Synthesis and Evaluation of Polysulfone/Chitosan/Polyvinyl Alcohol Integral Composite Membranes for the Removal of Mercury Ion

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Synthesis and Evaluation of Polysulfone/Chitosan/Polyvinyl Alcohol Integral Composite Membranes for the Removal of Mercury Ion

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Abstract: An integral composite membrane was fabricated from a blend of polysulfone/chitosan/polyvinyl alcohol (PVA) at various PVA polymer solution; 1, 3, 4 wt.%. The membranes were characterized in terms of thermal stability, water uptake, and were further evaluated through pure water flux, antifouling properties, and mercury removal. It was found that the composite membranes portrayed good thermal stability with enhanced hydrophilicity. The best performance portrayed by membrane with 4 wt.% PVA with good antifouling behavior, 46% IFR and 56% RFR, and able to remove more than 90% of mercury ions at much low pressure of 4 bars without jeopardizing the flux.

Keywords: composite membrane, characteristics, antifouling, mercury ion removal

1. Introduction

Rapid industrialization and urbanization have resulted in a large emission of heavy metals into the environment, particularly into water sources. One of the most toxic elements is mercury, Hg, which is carcinogenic, toxic, non-biodegradable, and highly soluble in water [1-3]. In industrial wastewaters, Hg is present at levels of parts per billion (ppb) and industries are required to adhere to strict discharge regulations [4]. Many of these industries are facing challenges in meeting the limits set by respective governing bodies.

Mercury is a heavy metal that is known as a toxic pollutant that contain in wastewater. The water that contains the pollutants usually came from the effluent of industrial process which needs to be treated before being released to the surrounding. The release of great amounts of heavy metals into water can give a huge impact to the human health and environment. Mercury that is released into river and lake water is fatal to human beings and aquatic life and upon consumed, these discharges may not be digestible in stomach and can lead to cancerous diseases.

Thus, to ensure the continuous supply of clean and fresh water which is becoming critical nowadays in the world due to an increase in the population growth, several methods have been implemented to minimize the amount of mercury in wastewater [5]. These include adsorption, absorption, filtration, coagulation, reverse osmosis, and chemical precipitation [6-8]. One of the methods that are being explored widely is membrane separation. Membrane separation technologies play significant part in today's growth of sustainable industrial processes for global chemical production. This growth mostly caused by the less energy used by membrane separation[9] compared to common separation process that being used by industry nowadays such as drying and distillation since membrane separation does not involve phase changes. According to Su et al. [10], the membrane separation is a practical with a mild operating parameters and does not require solvent, which is a preferred method to remove the heavy contaminant such as mercury ion in wastewater. Other than present in the form of soluble and ionic, mercury could be in the form of particulate/colloidal due to the formation of a complex of mercury with the dissolved matter found in the water. Meltem et al.[11] has conducted a research to investigate the abilities of four filtration processes that are microfiltration, ultrafiltration, nanofiltration and reverse osmosis to remove a significant amount of mercury ion from oil refinery's wastewater. The results show that all four types of filtration have met the target of discharged concentration level of mercury, where nanofiltration and reverse osmosis is performed at 20.7 bar of operating pressure. Due to the damage of water pollution is so chronic in the presence of mercury ion, it cannot be recovered through regular membrane that exist nowadays and special type of membrane need to be fabricated[12]. Apart from the advantages of membrane such as low energy requirement, high selectivity, greener process, and low maintenance cost, it suffers with fouling phenomenon that resulted in declining in water flux, which subsequently reducing the performance of the membrane [13]. Fouling occurs due to several factors such as adsorption of contaminant inside the membrane, formation of a cake layer from the deposition of the contaminant on the membrane surface and pore blockage. The surface characteristic of the membrane such as surface hydrophobicity, type of feed materials and parameter of process can also contribute towards the fouling [14].

