Cellulose Acetate-Polyethersulfone (CA-PS) Blend Ultrafiltration Membranes for Palm Oil Mill Effluent Treatment

Ani Idris*, Iqbal Ahmad

Department of Bioprocess Engineering
Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia, 81310 Skudai, Johor
Tel: +607-5535603, Fax: 607-5581463, Email: ani@fkkksa.utm.my

ABSTRACT

The objective of this research is to investigate the possibility of using ultrafiltration blended cellulose acetate (CA) and polyethersulfone (PES) membranes in the treatment of palm oil mill effluent (POME). Thus, series of distinctive formulations such as pure CA and blended CA/PES using N, N-dimethylformamide (DMF) as solvent were formulated and prepared by phase inversion method. The blended membranes were initially subjected to the separation of BSA and then POME. The performances of these membranes were evaluated in terms of pure water and permeate flux, percentage removal of total suspended solids (TSS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Blending of 19 % CA, 1 % PES and 80 % of DMF solvent were discovered as the best membrane formulation. The morphology of the blended membranes produced were analyzed using scanning electron microscope (SEM).

Keywords: blend membrane, cellulose acetate, polyethersulfone, palm oil mill effluent

INTRODUCTION

Ultrafiltration (UF) is a membrane process capable of separating or collecting submicrometer-size particles and macromolecules from a suspension or solution [1]. It has been widely used to concentrate or fractionate a solution containing macromolecules, colloids, salts, or sugars. Synthetic polymers such as polysulfone, polyethersulfone, cellulose acetate, etc. are widely used for the ultrafiltration membranes. Polyethersulfone is a hydrophobic polymer. It has wide pH tolerances, good chlorine resistance and easy to fabricate membrane in a wide variety of configurations. Polyethersulfone ultrafiltration membranes have advantages of good thermal stability because it has wide temperature limit and higher dry heat capability. Apart from that, it has good chemical resistance to aliphatic hydrocarbons, alcohols and acids [2]. Meanwhile CA being hydrophilic offers a good fouling resistance but is not suitable for more aggressive cleaning, has low oxidation and chemical resistances and poor mechanical strength and hence the modification of cellulose acetate gains importance [3,4,5]. New, less expensive types of materials with an extensive variety of properties intermediate between those of pure components could be obtained using

* Corresponding author: *Tel: +607-5535603, Fax: 607-5581463, Email: ani@fkkksa.utm.my*

polymer blending. Tomohiro et al. [6] and Sivakumar et al. [7] have reported that the blend membranes produced have better perm selectivity and permeability than that of membrane composed by the individual polymers and the synthesis of a polymer blend membrane is motivated by the necessity to superimpose requisite properties upon the basic transport properties of base polymer. Polymer blend membranes composing of hydrophobic and hydrophilic polymers such as polyacrylonitrile (PAN) with polyvinylchloride (PVC), cellulose acetate (CA) and polysulfone, (PSf), cellulose acetate (CA) and polyethersulfone, (PES),has been investigated [6,8,9,7]. In both of the later blends the additives polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) has been added as additives. Thus in this study the possibility of blending only cellulose acetate (CA) and polyethersulfone, (PES) without any additives for the treatment of POME is explored.

Membrane separation in wastewater treatment has been widely used and has successfully proven its efficiency in various types of industries. Several researches have been done on waste water treatment through membrane technology [10]. Turano *et al.* [11] successfully reduced the COD value to 90 % using an organic UF membrane for olive mill washing water. Sridhar *et al.* [12] used RO to treat vegetable oil industry effluent with resulting high rejection of TDS (99.4 %), COD (98.2 %) and also complete rejection of color and BOD. A combination of microfiltration (MF) and UF membranes has also been used for the treatment of kraft spent liquor with more than 80 % efficiency in silica rejection [13]. Afonso and Borquez [14] studied microfiltration (MF) and ultrafiltration (UF) membranes to treat wastewater from fishmeal production. They succeeded in recycling the water for plant use as well as recycle protein into fishmeal process. Mavrov and Belieres [15] carried out their research on recovery and recycling of water from food industry wastewater using nanofiltration (NF) and reverse osmosis (RO) combined with cartridge filtration and disinfection as a pretreatment. The combination of biological treatment with UF, NF and RO membranes in treating municipal wastewater was also studied by Rautenbach *et al.* [16] where 97 % water recovery was achieved.

