Jurnal Teknologi

Full paper

Preparation and Characterization of Polysulfone/Polyphenylsulfone/Titanium Dioxide Composite Ultrafiltration Membranes for Palm Oil Mill Effluent Treatment

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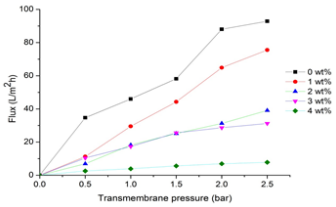
Article history

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

Graphical abstract



Abstract

Palm oil mill effluent (POME) is the largest pollutant discharged into the rivers of Malaysia. An efficient treatment system is highly desirable in palm oil mills in order to control the effluent discharged to any water bodies. In this study, composite ultrafiltration (UF) membranes were successufully prepared by incorporating polysulfone (PSF)/polyphenylsulfone (PPSU) blend membranes with inorganic TiO_2 nanoparticles in the range of 0–4 wt%. Prior to POME treatment process, the properties of the resulting membranes were first characterized with respect to pure water flux, BSA rejection, hydrophilicity and structural morphologies. Of the membranes tested, it is found that membrane without TiO_2 incorporation demonstrated the highest pure water flux, i.e. 82.81 L/m^{2}h with BSA rejection of 98% when tested at 2 bar. The decreasing water flux with increasing TiO_2 loading in the membrane is mainly due to the high viscosity of the dope solution which delayed the phase inversion process and resulted in reduced surface pore size. For the POME treatment process, the results showed that UF membrane could effectively treat the wastewater by removing up to 87% BOD_3, 90% COD and almost complete elimination of turbidity.

Keywords: Polysulfone; polyphenylsulfone; membranes; titanium dioxide; ultrafiltration; palm oil mill effluent, COD; BOD_3

1.0 INTRODUCTION

The palm oil industry forms the backbone of Malaysia, where the country today is the world's second largest producer and exporter of palm oil after Indonesia. In Malaysia, palm oil mill industry is identified as the one discharging the largest pollution load into the rivers throughout the country and it has been reported since last 3 decades.[1] Currently there are over 250 palm oil mills distributed in Peninsular Malaysia, generating over 20 million tonnes of effluent every year.[2] In addition, one of the most crucial problems that the oil palm industry faces is waste disposal, since about 2.5-3.0 cubic meters (m^3) of POME are generated for every tone crude palm oil produced.[3] An efficient treatment system is therefore highly desirable in palm oil mills in order to control the effluent discharge and to meet the standard parameters set by Malaysian Department of Environment (DOE).

There are several common POME treatment methods being adopted in Malaysia. One of the type of POME treatment is biological treatments of anaerobic and aerobic system. According to Perez *et al.*[4] anaerobic process is a suitable treatment method due to the organic characteristics of POME and thus is widely applied in Malaysia. However, the biological treatment process needs proper maintenance and closed monitoring as the efficiency of the process strongly depends on microorganisms to break down the pollutants which usually require long retention time and skilled personnel to handle.[5] An efficient POME treatment has always been considered a burden to industrial players since no profit is gained from this activity, although biogas can be potentially produced from biological treatment but it requires additional treatment process.[6] The pond systems have also been applied in Malaysia for POME treatment since 1982 and they are classified as waste stabilization pond.[7] More than 85% of palm oil mills exclusively use ponding systems due to their low costs. Ponding systems are easy to operate but still occupy a vast amount of land, relatively long hydraulic retention time (HRT) (between 45 and 60 days), bad odour and difficulty in maintaining the liquor distribution and biogas collection which result in harmful effect on the environment. In order to tackle this problem, membrane-based treatment process has become main focus among researchers due to their excellent performance in treating POME and producing permeate of high quality, in addition to its much smaller treatment footprint. This phenomenon can be reflected by the increasing number of technical papers published over the past 2-3 years.[8-10]