Polymer blending especially involves a blend of hydrophilic and hydrophobic polymers is a proven tool to obtain new types of material with a diverse intermediate property between those of pure components, that come together with an economical advantage [15]. Furthermore, blending of two different compounds are carried out to further enhance the membrane's properties such as enhancing the hydrophilicity of the resultant membrane to mitigate the fouling issue [16-17]. In the area of ultrafiltration, polysulfone membrane is widely used due to its good mechanical and thermal stability, and chemical resistant at a wide range of pH, good flexibility, oxidative and have reasonable price [18]. However, it suffers with high fouling and low permeability towards water due to its hydrophobic nature, which has given an impact on its service life. Therefore, blending of polysulfone with other hydrophilic polymeric materials such as polyethylene glycol, poly (vinyl alcohol), polyvinylpyrrolidone, glycerol and ethanol has widely been carried out to overcome that limitation [19]. Besides preventing fouling, addition of plasticizer or blending with other polymer could increase polymer chain mobility to increase the free volume, which could subsequently improve permeation flux [20]. The works of various researchers have found that integral composite membranes have better adsorption/absorption capabilities, chemical stability, tensile strength, thermal properties, and anti-fouling properties compared to pure membranes [21-23]. Furthermore, isotropic (integral) membrane is simpler to fabricate as only one layer to be controlled. In the search of suitable polymer for mercury removal, the presence of functional groups that could attract and adsorb heavy metals ions such as mercury ion is very important. These include acetamido group, amino, phosphate, carboxyl, hydroxyl and sulfates. Chitosan, biopolymer of natural polysaccharide is widely used in removing heavy metals including mercury ions at low concentration [24-25]. Chitosan is derived from chitin that comes from shell of seafood [26] and it contains amino and hydroxyl group. In addition, because of its characteristics which are non-toxic, biodegradable and biocompatibility, high selectivity and antimicrobial activity, chitosan is considered as environmentally friendly polymer [27].

Due to its hydrophilic properties, compatible structure, and high availability in global industry, PVA is being extensively used in a combination with other hydrophilic polymers particularly in polymer film manufacturing industries to improve the properties of films [28-29]. These advantages are the main reason why PVA is one of the best candidates to be used in the preparation of numerous commercial membranes. Therefore, in this research, polyvinyl alcohol (PVA) that has high water selectivity and dehydration properties was blended with polysulfone and chitosan. The effect of adding various concentration of polyvinyl alcohol polymer solution on the characteristic and performance of the integral membrane to reject mercury ions was evaluated. The performance testing on the membranes was conducted at a lower operating pressure of 4 bar compared to 20.7 bars as described from the previous study.

2. Materials and Method

2.1. Materials

The material used was chitosan powder with deacetylation degree 84.8 ± 1.2 mn% that was obtained from Central Drug House (P) Ltd, New Delhi. Polysulfone (PSf) pellet resins with molecular weight 44,000 – 53,000 Da and PVA pellets with a hydrolysis degree of 87-89% and molecular weight 85,000 – 124,000 Da respectively were obtained from Merck, Malaysia. Solvents such as acetic acid, Dimethyl sulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP) with purity of 99% respectively were also obtained from Merck, Malaysia. All materials were employed without further purification.

2.2. Methods

2.2.1 Preparation of composite membrane

0.02 g of chitosan powders was dissolved into 99.98 g of 2 wt% aqueous acetic acid solution. The solution was heated at 80˚C and stirred at 450 rpm for 2 hours. 13 wt.% PSf solution was prepared by adding slowly 13 g of PSf pellets into 87 g NMP at 80˚C for 9 hours while stirring at 500 rpm. 1 wt.%, 3 wt.% and 4 wt.% PVA polymer solution were prepared by dissolving 1 g, 3 g and 4 g of PVA powder into 99 g, 98 g, 97 g and 96 g of DMSO respectively. Each mixture was mixed with continuous stirring at 300 rpm and heating at 80˚C for 2 hours. The solution of blended polymers was prepared by taking PSf solution as a basis of 20 mL. With continuous stirring at 400 rpm and heating at 80ºC respectively, 0.1 mL of the prepared 1 wt.% PVA polymer solution was added to PSf solution. The solution was continuously heated and stirred at 450 rpm for 30 minutes. Then, 0.1 mL chitosan solution was added to the solution and the mixture was stirred at 600 to 1000 rpm for one hour. The above procedures were repeated by using 0.1 mL of other concentration of PVA polymer solution. The formulations prepared in this study are as shown in Table 1.

