

Development of Hybrid Polymeric Polyethersulfone (PES) Membrane Incorporated with Powdered Activated Carbon (PAC) for Palm Oil Mill Effluent (POME) Treatment

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Abstract: The development of water treatment system to produce low cost & high quality effluent has become extremely important nowadays. Since year 1960, membrane technology has transformed from laboratory stage to industrial applications stage. The development of newer membrane modules in recent years helps the membrane industry growth rapidly, but the technology is still not so universal due to membrane fouling issue. Additional of PAC directly into the treatment system has proven to be a promising strategy to reduce membrane fouling and improve efficiency of the system. However, there are also drawbacks caused by excessive PAC within a treatment system. In this study, the potential of integrating the PAC into PES membrane was evaluated and its performance was assessed. The result shows that the PAC integrated membrane has higher permeation rate, which is 231 L/m².hr compare to the one without PAC integrated membrane, which only has 89 L/m².hr. In addition, PAC integrated membrane was able to achieve up to 81% and 67% removal rate, compared to the one without PAC integrated which only can remove 10% and 35% of COD and color respectively. Besides, the structural property of the membranes was observed using scanning electron microscopy (SEM). The results showed a trend where the membrane with higher concentration of PAC integrated will have better performance in both pollutant removal ability as well as the membrane fouling control.

Keywords: Membrane technology, fouling, PAC, PAC integrated membrane, structural property

1. Introduction

In Malaysia, one of the major problems to deal with is the treatment for palm oil mill effluent (POME). High demand on palm oil world widely has triggered the country to have mass plantation and production which generated a relatively large amount of POME. POME consists of high concentrations of pollutants (e.g. chemical oxygen demand (COD), biological oxygen demand, and suspended solids) and would pollute the natural water resources if discharge without proper treatment [2].

Membrane filtration process is one of the common method which being used to treat wastewater. Membranes are the new type of filter which are slowly replacing conventional filter due to their excellent performance and ease of operation [3]. According to survey, the market for membrane technologies grew from \$4.4 billion in 2000 to \$10 billion in 2010, and the market for water treatment equipment could exceed \$10.4 billion in 2014, with one-third for desalination [4].

Membrane filtration process is driven by pressure (or vacuum) to force water to the other side of membrane while retaining impurities and some of the feed water. Membranes can be divided into four categories based on their effective pore size, which are microfiltration (MF),

ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [5]. There are many types of membranes of different materials and operational configurations available in the market. Most of the membranes used in water treatment are made of synthetic polymers such as polyvinylidene fluoride (PVDF), polypropylene (PP), polysulfone (PS) and polyethersulfone (PES) [3].

Membrane fouling and removal efficiency are both the major concern in a treatment system. In recent years, PAC additional into the system has been proven as a promising strategy to tackle those problems [6]. However, there are some drawbacks were detected. AWWA in [7] had stated that PAC in the system will cause additional sludge/solid handling problems. Besides, PAC is for one-time usage only, where replenish process must be followed up to maintain the PAC concentration as well as the performance of the system. Furthermore, the reaction between PAC and other chemicals in the system also an issue that needs to be aware of. According to [8], the removal efficiencies drop by 75% for 2-Methylisoborneol (MIB), and 40% for geosmin when oxidants and PAC were added simultaneously into the system.

This study was carried out to investigate the potential of integrating the PAC into the PES polymeric membrane

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for POME treatment. With PAC integrated, the membrane was expected to have better performance, better fouling control, and able to lower down the operating cost as amount of PAC needed to be refurbished will be lesser.

2. Materials and Methods

2.1 Palm Oil Mill Effluent (POME)

The sample for POME in this study was obtained from Tian Siang Oil Mill (Air Kuning) Sdn. Bhd. which is a palm oil mill industry located at Perak.

2.2 Dope preparation and membrane fabrication

Polyethersulfone (PES) as polymer and N-Methyl-2-pyrrolidone (NMP) as solvent were used to produce polymeric membrane in this study. PAC was integrated into the membrane by 1wt.%, 3wt.%, 5wt.%, 7wt.%, 9wt.% and 11wt.% based on the polymer weight percentage to produce hybrid membranes. Membranes were produced by dry-wet phase casting technique using semi-automated membrane casting machine. The whole processes were done in ambient temperature (27oC to 30oC). Thickness of the membrane was set to 5 micrometer. After the dope being casted on the glass plate, it was submerged into a water bath immediately. A thin layer of polymeric film will be formed and separated itself from the glass plate. The formed membrane was then transferred to coagulation bath and remained for 24 hours, followed by post treatment in methanol for 8 hours. Finally, the membrane was dried and ready for filtration process.