Membrane technology particularly ultrafiltration (UF), appears to be a potential treatment process to treat POME

efficiently owing its to micrometer (μm) range pore size. Industrially, UF membranes have been successfully implemented in municipal and industrial wastewater treatments. It is gaining importance for water and industrial wastewater treatment especially in the recovery of chemicals from the industrial wastewater, desalination, drinking water purification, and removal of oil from oil–water emulsions.[11] These include Mameri *et al.*[12] which successfully reduced the COD value to 90% using an organic UF membrane for olive mill washing water. Lo *et al.*[13] and Wu *et al.*[14] also supported that PSF UF membranes were able to treat and reclaim the protein from poultry processing wastewater and POME, respectively with significant efficiency. In the previous study, the effect of hydrophobicity of the membrane material on UF of protein has also been the subject of many studies and hydrophilic membranes are preferentially used because of their low-binding properties.

The main objective of this work is to improve the properties of UF membrane made of PSF by blending the membrane with the third member of the PSF family i.e. polyphenylsulfone (PPSU). It has been reported that PPSU has even better properties than PSF and polyethersulfone (PES) due to its unique characteristics of polysulfone family. This PSF/PPSU blend membrane with further incorporated with TiO_2 nanoparticles at different loading in order to produce composite UF membrane for POME treatment process.

2.0 EXPERIMENTAL

2.1 Materials

Polysulfone (Udel-P1700, MW: 35400 g/mol) obtained from Amoco Chemical was used in this study as membrane forming material. Another type of polymer - polyphenylsulfone (MW: 53,000-59,000 g/mol) purchased from Sigma-Aldrich was used together with PSF in preparing PSF/PPSU blend membranes. Titanium dioxide (Degussa P25, average particle size ~ 21 nm) from Evonik was used as inorganic additive. 1-methyl-2-pyrrolidone (NMP) with analytical purify of 99.5% purchased from Merck was used as solvent. Bovine serum albumin (BSA, 67 kDa) purchased from Sigma Aldrich was used as test solute by dissolving it in DI water.

2.2 Membrane Preparation

All membranes were fabricated using dry-jet wet spinning technique. The formulation of each dope solution is tabulated in Table 1.

Table 1 Composition of the dope solution for the preparation of PSF/PPSU/TiO_2 blend membranes

Membrane designation	Weight ratio PSF : PPSU	Dope solution composition (wt%)		
		Total polymer	NMP	TiO_2
50PSF/50PPSU	0.5 : 0.5	20	80	-
50PSF/50PPSU-T1			79	1
50PSF/50PPSU-T2			78	2
50PSF/50PPSU-T3			77	3
50PSF/50PPSU-T4			76	4

2.3 Membrane Characterization

The morphologies of the membranes were observed by a tabletop scanning electron microscopy (SEM) (TM3000, Hitachi). Cross sections of samples were prepared by fracturing of membrane in liquid nitrogen. The hydrophilicity of membranes was studied by measuring the angle between the membrane surface and the meniscus formed by the water using contact angle system (Model: OCA 15EC, Dataphysics). Dope solutions viscosity was measured using Basic Viscometer (EW-98965-40, Cole Parmer).

2.4 UF Experiment

The permeation flux and BSA rejection of membranes prepared were measured by a cross-flow UF system as illustrated in Figure 1.In this study, the pressure was applied on the shell side (feed side) of the hollow fiber membranes. A module consists of 10 fibers in 21 cm long (equivalent of 72.57 m^2 effective membrane area) was housed in a pressure vessel of maximum 1 L capacity. The filtration pressure was supplied by a vacuum pump and controlled by needle valve at 2 bar. Pure water flux was measured after the flux was steady, then calculated as

$$J_{PWF} = \frac{V}{AT} \quad (1)$$

where J_{PWF} is the pure water flux (L/m^2h), V is the permeate volume (L), A is the membrane surface area (m^2), and T is the time (h).

