Removal of Mercury by Using Thin Film Composite Membrane

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Abstract— **In this study, a thin film composite membrane was synthesized by coating a layer of polyvinyl alcohol, polyethylene glycol and chitosan hybrid solution crosslinked with tetraethylorthosilicate on a polysulfone support membrane. The aim of this experiment is to study the effect of varying the PVA concentrations on the characterization and performance of the TFC membrane. Two different concentrations were selected and used which are 5 wt% and 6 wt%. FTIR and TGA were used in order to find the membrane structure meanwhile for the performance testing; pure water permeability was used for water flux, antifouling properties and mercury removal. Results show that 5 wt% PVA concentrations have superior membrane characterization and performance. Moreover, the blend membranes showed improvements in the removal of heavy metal ions.**

Keywords—**Thin film composite membrane, Polyvinyl alcohol, Antifouling, Blend membrane, Permeation**

I. INTRODUCTION

Nowadays, composite membrane has been widely applied in a various applications in the industries with the significant improvement of technology. The ability to sustain water quality level has become harder with the increasing of water pollution (Habiba et al., 2017). Furthermore, the release of wastewater into the water sources such as domestic effluent and factory discharge affect the ecosystem and human health (Medhat Bojnourd & Pakizeh, 2018b). With the development of cities and industries over the past few years, population growths have caused many environmental problems ultimately contamination (Medhat Bojnourd & Pakizeh, 2018a). Heavy metals pollutants such as mercury that are found in the industrial waste waters can be toxic to living species where toxic metal poisoning is becoming a significant environmental issue today (Abu-Saied et al., 2017). Therefore, an effective removal of heavy metals contaminants is essential to protect the environment and living creatures. Application of more efficient wastewater treatment system has been suggested by the World Health Organization in order to solve this matter which existing treatments include coagulation-flocculation, adsorption, oxidation and advanced oxidation, biological treatment and membrane separation (Medhat Bojnourd & Pakizeh, 2018b).

Membrane separation technology has much advantages over the conventional separation processes which include lower power consumption, smaller footprint, ability of being manufactured with different size and modules, favorable mass transport, lower pressure drop, usability for materials sensitive to temperature, regeneration capacity, high efficiency, easy scale-up and ability to be hybridized with other separation processes (Vatanpour, Salehi, Sahebjamee, & Ashrafi, 2018).

One of the most common polymers used in membrane is polysulfone due to its thermal stability, mechanical strength, chemical inertness and excellent tolerance for all sterilization techniques (Chen, Tang, Luo, & Wan, 2017). Apart from that, it is reasonably cheap price and good resistance to extreme pH. The chemical and physical properties of polysulfone make it to be preferred material for use in a membrane (H.-L. Huang & Yang, 2006). However, it is still restricted by several obstacles such as trade off relationship between permeability and selectivity and low resistance to fouling (Khalid, Abdel-Karim, Ali Atieh, Javed, & McKay, 2018). Additives are essential and have important effect on the preparation process of the polysulfone membrane. The effects are on the formation of membrane structure by enlarging or preventing macrovoid formation, enhancing pore formation, improving pore interconnectivity, and introduce hydrophilicity to the membrane structure (Chen et al., 2017). One of the best additives in polysulfone membrane preparation is polyethylene glycol.

Due to its excellent characteristics, the membrane separation using polysulfone is continued. They help in the formation of interpenetrating networks with blends while preserving the mechanical and thermal properties (Shah & Murthy, 2013). The conditions for facilitated and enhanced mass transport through the membranes are provided just by having these characteristics. Heavy metal ions can be separated even at trace concentrations of less than 10 ppm (Vatanpour et al., 2018).