2.3 Analytical parameters methods

2.3.1. Water permeability test.

Under room temperature, the permeate flux was calculated as follows:

$$\text{Flux, } J = \frac{V}{(A \times t)}$$

Where,

V = Volume of permeate solution collected (m³)

A = Effective area of membrane (m²)

t = Time (s)

J = Water flux (m³/m².s)

Dead-end filtration was used to test the water permeability of the membranes. Distilled water was used as feed in the filtration. To calculate the flux, the collected volume fixed at 10ml & pressure fixed at 0.3 bars, the time taken is recorded. After calculated the data obtained, graph of pure water flux against pressure is plotted.

2.3.2. COD removal efficiency

0.2 mL of diluted supernatant is pipetted into the HR+ vial and placed into the COD digester at 150°C for 2

hours. After that, the vial is cooled down to room temperature and measured by using DR-6000 UV-vis spectrophotometer.

2.3.3. Colour removal

5mL of feed and respective effluent samples were collected from the POME treatment process. The absorbance of the samples was measured by using DR-6000 UV-vis spectrophotometer at 455 nm using 1 cm quartz cells.

2.3.4. Cross section structural properties.

Scanning Electron Microscopy (FESEM- JEOL 6701-F) is used as the equipment to identify the morphology of the membranes. The images were captured at magnification of 2000x.

3. Results and Discussion

In this study, two different types of methods were approached in dope preparation. In first method, PAC was mixed with solvent (NMP) and the mixture was gone through the sonication process before added with the polymer. In second approach, dope was prepared first by dissolving the polymer in the solvent, followed by PAC addition into the dope before gone through the sonication process. When carry out the first method, it was observed that PAC was unable to mix homogenously into the solvent after gone through several hours of sonication. Since it was unable to obtain a homogenous mixture for dope preparation, first method was considered not suitable to apply in this study. While proceed with the second method for dope preparation, the problem faced in first method was able to minimize. It was hardly observed any PAC residue in the dope prepared after 8 hours sonication process. However, some residue still can be spotted in dope contain high PAC concentration. It is believed that the PAC addition in the mixture has reached it maximum capacity.

3.1 Flux production of different PAC membranes in pure water permeation test

The test was determined using dead-end filtration with different wt.% PES/PAC membranes and the pressure was fixed at 0.3 bar. The time taken to collect 10 mL of permeate was recorded, and the data was used to calculate the pure water flux. The diameter of membrane was 0.047 m, which has an effective surface area at 1.734 × 10⁻³ m². Table 4.2 shows the result obtained from the test.

Table 1 Pure water permeation of produced membranes at 0.3bar

Samples	Pressure (Bar)	Time (Sec)	Flux (L/m ² ,hr)
PES(Without PAC)	0.3	232.50	89.30
1wt. % PES/PAC	0.3	164.58	126.15
3wt. % PES/PAC	0.3	175.57	118.25
5wt. % PES/PAC	0.3	155.62	133.94
7wt. % PES/PAC	0.3	132.34	156.88
9wt. % PES/PAC	0.3	122.48	169.51
11wt. % PES/PAC	0.3	89.72	231.39

The result clearly shows that the higher the PAC concentration in the membrane, the lesser the time for 10 mL permeate collection, which means that more flux production by the membrane with higher PAC integrated. The data can be visualized in the Figure 1.

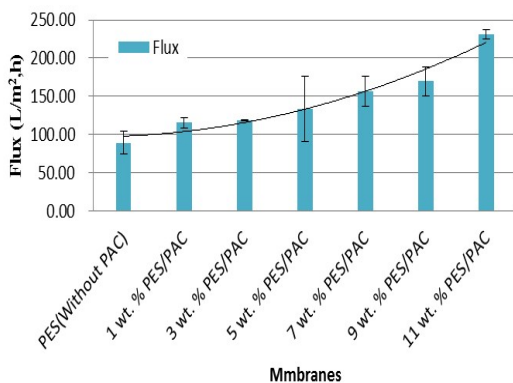


Figure 1 Flux production by the produced membranes at 0.3 bar

Based on the Figure 1, the membrane with higher concentration of PAC integrated able to produce more flux at the same pressure applied. This shows that PAC as additives is able to enhance the porosity of the membranes, which directly increased the flux production when more PAC was integrated into the membrane [2].