The palm oil industry is one of the major agro-industries in Malaysia. It requires a large amount of water for its operation and discharges considerable quantities of wastewater. This creates a serious threat to the environment and sources of potable water. Membrane technology is a highly potential solution for the treatment of POME since current conventional treatment system shows its lack of efficiency and leads to the environmental pollution issues [17]. It is important to develop locally-made membranes in Malaysia not only to gain better approach in terms of the technology but also to reduce the production cost. In order to achieve this mission, self made ultrafiltration blended membrane from cellulose acetate (CA) and polyethersulfone, (PES) without any additives were fabricated and the performances of the membranes produced were evaluated using palm oil mill effluent waste water in terms of flux and percentage rejection of total suspended solids, COD, BOD and turbidity. The morphology of the cross section of PES membranes were obtained by high voltage scanning electron microscope.

MATERIAL AND METHOD

Polyethersulfone (PES) was the polymer used which was supplied by BASF. N, N-dimethylformamide (DMF) was purchased from Labscan Asia Co. Ltd, as solvent without further purification. Bovin serum abumine (BSA) with molecular weight of 69000 Daltons was supplied by Merck and was used as the feed solution. Cellulose

acetate (CA) with 39.8 acetyl content from Acros organic was used. For UF experiments, samples of palm oil mill effluent (POME) at 80 °C were collected from the Felda Bukit Besar Kulai, Johor. These samples were allowed to cool to room temperature and left to sediment by filtration process. Portions of the suspension were withdrawn and analyzed.

Dope Preparation

Polyethersulfone and cellulose acetate were dried before dope solutions were prepared. The blend polymer concentration was fixed at 20% and their proportions are shown in Table 1. A 500 ml Schott Duran is used as the sample reaction vessel at atmospheric pressure.

Membrane Casting

In this study, the membranes are prepared by phase inversion method. The dope solution thus obtained was spread over a smooth glass plate with the help of a knife edge. The thickness of the membranes was controlled by varying the thickness of

Table 1: Dope solution compositions.

Dope Solution	Composition in Wt. %		
	CA	PES	DMF
1	20	0	80
2	19	1	80
3	18	2	80
4	17	3	80
5	16	4	80
6	15	5	80

adhesive tapes at the sides of the glass plate. The glass plate was kept in an environment of controlled temperature and humidity during membrane casting. No deliberate solvent evaporation period was allowed. The glass plate was subsequently immersed in a gelling bath, which is generally distilled water maintained at a known temperature.

Pretreatment for POME Wastewater

The raw POME was collected from oil palm refinery of Felda Bukit Besar, Kulai. The sample was treated via filtration process to remove the suspended matter. The pH of POME before the treatment was 8 and after the pretreatment process was 6.5 and density was 1.25gm/cm^3 at 30 °C. The POME was also analyzed in terms of turbidity, TSS, BOD and COD.

Experimental Method

Membrane performances were investigated by ultrafiltration experiments with POME samples after pretreatment. Pure water or the feed solution was pumped to the flat sheet module by a pump at 3.5 bar, and was circulated through the module for 1 h (pressure drop = 0.5 psig). Then, permeate was collected for a predetermined period and the permeate volume was measured. The permeate sample was further subjected to a series of analysis. After the completion of each ultrafiltration experiment, feed POME solution was switched to pure water and the system was washed for 3 h by circulating the pure

water. The pure water flux (PWP) was calculated from the equation (1)

$$\text{Pure water flux } (l/m^2hr) = Q / At \qquad (1)$$

where Q is the volume of permeate (l), A is the area of the membrane (m^2) and t is the permeation time. In POME ultrafiltration process, permeate comes out from each membrane was collected after 1 hour.

Analytical Methods

Chemical Oxygen Demand Test

2 ml sample was put into contact with the oxidizing acid solution that was then held at 148 °C for 2h. After cooling, the sample was then analyzed in the HACH DR/2000 and DO readings were taken at 435 nm wavelengths. The color of the sample varied from orange to dark green indicating COD strength in the range of 0 – 15,000 mg/L.