Chitosan are natural polysaccharide copolymers which are found in a variety of natural resources including shrimp shells and crab. It is the second most abundant natural copolymer after cellulose and it is a renewable resources. It has wide range of availability and versatile applications. It is also commonly used in adsorption, chromatography and ion-exchange process, mainly for its hydrophilicity, non-toxic, biodegradability and biocompatibility (Salehi & Madaeni, 2014). Modifications on the membrane's surface and pores increase the membrane's fouling resistance by increasing the hydrophilicity of the membrane (Bin Darwish, Al Abdulgader, AlRomaih, & Alalawi, 2019). In many water treatment and separation processes applications, membrane modification by chitosan has shown a promising result (Bin Darwish et al., 2019). It contain amino and hydroxyl groups which serves as coordination sites and good complexation which are suitable for adsorbing wide range of contaminants including heavy metals. Making full use of this abundant and low-cost polymer is beneficial to turn them into treasure (Zheng et al., 2019).

Other polymers such as alginate, cellulose, polyacrylonitrile and polyvinyl alcohol have been used in removal of hazardous metal ions from wastewater. Among these polymer, polyvinyl alcohol is particularly fascinating from an economic and biodegradability perspective, widely used in drug delivery system and also metal removal (Yoon, Zhang, Kim, Harbottle, & Lee, 2019). Polyvinyl alcohol is biocompatible, non-toxic and chemical resistant polymer that is substantially used in blend membranes. However, limited mechanical properties and thermal stability of this polymer limits its applications especially in high temperature environment. Nevertheless, these properties are usually modified by many physical and chemical methods such as blending, crosslinking and grafting which is the blending turned out to be an effective approach by forming strong intermolecular interactions between polymers (Zhang et al., 2018).

In this study, chitosan/polyvinyl alcohol thin film composite supported with polysulfone membrane have been synthesized and examined for their performance in removal of mercury. Polyethylene glycol was applied to generate pore in the dense polymeric background of chitosan/polyvinyl alcohol membrane (Salehi & Madaeni, 2014). The membrane were test with FTIR and TGA to study on the structure and performance testing to measure water flux, antifouling and also mercury removal. Prior to performance testing on antifouling and mercury removal, it was characterized in term of functional group and thermal stability.

II. METHODOLOGY

A. Materials

Polyethylene glycol, MW=1,500, polyvinyl alcohol, MW=60,000, chitosan powder, MW=100,000-300,000, Tetraethylorthosilicate (TEOS) (98%) were purchase from Sigma Aldrich, N-methyl pyrrolidone (NMP) were purchase from Merck KGaA, aqueous acetic acid solution, polysulfone flakes, humic acid, mercury solution and hydrochloric acid (37%) .

B. Preparation of polysulfone solution

13 wt% polysulfone flakes were dissolved in 87 ml wt% NMP solvent in 100 ml solution. Then the solution was stirred above the hot plate at 60°C and 400 rpm for 4 hours.

C. Casting of polysulfone support membrane

About 2 ml of PSF solution was poured onto the glass casting support. Then the membrane film was formed with thickness 90 micrometer with the aid of doctor blade. Then, the glass plate was immersed into a container of tap water immediately to remove any residual solvent and the film membrane layer will be removed from the glass support by itself. Next, the membrane was transferred into another container filled with tap water for a day and later was hanged for another day.

D. Preparation of hybrid solution

0.02g of chitosan (CS) powder was dissolved in 2 wt% acetic acid solution at room temperature and 450 rpm for 1 hour until fully dissolved. Then 0.01g of polyethylene glycol (PEG) was added in the solution with the ratio of 2:1 at 80°C and 450 rpm for 4 hours. Next, 5wt% of polyvinyl alcohol solution was prepared by dissolving the PVA with distilled water. Lastly, all the 3 mixtures were added together along with 3wt% of TeOS as crosslinker and 1wt% of hydrochloric acid as catalyst and were stirred for 7 hours at 40°C. The same solution of 6wt% polyvinyl alcohol was later prepared.

E. Preparation of thin film composite membrane

About 4 to 5 drops of hybrid solution were coated evenly onto the surface of each PSF membrane casted using glass rod and hanged to dry for a day. Next, the coated membranes were then dried in oven for an hour at 45°C.