After determine the J_{PWF}, the distilled water was then replace with Bovine serum albumin (BSA) protein solution at the operational TMP 2 bar. The rejection for BSA solution was determined by measuring the concentration in the fed and filtrate solution. The feed and permeate solute concentration was determined using HACH DR5000 UV-Vis spectrophotometer at the wavelength 254 nm (UV_{254}). The permeate was periodically taken for each10 minutes throughout the 180 min of the filtration times. The percentage of rejection was calculated as:

$$R = (1 - \frac{C_p}{C_f}) \times 100 \quad (2)$$

where R is the BSA rejection (%), c_p is the concentration of the permeate (mg/L), c_f is the concentration of the feed (mg/L).

2.5 POME Analysis

Analytical tests were carried out to evaluate the quality of the POME after and before membrane treatment process. Chemical oxygen demand (COD) tests were carried out by putting 2 ml sample into the oxidizing acid reagent solution and then were held at 150 °C for 2 h. After it was cooled down to ambient temperature, the COD value of sample was analyzed using a colorimeter (DR/890, Hach) with readings taken at 435 nm wavelength. Biological oxygen demand (BOD) tests were carried out according to BOD_3. Initial dissolved oxygen (DO) of each solution was first determined using a portable dissolved oxygen meter (PRODO, YSI). After 3 days of incubation in

20°C, the samples were then analyzed and the final readings were used to calculated BOD. With respect to sample turbidity, a portable turbidimeter (2100Q, Hach) was used for measuring the turbidity of feed and permeate sample at room condition.

■3.0 RESULTS AND DISCUSSION

3.1 Effect of TiO_2 Nanoparticles Loading on PSF/PPSU Membrane Properties

3.1.1 Morphological Studies

Asymmetric PSF/PPSU blend membranes with different TiO_2 loading were prepared through the phase inversion process. Figure 2 shows SEM micrograph of PSF/PPSU membranes prepared from different TiO_2 loading i.e. 0 wt%, 1 wt%, 2 wt%, 3 wt% and 4 wt %. It was experienced that TiO_2 nanoparticles were dispersed uniformly in the dope during solution preparation. As can be seen, all the membranes prepared with and without TiO_2 nanoparticles solution exhibited porous structure. From the membrane cross section TiO_2 nanoparticles are uniformly distributed on the 50PSF/50PPSU-T1, 50PSF/50PPSU-T2, 50PSF/50PPSU-T3 and 50PSF/50PPSU-T4 membrane. However, by increasing the TiO_2 nanoparticles loading in dope solution, it tended to form agglomeration in membrane. This can be seen by SEM images. As TiO_2 nanoparticles have a large specific area and high surface energy, the addition of them in dope solution would increase viscosity of solution, delaying demixing process Yuliwati *et al.*[15].. In their study also reported that higher TiO_2 concentration resulted in the formation of a highly viscous dope solution. This would slow down the formation process of the membranes and produced a denser sponge-like substructure (i.e. reduced pore size).

In the previous study conducted by Machado *et al.*[16], it was stated that the addition of an additive into the casting solution produces two opposite effects. Depending on the molecular weight, additives may reduce the miscibility of the casting solution with water, which causes the thermodynamic enhancement of the phase separation (thermodynamic factor). At the same time, they may increase the viscosity of the casting solution to a certain extent which causes kinetic hindrance against phase separation (rheological factor) Strathmann *et al.*[17]. So impact of thermodynamic or rheological factors on membrane morphology depends on the molecular weight of additives.