Table 1. Formulations of integral membrane

	Composition (mL)		
Membrane	PSf	PVA	CS
M0	20	-	-
M1	20	0.1 mL PVA 1 wt%	0.1
M2	20	0.1 mL PVA 3 wt%	0.1
M3	20	0.1 mL PVA 4 wt%	0.1

2.2.2 Membrane Casting

The blend membrane solution was being allowed to cool down before it was cast on a glass plate using a Baker Film Applicator. The film thickness was set at 90 µm. The membrane film was immersed in deionized water for 24 hours. Then, the membrane was dried at room temperature for 24 hours. The dried membrane was then heat-cured for 1 hour at 45˚C in the oven.

2.3 Membrane Characterization

Thermogravimetric analysis was carried out to measure the weight loss of the integral membrane subjected to continuous heating from 30ºC to 900°C at a heating rate of 10˚C min^{-1} under a nitrogen atmosphere. It was conducted by using Thermogravimetry Analyzer, Mettler Toledo model Star^{e} SW. The sample weight was ranged from 5 to 10 mg. The weight losses at different stages were analyzed and the data collected were plotted.

In the analysis of water uptake, the membranes were cut into 1 cm^2 and immersed in deionized water. After 24 hours, the wet samples were removed and weighed immediately (m_{wet}). Next, the samples were oven dried at 50˚C for 24 hours. The dry weight of the membrane (m_{dry}) was then recorded. Based on the average obtained from 3 samples, the water uptake was calculated [30]. The % water uptake was calculated using Equation (1).

$$Water\ uptake\ = \frac{m_{wet}-m_{dry}}{m_{wet}} x\ 100 \qquad (1)$$

2.4 Performance testing

2.4.1 Pure water flux

The dead-end mode of membrane filtration rig was used for the experiment. The set-up is as shown in Fig. 1. Firstly, the membrane sample was cut into a circular shape with surface area of 19.63 cm^2 and then placed in the sample section as shown in Fig. 2. Then, 300 mL of deionised water was filled inside the stainless-steel filtration cell as the feed solution. A 4 bar of pressure for the filtration process was applied using nitrogen gas. The amount of permeate was recorded at an interval of 15 minutes during a 1 hour period [31]. Water flux was determined using Equation (2).

$$J_w = \frac{Q}{A\Delta t} \qquad (2)$$

Where
J_w is the pure water flux in (L/m^2.h)
Q is the volume of permeate (L)
A is membrane area, m^2
Δt is the sampling time (h)

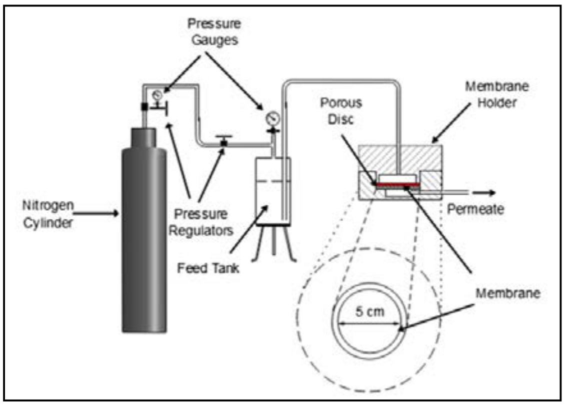

Fig. 1: Schematic view of the membrane filtration rig[32]