Biochemical Oxygen Demand Test

Samples may have to be diluted in order for the DO range to be detected by the meter. Once all the bottles have been filled, in a 500 ml BOD flask the initial DO's of each solution is determined using dissolved oxygen meter (model YSI 5402). Once recorded, the bottles are capped with ground glass stoppers to avoid excess bubbles. After five days of incubation at 4 °C, the samples are ready to be analyzed. The samples are removed from the incubator and allowed to equilibrate to room temperature. Once the DO meter is calibrated, the samples are read starting with the blanks and ending with the actual samples. The final DO of each solution is recorded and the initial and final readings will be used to calculate the BOD.

Turbidity and Total Suspended Solid Test

The turbidity of the samples was measured using HACH Ratio/Xr Turbidimeter which was calibrated. Total suspended solids were measured by inserting a glass microfiber filter disc with wrinkled side up in the filtration apparatus. Vacuum and wash disc with 50 mL of reagent-grade water is then applied. Suction is sustained to remove all traces of water. Next, the vacuum is then turned off. Sample is to be dried in an oven at 103 to 105 °C for an hour. Next, the sample was then cooled down to room temperature before weighing. The cycle of vacuum, drying, cooling and weighing with 20 ml of sample is repeated. The total suspended solid is calculated according to equation 2.

$$\text{Total suspended solids mg/L} = \frac{(A-B)\times 1000}{v} \qquad (2)$$

where A is weight of filter + dried residue, mg, B is weight of filter, mg and v is volume of sample used.

Total Removal of the Component

The efficiency of the membrane fabricated is highly dependent upon the total removal of the component using the following equation:

$$\text{Total removal (\%)} = \left(\frac{\textit{Initial Concentration} - \textit{Final Concentration}}{\textit{Initial Concentration}}\right)\times 100 \qquad (3)$$

Scanning Electron Microscope (SEM)

CA/PES blend membrane's cross section was obtained by a high voltage scanning electron microscope. Samples of membranes were frozen in liquid nitrogen which gives generally clean break [18]. The samples were placed on a sample stand and sputtered coated with gold before being viewed with the SEM Model SUPRA 35VP.

RESULTS AND DISCUSSION

BSA Separation and Pure Water Permeation

The efficiency of the blend membranes produced were tested using solutions of both BSA solutions and POME. The pure water permeation and BSA rejection rate results were depicted in Figure 1 and 2 respectively. The performances of the membranes in terms of pure water permeate produced from the various solutions were depicted in Figures 1. It is observed that the membranes produced from dope solution 5 containing 5% PES exhibits highest pure water permeation rates compared to those produced by from dope solutions 1-4. However the rejection rates of this membrane is the lowest compared to the other membranes containing less amounts of PES in CA. Apparently membranes produced from the dope solution 1-2 exhibits highest rejection rate with molecular cut off (MWCO) at 90% of approximately 69 kDa (BSA) as shown in Figure 2.