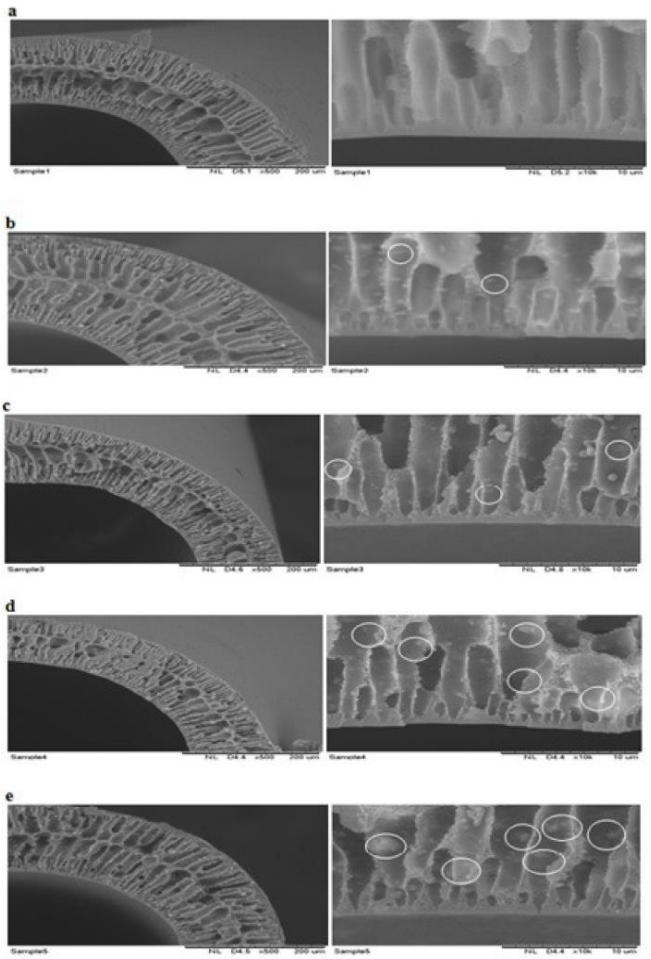


Figure 2 SEM micrograph of PSF/PPSU membranes with different TiO_2 loading: (a) 0 wt%, (b) 1 wt%, (c) 2 wt%, (d) 3 wt% (e) 4 wt%

3.1.2 Pure Water Flux and BSA Rejection

The water flux–pressure relationships obtained for the composite membranes are illustrated in Figure 3. It can be seen that the pure water flux decreased with increasing TiO_2 content in composite membranes when tested at pressures of 0.5-2.5 bar. The water flux of all the membranes increased with increasing operating pressure since the driving force for permeation of water is dependent on the applied pressure. Unlike other studies which reported the flux enhancement upon TiO_2 addition, the use of TiO_2 in PSF/PPSU blend membrane was experienced to have negative impact on permeate flux. This might be due to the surface pores plugging by TiO_2 nanoparticles and/or reduced surface pore size resulted from increased solution viscosity upon TiO_2 addition.

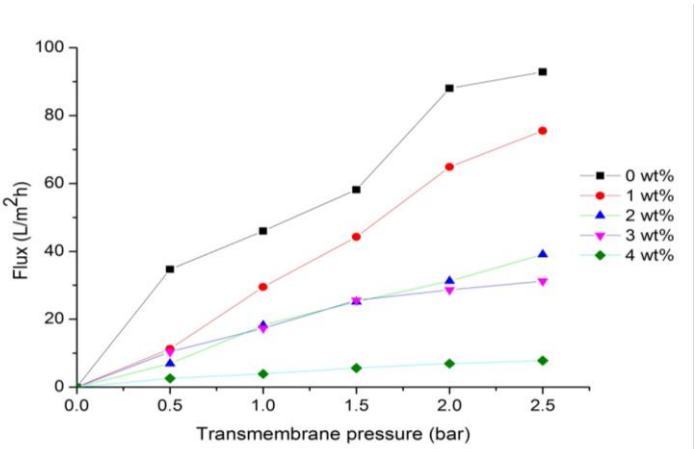


Figure 3 The effect of pressure on the pure water flux of different TiO_2 composition

As observed in Figure 4, the addition of TiO_2 nanoparticles had greatly increased the spinning dope viscosity. It is generally accepted that the spinning dope viscosity would influence the multi transfer between solvent and non-solvent, or kinetic effect for membrane formation. In this study, the viscosity was increased linearly with increasing TiO_2 loading from zero to 4 wt%. High viscosity of the spinning dope would decrease the mutual diffusion between solvent and non-solvent in the coagulation bath (kinetic effect), delaying phase inversion process. The delaying demixing process is the main reason reducing the surface pore size of membrane, causing the pure water flux decreases from around 83 L/m^2.h in 50PSF/50PPSU membrane to less than 10 L/m^2.h in 50PSF/50PPSU-T4 membrane.