3.2. Performance of produced membranes in treating POME wastewater (COD and color removal)

Based on the flux production ability, four membranes with low, median, and high concentration of PAC integrated (0wt.%, 3wt.%, 9wt.% and 11wt.%) were choose for COD and color removal evaluation. Sample for POME was flow through the cross-flow filtration system with 1 bar of pressure applied. Time needed for a fixed amount permeate collection was recorded during the filtration process for flux determination. Table 2 shows the details and result for the COD removal test for each membrane respectively.

Table 2 COD removal ability by different membranes.

Sample	Pressure (Bar)	Time (sec)	Flux L/m ² , hr	Initial COD mg/L	Final COD mg/L	Removal rate %
0wt.% PAC	1.0	583	17.81	18800	16900	10.11
3wt.% PAC	1.0	404	25.69	18800	10550	43.88
9wt.% PAC	1.0	386	26.89	18800	4760	74.68
11wt.% PAC	1.0	348	29.83	18800	3450	81.65

According to the Table 2, total time needed to collect the fixed amount of permeate was decreased with the increasing of the concentration of integrated PAC within the membrane. The finding shows that the higher concentration of PAC integrated will contribute to the higher flux production. Same trend was observed for the COD removal ability as well, where the removal rate was improved tremendously from 10.11% to 81.65% when 11 wt.% of PAC was integrated into the polymeric membrane during filtration.

Figure 2 clearly illustrated that all membrane with PAC integrated are performed better in both COD removal and flux production compared with the membrane without PAC integrated. Low COD removal rate which is 10.11% was obtained by the membrane without PAC integrated, and the removal ability was increased dramatically to 43.88%, 74.68% and 81.65% after 3wt.%, 9wt.% and 11wt.% of PAC was integrated into the membrane accordingly. In addition, it was also found that the membrane with higher PAC integrated become more permeable with higher flux production compared with the membranes without and with lower PAC concentration.

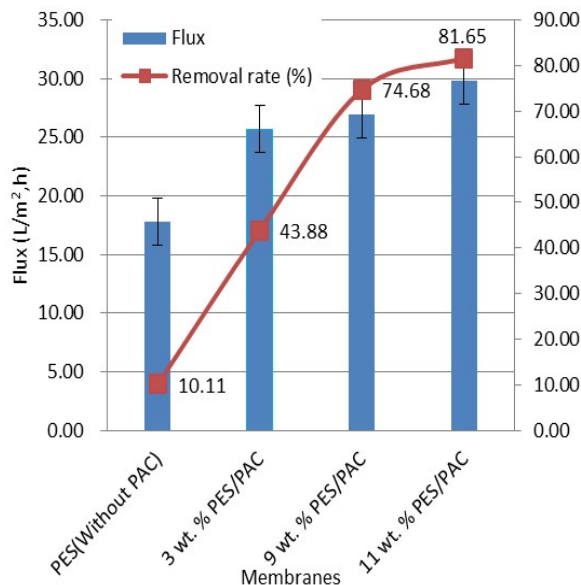


Figure 2 Flux production and COD removal efficiency between the produced membranes

Selected membranes were then tested for their ability in colour removal on POME wastewater. The sample before and after filtration was collected and the absorbance reading was compared. Table 3 shows the absorbance reading obtains from the spectrophotometer. The reading shows that the removal rate of membrane without PAC is 35.43%, which is the lowest among the produced membranes. This followed by the membranes with 3wt.%, 9wt.%, and 11wt.% of PAC integrated which achieved a removal of 50.71%, 61.03%, and 67.21% respectively. The finding indicated that with the increasing of PAC concentration integrated, the membrane can performed better in color removal.

Table 3. Color removal rate of different wt. % PES/PAC membranes

Samples	Initial reading (PtCo)	Final reading (PtCo)	Removal rate (%)
PES (Without PAC)	988	638	35.43
3wt. % PES/PAC	988	487	50.71
9wt. % PES/PAC	988	385	61.03
11wt. % PES/PAC	988	324	67.21

PAC integrated membrane was able to performed well for both COD and color removal in POME treatment. The removal ability was observed to increase with the amount of PAC concentration which integrated within the membrane. The good performance of the PAC integrated membrane could cause by the absorbance properties of PAC which absorbed the pollutants during the filtration process [2].