Fig. 2: Membrane setup for pure water flux experiment

2.4.2 Anti fouling analysis

The antifouling experiment was carried out in 3 stages at a pressure of 6 bars [33]. In the first stage, the membrane was filtered with deionized water for 30 minutes and the stabilized flux was recorded as J_{w1}. Then, permeation using humic acid solution (10 g humic acid in 1 L of 1000 ppm sodium hydroxide) as the feed solution was carried out for 2 hours. The volume of the permeate stream was recorded every 20 minutes, where the final flux was recorded as J_{HA}. Prior to the final stage, the membrane was backwashed for 30 minutes to remove the foulant material on its surface. It was conducted by immersing it in a beaker, which contains deionized water, and the solution was then stirred at 150 rpm. Then the procedures in the first stage were repeated, and the pure water flux was recorded as J_{w2}. Finally, the FRR (flux recovery ratio), RFR (reversible fouling ratio) and IFR (irreversible fouling ratio) were calculated using Equations (3), (4) and (5)[33] respectively.

$$FRR = \frac{J_{W2}}{J_{W1}} x\, 100 \qquad (3)$$

$$RFR = \frac{J_{W2} - J_{HA}}{J_{W1}} x\,100 \qquad (4)$$

$$IFR = \frac{J_{W1} - J_{W2}}{J_{W1}} x\,100 \qquad (5)$$

2.4.3 Mercury Removal

The performance of the composite membrane on the removal of mercury ion was tested using the same rig as described in Section 2.4.1 but using 3 ppm mercury pure solution as the feed solution. The pressure for nitrogen gas system was set at 6 bars. The concentration of mercury in the permeate (C_p) and feed (C_f) streams were determined by using ICP-OES. The percentage of mercury ion removal was calculated using Equation (6).

$$R(\%) = \frac{C_f - C_p}{C_f} x\,100 \qquad (6)$$

3. Results and Discussion

3.1 Thermal analysis

As shown in Fig. 3, for M0, the initial weight loss in the temperature range of 109.18 to 514.61°C corresponded to the removal of moisture and solvent from the sample [34]. The degradation of the membrane started at 523.46°C and continued to 869.78°C. The weight loss of the composite membranes, M1, M2 and M3 at temperature range 117.63 to 514.73°C, and 444.65 and 515.28°C respectively are associated with the loss of adsorbed and bound water [30]. When the temperature reached the range of 523.61 to 585.64°C, the weight loss of M1 happened rapidly almost the same rate with M0, which indicated that PSf and PVA have decomposed into CO_2 and H_2O [35]. M2 and M3 also decomposed at the same temperature range but at slower rate. Hence, it was obvious that the blend membranes show better thermal stability compared to pure PSf membrane due to improved packing and H-bonding between the components of the membranes [36]. However further increase in PVA concentration leads to declining in residual weight percentage of the membrane, where M2 exhibits the highest thermal stability compared to M3. This claim is portrayed through Fig. 3 where M2 maintaining the slightly higher residual weight as compared to M3 until 900°C. This result portrays that M2 and M3 possess good thermal stability where the polymer chain network might not plasticize that lead to losing strength of the membranes particularly at high temperature. Although membrane normally operates at normal room temperature but inadvertently the feed wastewater can flow into the filtration system at higher temperature due to hot weather or as a result from prior process [37].

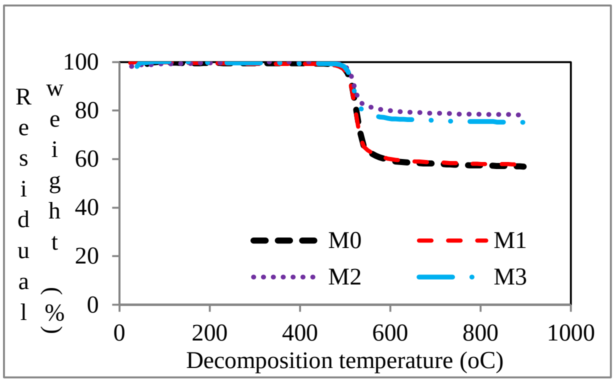

Fig. 3: Thermal stabilities of diferent formulation of membranes

3.2 Water uptake analysis

Water uptake or swelling behaviour of polymers depend on the type of polymer, its cross-linking degree, and its compatibility with solvent [38]. Table 2 show the water uptake of the membranes. The percentage of water uptake is lowest in PSf membrane and shown an increment with the presence of PVA in the formulation. The increase in water uptake in the blend membranes is due to the increase in –OH groups from PVA in the membranes, which reflect the higher hydrophilicity of the blended membranes, where comparable result was also obtained in another study by Casey & Wilson [36]. This hydration layer creates the water-binding capability to enhance the permeation of water through the membrane and lessen the fouling effect, where the adsorption of foulant on the membrane's surface is prevented [39-40].