F. Characterization

i. Fourier transform infrared spectroscopy (FTIR) analysis

Fourier transform infrared spectroscopy (FTIR) was used in order to identify the functional groups and types of bonding in the integral membrane. Each of the membrane samples were cut off into tiny little pieces to be send for analysis.

ii. Thermogravimetric analysis (TGA) analysis

Thermogravimetric analysis (TGA) was used to investigate the thermal decomposition behavior and stability of the integral membrane. The equipment is also able to identify the weight loss of material as a function of temperature. The samples of hybrid solution were coated onto glass plate and then later were scrap to obtained about 3 mg for analysis. Then the sample was heated from 30oC to 900°C at a heating rate of 10 °C/min under nitrogen gas.

G. Performance test

i. Pure water permeability (PWP)

PWP was used to determine the amount of pure water that can permeate into the membrane. The equipment used is the dead end filtration mode of membrane testing rig. Firstly, the sample membranes were cut off into a circle shape with the surface area of the apparatus plate which is 19.63cm^2. Then, 200 ml of deionised water was poured into the filtration cell. The apparatus must be tightly closed before applying the pressure of 4 bar using nitrogen gas. After that, the permeate sample was collected in a beaker. The time taken for this test is approximately 1 hour and 15 minutes with 15 minutes interval to measure the volume of collected permeate sample. This test can identify the permeate flux and permeability where the permeate flux is usually used to characterise whether the membrane is asymmetric or composite while permeability was used to characterise dense film. The permeate flux, J (mL/cm^2.min^{-1}) was determined analytically from the total volume of permeate collected against time by dividing the total volume collected with area times with total time taken.

$$J = \frac{\Delta V}{A.\Delta t}$$

ii. Anti-fouling properties

Humic acid solution was obtained by dissolving 1g of humic acid in distilled water to obtained 500 ppm sodium hydroxide solution. The solution was then stored in a glass bottle then put in the refrigerator to cool and maintain it at 5°C. The same equipment was used which is dead-end filtration rig. However, the filtration was divided into three stages.

Firstly, deionized water as feed solution for 30 minutes was recorded and the stabilized will denote as J_0. Secondly, the membrane was tested with the humic solution for 2 hours with 30 minutes time interval to collect the permeate samples. Lastly, the back-washing method was done by immersing the membrane in 20 ml of deionized water and stirred in a shaker at 200 rpm for 30 minutes. It is then later used again and the permeate sample was recorded again for 30 minutes, and the final flux is donated as J_1. All of the data were collected to calculate the Relative flux Decay (RFD) and Relative Flux Recovery (RFR) based on the equation below.

$$RFD = \left[\frac{(Jo - Jp)}{Jo} \right] \times 100$$

$$RFR = \left(\frac{J1}{Jo} \right) \times 100$$

iii. Mercury water permeability

The same method was used in PWP but pure water was replaced with 1 ppm of mercury solution. 1 ppm of mercury solution was prepared by adding 1 ml of 1000 ppm mercury stock solution into a 1 liter volumetric flask. The volumetric flask was then diluted to mark with deionized water.

III. RESULTS AND DISCUSSION

A. Characterization

i. Fourier transform infrared spectroscopy (FTIR) analysis

From the graph in Fig. 3.1, there are broad peak from 3600 to 3000 cm^{-1} indicates the presence of O-H group. Both graphs shows peak at 2900 cm^{-1} means that the presence of C=OH occur in the membrane. Apart from that, this functional group also shows peak at 1400 cm^{-1}. The ether functional group C-O-C was also present in the membrane where the peaks occur at 1515, 1150 and 1105 cm^{-1}.

Peaks occur at near to 1600 cm^{-1} indicates that C-C stretch ring. At peaks 1350 cm^{-1}, aromatic C=C group was identified on both membrane due to conjugation of benzene ring (Kumar, Isloor, Ismail, Rashid, & Matsuura, 2013). Adsorption peak at 1250 cm^{-1} and 550 cm^{-1} indicates that both membrane have the O=S=O functional group which correspond to the stretching of sulfonated group.