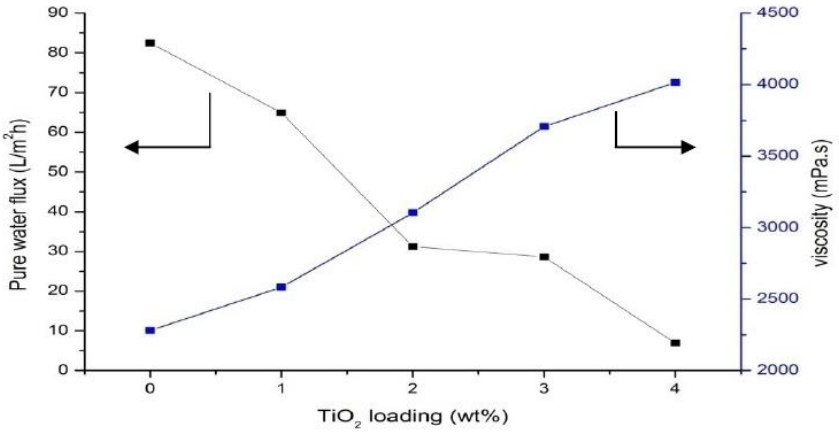


Figure 4 The viscosity and pure water flux of PSF/PPSU spinning dope with various TiO_2 content at 2 bar

The separation performances of composite membranes were also evaluated using bovine serum albumin (BSA) as test solute. The experiments were conducted at 2 bar using 1000 ppm BSA solution and the results are shown in Figure 5. As shown in the figure, PSF/PPSU membrane without TiO_2 addition showed the highest permeate flux (i.e. 37.18 L/m^{2}h) but tended to decrease when TiO_2 nanoparticles were incorporated. Overall the permeate fluxes of all membranes were lower than their pure water fluxes. This is mainly due to the protein adsorption or convective deposition, restricting the water molecules to flow through membrane matrix.

With respect to BSA rejection, it is reported that all the membranes studied showed a very promising rejection against BSA solute. This indicated that these membranes having pore size much smaller that the particle size of BSA. Although these membranes showed similar BSA rejection, the decrease of

membrane water flux with increasing TiO_2 loading could be an indication of pore size reduction. According to Bae and Tak[18], it is difficult to predict the performance change of membrane because of conflict effects of TiO_2 nanoparticle. Although TiO_2 is hydrophilic in nature, the existence of it in membrane matrix might plug membrane pore, compromising its positive effect.

As shown in Figure 6, it is found that hydrophilic TiO_2 nanoparticles did not improve hydrophilicity of membrane by reducing the contact angle value. Instead, the contact angle of all membranes incorporated with TiO_2 nanoparticles have shown significantly higher value compared to the PSF/PPSU blend membrane without TiO_2 addition. The increase in contact angle value could be due to the increase in membrane surface roughness (upon TiO_2 addition) according to Cassie and Wenzel effect.

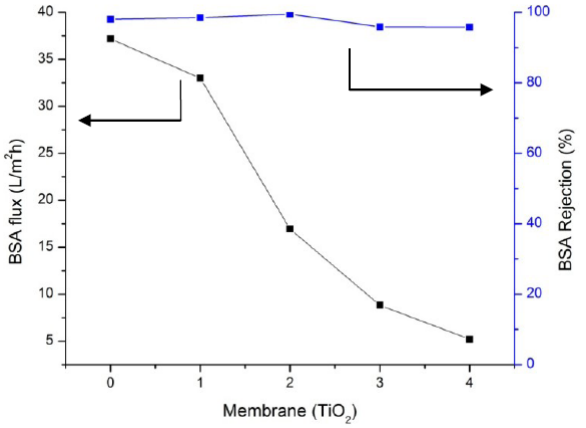


Figure 5 Flux and BSA rejection of PSF/PPSU membranes with different TiO_2 loadings tested at 2.0 bar