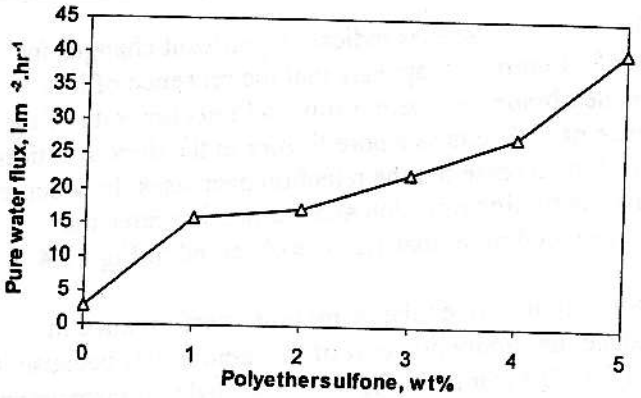


Figure 1 Pure water permeation flux of blend membranes

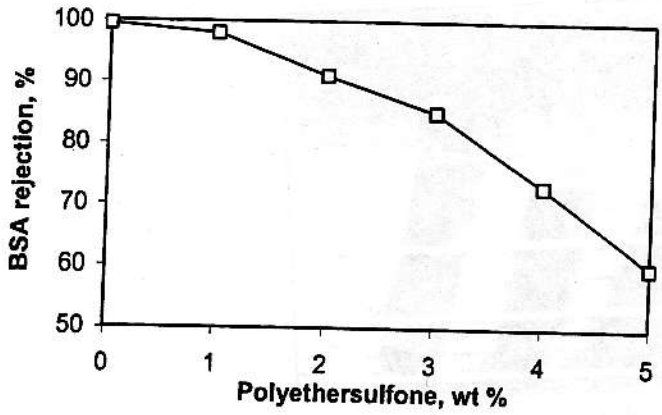


Figure 2 BSA rejection rate versus amount of PES in the blend membranes

POME Separation

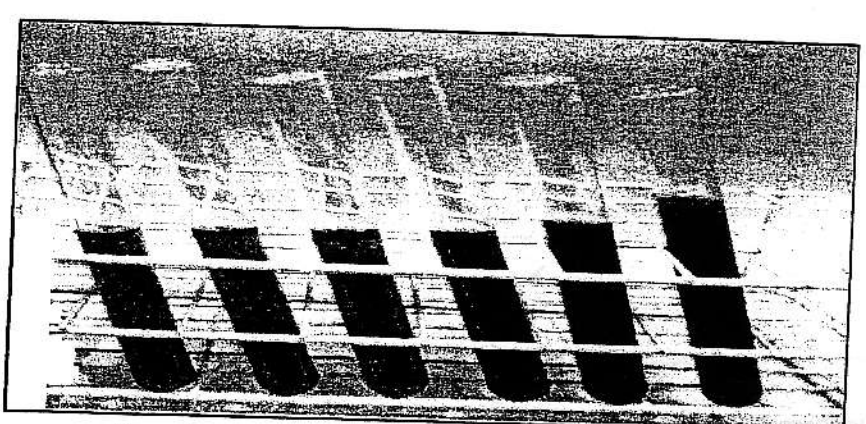
In the case of the POME separation, filtration is used as pretreatment for the samples before undergoing ultrafiltration process. Pretreatment steps indicate that it would eliminate a large portion of solid fraction in the samples. As shown in Table 2 and Figure 3(E) and (F), it is observed that the raw POME sample has high concentration of waste. This study abides by the same trend of pretreatment via centrifugation, a process which is used to remove organic pollutant loads before ultrafiltration experiments. The results indicates that there is a reduction of 186 mg/L or 41.24 % in BOD, 1294 mg/L or 41.0 % in COD, 11400 mg/L or 95.12 % of suspended solids and 6826 NTU or 95.12 % turbidity. This implies that some of the organic and suspended solids content has been removed by filtration before ultrafiltration process.

Table 2: The efficiency of pretreatment

	Raw POME	POME After Filtration	Reduction	Percentage of Removal, %
TSS (mg/L)	11985	585	11400	95.12 %
Turbidity (NTU)	7140	314	6826	95.602 %
COD (mg/L)	3156	1862	1294	41.0 %
BOD (mg/L)	451.00	265.00	186.00	41.24 %

Results obtained from 1% PES flat sheet membranes indicate significant changes in visual display on samples as shown in Figure 3. It appears that the presence of low amounts of PES has improved the membrane permeation flux and rejection rate of the membranes. Apparently the presence of PES acts as a pore former in the dope solution where permeation rates are observed to increase but the rejection decreases. In order to produce membranes which exhibited both high rejection and permeation rates the percentage of PES added should not exceed more that 1.5% as observed in Figure 4.

The presence of higher % of CA not only improved the membranes performance in terms of rejection rates but also reduce the production cost of the membranes because it is a cheaper polymer compared to PES. The results in Figure 4 revealed that membrane 6 which consists of 5% PES exhibits the highest permeate flux during the POME



Samples: 2 3 4 6 E F

Figure 3: The visual display of samples, E is sample after pretreatment and F is raw POME