Table 2**.** Percentage of water uptake for different membranes

Membrane	Water uptake (%)
M0	34
M1	72
M2	198.48
M3	204.12

3.3 Pure water flux

The result of pure water flux has a relation with hydrophilicity of the membrane. Based on Fig. 4, M0 and M1 show the lowest flux even after an hour filtration time. On the other hand, M2 and M3 exhibited higher flux at the beginning and show a slow declining rate of the flux until one hour of filtration time. The significant increase in permeation of water through M2 and M3 membranes is resulted from the presence of PVA that increases the hydrophilicity of the membranes [41]. PVA's hydrophilic nature also give rise to higher porosity of both blend membranes, which enhancing the permeation of water through the membrane [42-43]. This result agrees with Table 2 on the water uptake.

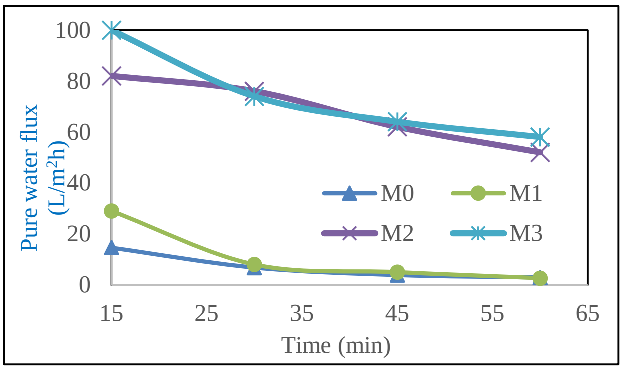

Fig. 4: Pure water flux at various concentration of PVA

3.4 Antifouling behaviour

The results from antifouling experiment are shown in Table 3. Membranes M1 has very low flux recovery ratio (FRR) and high values of the irreversible fouling ratio (IFR) that are due to their fouled surface, which exhibit irreversible fouling mechanism. This condition is attributed to concentration polarization which occurs when there is high concentration of solute at the membrane interface [44]. In this case, high deposition of humic acid on the membrane's surface had blocked the pores and constricted the flow of the solute. On the other hand, membrane M2 and M3 have better FRR and RFR (reversible fouling ratio) respectively. It was attributed to the negative charges of the hydroxylated groups in the membranes because they have more OH groups, which are abled to prevent fouling and flux decline [45]. This steric stabilization effect forms a strong hydrogen bond between the water molecule and the PVA particularly at the oxygen atom [46-47].

Generally for flux and antifouling analysis, porosity and hydrophilicity are key factors that determine the membranes' performance [45]. Although not much increment on the flux recovery ratio and reversible flux ratio portrayed by membranes M2 and M3 as compared to M1, there is still opportunity to improve the antifouling behaviour of the membranes, where it was proven that blending with PVA do indeed increase the antifouling properties of polysulfone membranes. Furthermore, this study uses quite high concentration of humic acid (10 g/L) that induced very severe fouling on the membrane's surface as compared to some similar studies, which uses a much lower concentration of humic acid, 1 g/L [46] and 0.2 g/L [48].