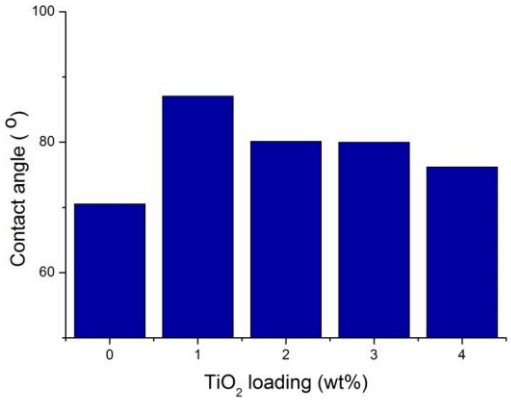


Figure 6 Contact angle of PSF/PPSU membranes incorporated with different TiO_2 loading

3.2 POME Analysis

Figure 7 shows the separation of POME in terms of BOD_3, COD and turbidity. As can be seen, PSF/PPSU membrane without TiO_2 incorporation demonstrated the highest COD rejection (90.77%) followed by PSF/PPSU membrane with 1 wt% TiO_2 (88.41%), 2 wt% TiO_2 (86.94%), 3 wt% TiO_2 (85.27%) and 4 wt% TiO_2 (83.00%). Similar trend was also observed for BOD_3 rejection but with lower separation efficiency. The decreasing COD and BOD_3 rejection with increasing TiO_2 content on the PSF/PPSU membrane can be explained by the fact that the addition of TiO_2 caused particle agglomeration on membrane surface which affected the integrity of membrane structure, leading to surface defects.

On the order hand, it is found that all membranes showed a very promising turbidity rejection (at least 99.9%) regardless of the TiO_2 loading added into the membrane matrix. The complete elimination of sample turbidity can be explained by the presence of large particulates in POME which in general were much larger in terms of size in comparison to the pore size of UF membranes.

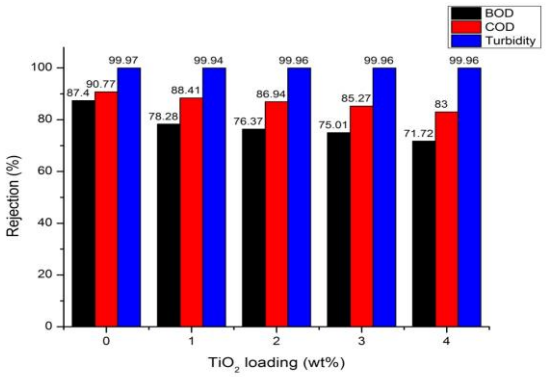


Figure 7 Rejection of BOD_3, COD and turbidity for the PSF/PPSU membrane prepared from various TiO_2 loading for POME treatment

4.0 CONCLUSION

PSF/PPSU/TiO_2 composite UF membranes were successfully fabricated via dry-jet/wet spinning method. In addition to the characterizations using SEM and contact angle goniometer, the performances of the composite membranes were evaluated with respect to BSA rejection and separation efficiency in treating POME. Of the membranes tested, it is found that membrane without TiO_2 incorporation demonstrated the highest pure water flux, i.e. 82.81 L/m^{2}h with BSA rejection of 98% when tested at 2 bar. The decreasing water flux with increasing TiO_2 loading in the membrane is mainly due to the high viscosity of the dope solution which delayed the phase inversion process and resulted in reduced surface pore size. For the POME treatment process, the results showed that UF membrane could effectively treat the wastewater by removing up to 87% BOD_3, 90% COD and almost complete elimination of turbidity.

Acknowledgement

The outhor would like to express sincere gratitude to Ministry of Higher Education (MOHE) for the sponsorship and Ministry of Science, Technology and Innovation (MOSTI) for the financial aid Research University Grant (Tier 1) (Grant no. Q.J.130000.2542.04H86).

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