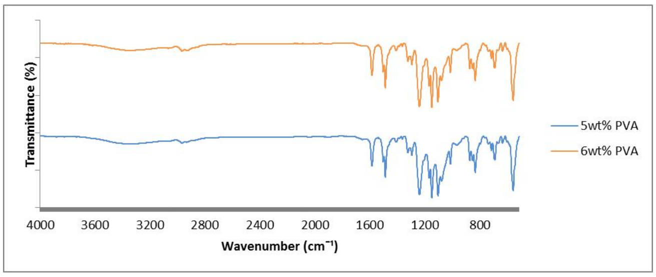

Fig. 3.1: FTIR spectra for TFC membranes with different PVA concentration

ii. Thermogravimetric analysis (TGA) analysis

Based on the Fig. 3.2, both membranes have quite similar pattern curves. The hybrid membranes have similar weight profile started at 20 °C and 33 °C to 65 °C respectively due to evaporation of adsorbed and bound water from the membrane phase with average of 1 mg. the slight pattern at 200 °C indicates that degradation of chitosan which present in the membrane. However, due to higher percentage of PVA in 6 wt%, the degradation of the membrane and loss much further because of higher PVA concentration limits the thermal stability of the membrane (H. Huang et al., 2018).

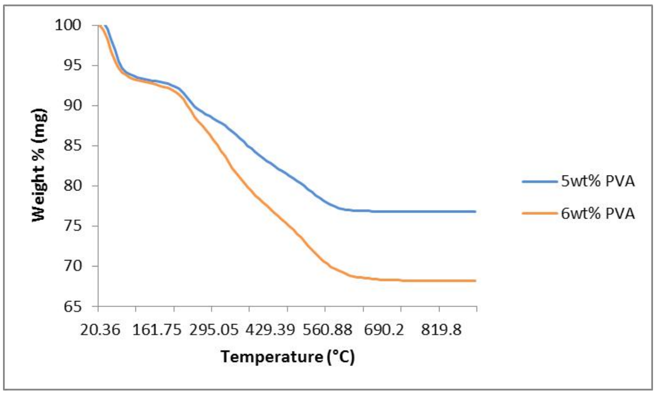

Fig. 3.2: TGA curves for TFC membranes with different PVA concentration

B. Performance test

i. Pure water permeability (PWP)

Fig. 3.3 shows average water flux for thin film composite membranes with difference PVA concentration of 5wt% and 6wt% respectively. As the time increase, the flux decreases for both membrane samples. At first, initial flux such as 0.056 ml/cm^2.min for 5% and as 0.037 ml/cm^2.min for 6%.

After 1 hour, the average flux for both 5% and 6% are very slightly different which both are close approximately to 0.001 ml/cm^2.min. This test was applied on the TFC membranes to determine the membrane porosity and its stability by measuring the water permeability which is high permeability indicates high porosity of a membrane (Chong, Wang, Mattevi, & Li, 2018).

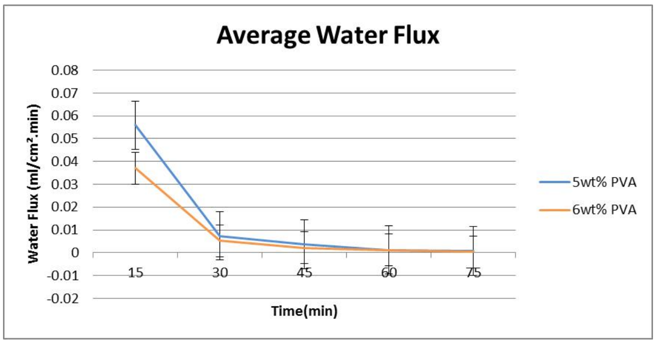

Fig. 3.3: Average water flux for TFC membranes with different PVA concentration

ii. Anti-fouling properties

Fig. 3.4 shows average flux using humic acid solutions as foulant in the treatment through thin film composite membrane. Based on the graph, both membranes have flux decrease greatly with time increasing compared to PWP graphs due to concentration polarization and membrane fouling.

Solutes are trapped and accumulated on the membrane surface and pores due to strong hydrophobic interaction. Increasing in polymer membrane will reduce the porosity and the size of the pores thus more solute will agglomerate on the membrane surface and inside pores (Kumar, Isloor, Ismail, & Matsuura, 2013). The hydrophobicity of the membrane increases with high amount of polymer concentration.

