ridge-and-valley on the membrane surface can also be attributed to the nodular shapes of TiO_2 nanoparticles that present in the membrane.

3.2 Effect of Different Molecular Weight of PVP on Membrane Flux and Oil Rejection

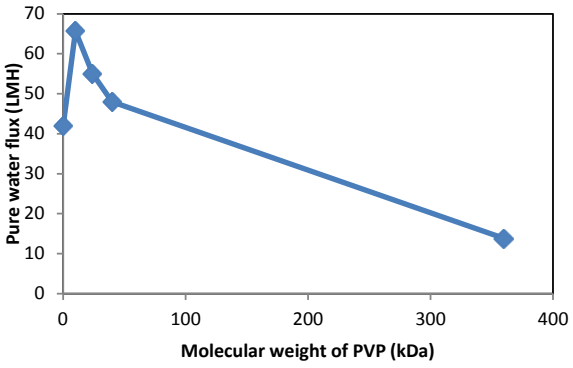
Figure 3(a) shows that pure water flux of PVDF-TiO_2 membranes prepared from different M_w of PVP. As can be seen, the pure water flux of PVDF-TiO_2 membrane decreased from 65.73 to 13.81 L/m^2.h with the increasing M_w of PVP from 10 to 360 kDa, which has exhibited approximately 179 % reduction in water permeability. The neat PVDF-TiO_2 membrane showed lower flux due to less macrovoids that presented in the membrane surface. When PVP was added into membrane dope solution, the flux was increased initially and then declined with further increasing M_w of PVP. The decreasing trend of flux may be attributed to the formation of membranes with smaller pore size and thicker sponge layer due to the addition of higher M_w of PVP. As evidenced by other researchers [17-19], low M_w of PVP could act as an enhancer to the membrane hydrophilicity and resulted in important changes in the performance of UF membrane such as solute retention and fouling control on the membrane surface. From Figure 3(b), the permeate flux of PVDF-TiO_2 membranes blended with PVP were higher than that of neat PVDF-TiO_2 membrane. With increasing M_w of PVP, the permeate flux of PVDF-TiO_2 membrane decreased from 55.29 to 11.43 L/m^2.h. The permeate flux obtained was lower than pure water flux as the presence of oil molecules in the feed solution tended to accumulate on the membrane surface, creating an additional resistance for water molecules to permeate and decreased water flux production. With respect to oil rejection, PVDF-PVP10k membrane exhibited lower separation efficiency compared to that of neat PVDF-TiO_2 membrane but the oil rejection was increased with increasing M_w of PVP. It was believed that the mean pore size of PVDF-TiO_2 membranes was reduced with increasing M_w of PVP, hence eliminated most of the oil droplets presented in the feed solution, consequently resulted in higher oil rejection.

4.0 CONCLUSION

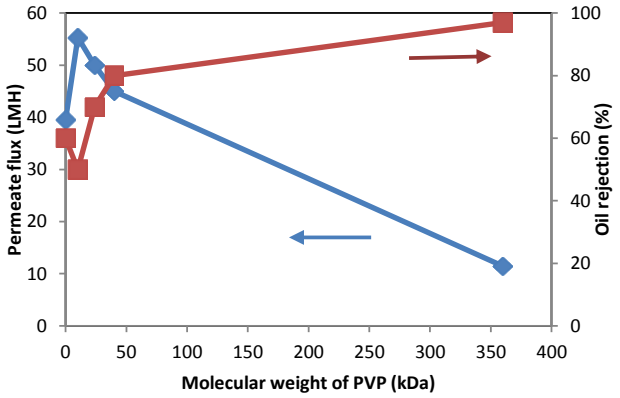
The permeation performance of PVDF-TiO_2 membranes with different M_w of PVP were evaluated under submerged conditions. The results obtained showed that the membrane properties were affected with the use of different M_w of PVP as additive during membrane preparation. The main conclusions are as follows.

(i) The macrovoids were suppressed and thicker sponge layers were formed, which enhanced the mechanical properties to the membrane structure.
(ii) The viscosity and contact angle were increased whereas porosity and membrane surface roughness were decreased due to relaxation of the orientated macromolecules and result in smoother surface.

(iii) The rejection of BSA, EA and trypsin was increased due to pore blocking effect caused by the M_w of protein and pore sizes on the membrane surface layer.
(iv) The pure water flux and permeate flux was decreased whereas oil rejection was increased, due to smaller pore size and thicker sponge layer with the addition of higher molecular weight of PVP.
(v) PVDF-TiO_2 membrane added with PVP40k is concluded as optimum membrane due to the high flux and rejection achieved in the oil filtration.



(a)



(b)

Figure 3 (a) Pure water flux (b) Permeate flux and oil rejection of PVDF-TiO_2 membranes prepared at different M_w of PVP (Operating conditions: temperature = 25 °C, oil concentration = 250ppm, air bubble flow rate = 5 ml/min and vacuum pressure = –15 inHg)

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