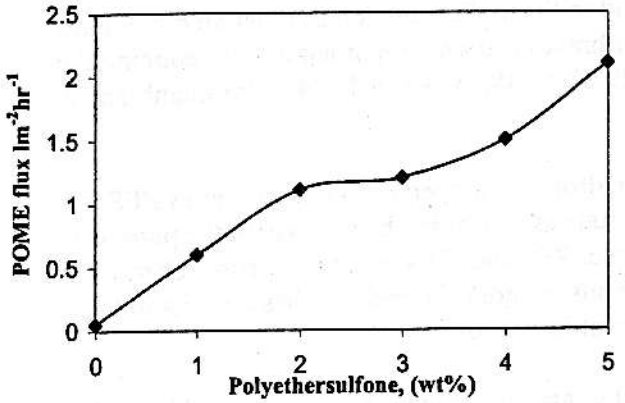


Figure 4: Flux during POME separation

ultrafiltration process, followed by membrane 5, 4, 3, and 2. However the permeate flux decreased with time regardless of % of PES in blend membranes due to concentration polarization.

Results in Figure 5 shows that the separation performance of POME in terms of total suspended solids (TSS), turbidity (NTU), COD and BOD for the membranes tested. The blended membranes fabricated are capable of reducing POME turbidity to 95.602 % and its total suspended solid by 95.12 %. This directly implies that some content of suspended solids has been removed prior to membrane treatment stage. The results also proved that blended CA-PES membranes exhibit excellent performance in POME waste water treatment. Membrane 2 shows the best result with 99.972 % of turbidity removal and 98.71 % in removal of TSS. This is followed by membrane3, membrane 4, membrane 5 and membrane 6.