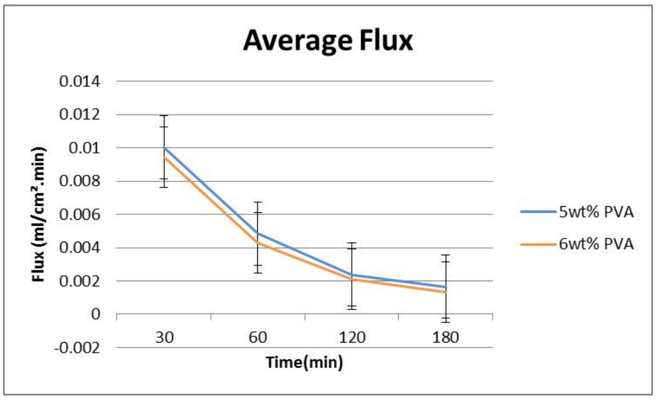

Fig. 3.4: Average flux for TFC membranes with different PVA concentration

Table 3.1 and 3.2 show the Relative flux recovery (RFR) and relative flux decay (RFD) in order to determine the antifouling property of the membrane. High efficiency of hydraulic cleaning and good fouling resistant ability indicates with the high value of RFR and low value of RFD, otherwise its vice versa (H. Huang et al., 2018).

TFC membrane with 6wt% PVA concentration has the highest RFR value (90%) and lowest RFD value (46%). This indicate that solute deposited on the membrane surface of 6% were harder to remove by hydraulic cleaning compared to membrane with 5% of polymers.

Table 3.1: Relative flux recovery (RFR)

PVA wt%	RFD
5	49.08466819
6	46.05614973

Table 3.2: Relative flux decay (RFD)

PVA wt%	RFR
5	82.8375286
6	90.37433155

iii. Mercury water permeability

Figure 3.5 shows the mercury flux of both 5 and 6 wt% PVA concentration membranes decline over time. The degree of decline, however, in 5 wt% is higher and steeper than that of the 6 wt%. In other word, 5 wt% membrane is more efficient to mercury removal than the 6 wt% membrane. After 30 minutes of filtration, the flux of 6 wt% membrane lowered steadily than the 5 wt%.

The results clearly show that higher concentration of polymer does make the membrane prone to fouling where the mercury ions traps and agglomerates on the surface of the membrane (H. Huang et al., 2018). The filtration of mercury solution in both membranes shown in the graph indicates that lower PVA concentrations means less fouling on the surface of the membrane.

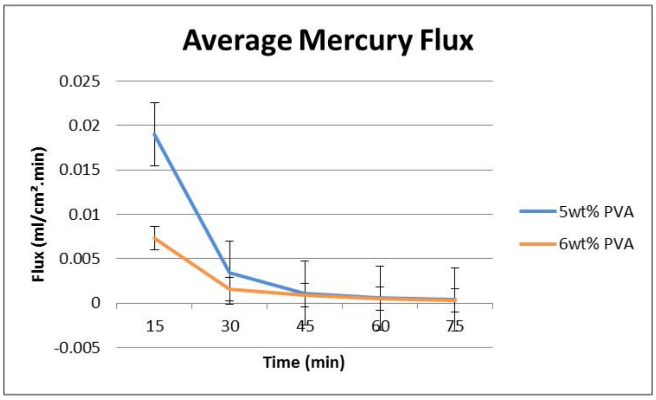

Fig. 3.5: Average mercury flux for TFC membranes with different PVA concentration

IV. CONCLUSION

The synthesis of thin film composite membrane was successful. The method for the support layer membrane was phase inversion method and hybrid solution of CS/PEG/PVA was also successfully blended with TeOS as crosslinker. TFC membranes with 5 wt% of PVA have greater flux rate, good antifouling properties and high value of RFR. The modification of TFC membranes with different PVA concentrations was to study hydrophilicity and reduce fouling.

During the mercury filtration, lower PVA concentration showed the bes anti-fouling properties. However, further studies need to be done in order study the modification of other polymers as well.

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