3.5 Performance of membrane on the mercury removal

Fig. 5 shows the permeate flux and percentage of mercury removed by the membranes. Based on the figure, M1 was able to consistently remove 100% of the mercury throughout 60 minutes of filtration but it suffered with high concentration polarization, which was observed through Fig. 6 as it has a consistently low permeate flux of 0.0001 L/m^{2}h. As mention earlier that PVA also acts as pore former agent, therefore in the absence of PVA, M0 has a dense structure that led to low permeation of water [42-43]. The adsorption of mercury ions creates a cake layer formation that further blocking the pores of membrane, which explain high rejection of mercury ions but lowering the flux for M0 [13]. As for M3, it was able to allow higher permeation of water, while providing a good absorption of mercury ions on its surface. It can be observed through Fig. 5 and 6 respectively on its performance to consistently remove more than 90% of mercury ion from the solution from 15 minutes until 1 hour of the filtration period without jeopardizing too much the flux. A slow declining in flux was still occur because of concentration polarization but not too severe as compared to membrane M0. Generally good hydrophilicity of membrane not only reduce the concentration polarization but also enhances the binding between the metal ions and the membrane's surface since hydroxyl group is one of the chemical groups that serve as chelating sites for mercury ions [49]. So higher loading of PVA in membrane M3 contributes to enhancing the hydrophilicity of the membrane, which consequently adsorb more mercury ions and allow high permeation of water. Although the FRR and RFR for M2 are higher than that of M3 respectively, the differences are marginal and M3 displayed good performance in removing the mercury ions as portrayed through Fig. 5 and 6.

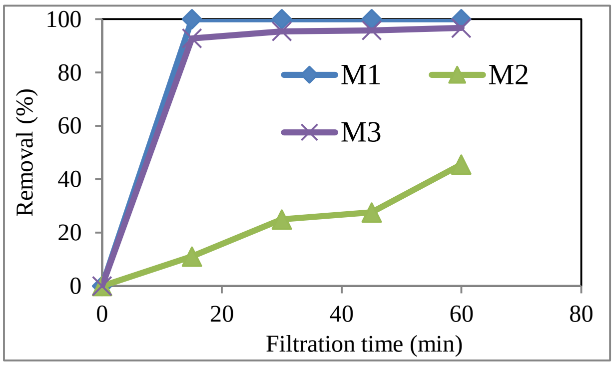

Fig. 5: Percentage removal of mercury ion against filtration time for various membranes

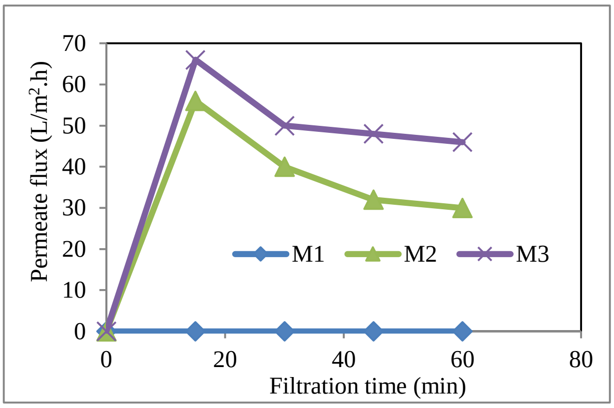

Fig. 6: Flux against filtration time during mercury removal analysis

Table 3. Performance of the Membranes in Term of Antifouling Behaviour

	L/m^{2}h			%		
Membrane	J_{w1}	J_{HA}	J_{w2}	FRR	RFR	IFR
M1	122.23	7.56	22.41	18.33	12.15	81.67
M2	223	3.9	130	58.30	56.55	41.70
M3	279	4.8	152	54.48	52.76	45.52

4. Conclusion

Integral membranes consisting of PSf, CS and PVA were successfully fabricated based on a v/v ratio. In addition, increment in wt% of PVA polymer solution greatly enhanced the hydrophilicity of the integral membranes. This was depicted through the water uptake and pure water fluxes of M2 and M3. M3, which contained more OH groups than M2, showed the highest water uptake and pure water flux respectively. Aside from that, the integral membranes have good thermal stabilities. In term of mercury removal, M3 showed superior ability than M2 due to the rejection of more than 90% of mercury as compared to 46% of the M2 without jeopardizing the flux. The increase loading of PVA also improves the antifouling behaviour of the membranes, where the FRR and RFR were more than 50% as compared to 18% and 12% respectively for membrane from PSf/CS. The average value of RFR could represent good antifouling behaviour since the concentration of humic acid used in this research was too high.

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