3.3 SEM images of the produced membranes

The SEM images of seven membranes were shown in Figure 3(a) to (g). According to [9], membrane consists of an asymmetric structure with finger-like structures at the top surface, whereas a sponge-like structure can be found at the bottom of cross section. In this study, produced asymmetric membranes shows the structural properties with increment of porosity from membrane without PAC integrated to the membrane with the highest concentration of PAC integrated.

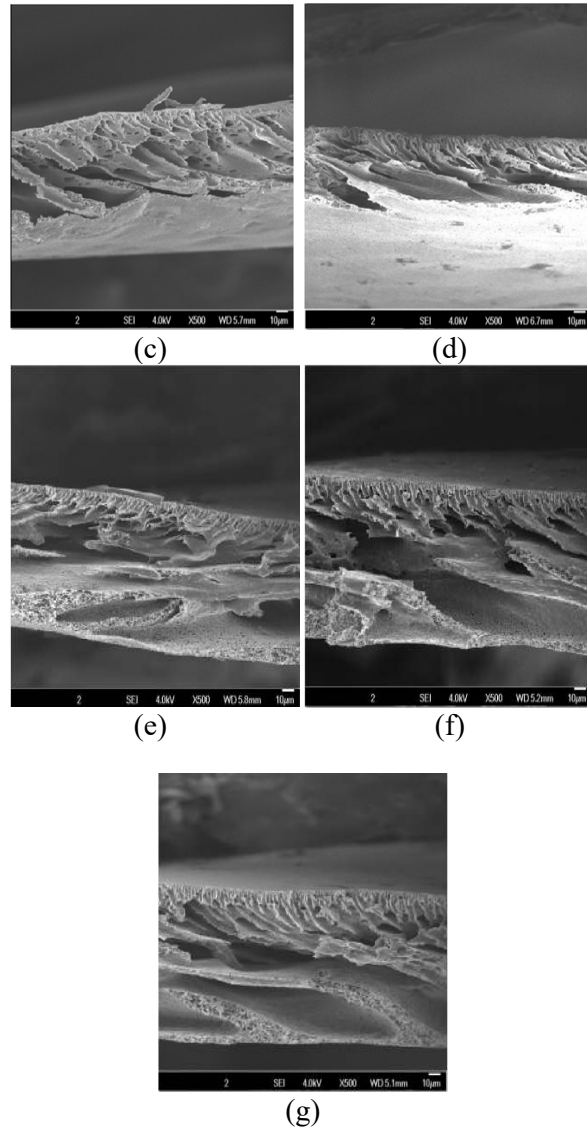
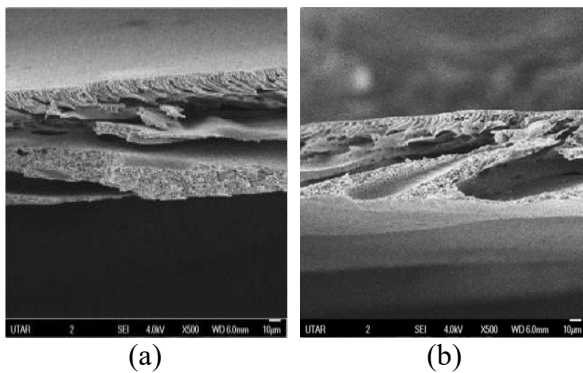


Figure 3. Cross sectional morphological structures of PES membranes (a) to (g) with different concentration of PAC, ranges from 0wt.%, 1 wt.%, 3 wt.%, 5 wt.%, 7 wt.%, 9 wt.% and 11wt.% respectively.

4. Summary

Membrane with PAC integrated was proven to have good quality in terms of COD and color removal, as well as higher flux production in POME treatment. It was observed that the performance of the membrane were increased with the higher concentration of PAC integrated into the membrane. In this study, membrane with 11 wt.% of PAC integrated was showing the better performance compare to other membranes, which achieve a 231.39 L/m².hr of flux rate, 81.65% of COD removal, and 67.21% of color removal. SEM image revealed that the PAC additional would trigger the forming of large microvoids which increased the porosity of the produced membranes.

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