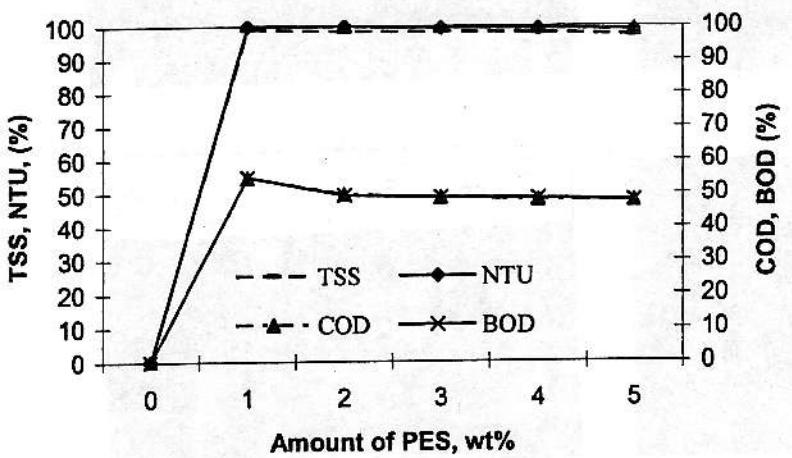


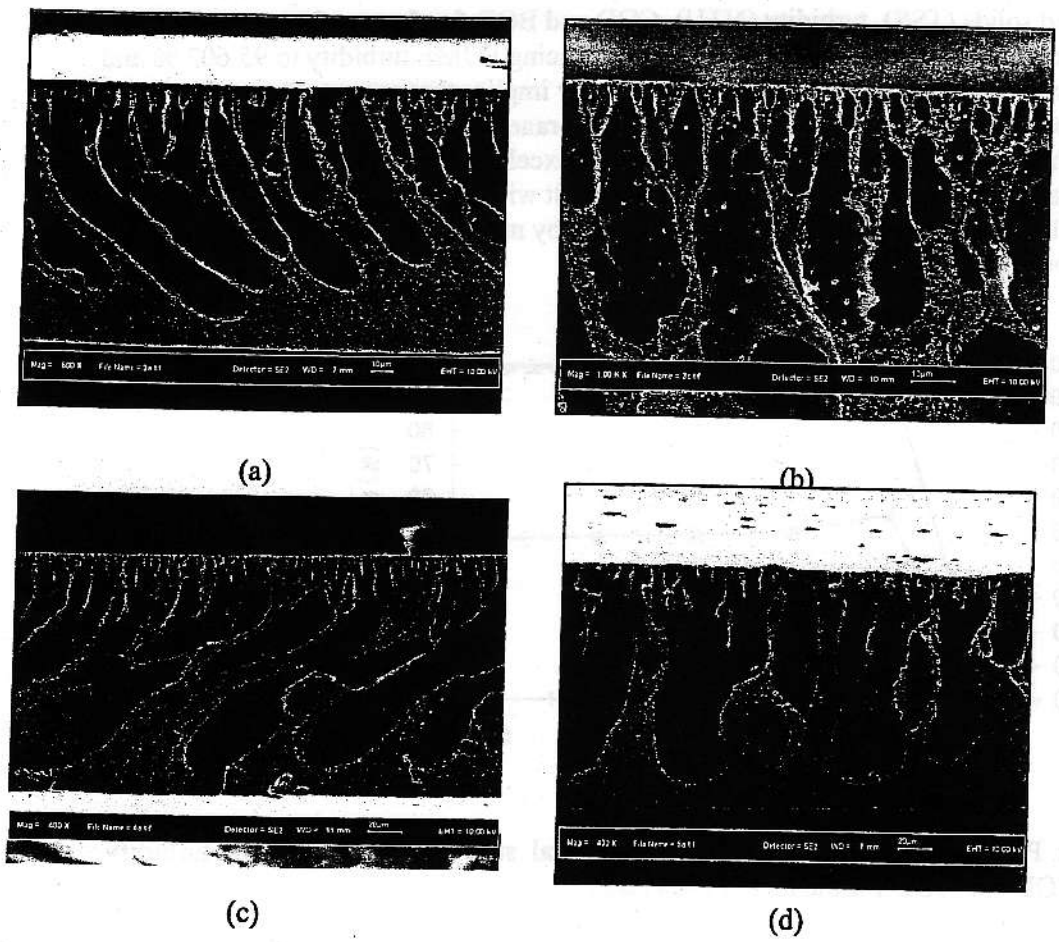
Figure 5: Percentage of removal in terms of total suspended solid (TSS), turbidity (NTU), COD and BOD for the membranes tested

COD is an indication of the overall oxygen load that a wastewater will impose on an effluent stream. COD is equal to the amount of dissolved oxygen that a sample will absorb from a hot acidic solution containing potassium dichromate and mercuric ions. The performance of COD shows the reduction by 54.75 % for the membrane 2, 49.37 % for membrane 3, 48.73 % for membrane 5 and 47.72 % for membrane 6. The BOD of wastewater expresses the amount of oxygen used by biodegradable organic substances.

The BOD reduction shows a similar trend to the COD reduction as illustrated in Figure 5. The amount and presence of PES membranes plays an important role in reducing the BOD percentage to 54.55 %, 54.77 %, 49.38 %, 48.75 % and 47.74 % for membrane 2, 3, 4, 5 and 6 respectively.

The evidence seems to suggest that the hydrophilic property of aromatic series PES is raised when it is mixed with cellulose acetate as shown by the increase in the pure water permeate flux and POME flux [6]. However PES and CA are not compatible chemically since the hydrophobic and hydrophilic bonds are not balanced and these results in the rejection rate to decrease as the PES content is increased.

The scanning electron microscope (SEM) images indicated that the CA-PES blended membranes have semi-permeable membrane structure. It can be observed from Figure 5 that PES/CA blended membranes have big macrovoids and nodules. As shown in Figure 5 macrovoids increased in size as higher percentage of PES was added. The higher amounts of PES in PES/CA blended membranes have higher fluxes but lower rejection rates. SEM images of PES/CA blended membranes exhibit finger-like macrovoids in the support layer with the presence of nodules.



(a) (b)

(c) (d)

Figure 6: SEM images of CA-PES blends (a) 1% (b) 2% (c) 3% (b) 5% PES

CONCLUSION

The performance of blended CA-PES ultrafiltration membranes fabricated has been tested using BSA solution and POME and found to be capable of giving good separation

in terms of percentages of removal for turbidity, TSS, COD and BOD and exhibit good permeate flux,. The performances of the PES ultrafiltration membranes revealed that membranes with the formulation, 1 % PES, 19 % CA and 80 % DMF exhibited the best rejection rates and reasonably high fluxes. The pure water permeate flux of the best formulation membranes was 15 l/m^2.hr, the percentages of removal for turbidity, TSS, COD and BOD were 99.975 %, 99.12 %, 54.75 % and 54.77 % respectively.

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