HEAVY METAL REMOVAL BY MEMBRANE FILTRATION

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Abstract—The heavy metals ate the bad things that exist in water and may affect the ecosystem for the long term effect. One of the dangerous of the heavy metal is mercury that can cause paralysis, blindness and chromosome breakage due to central nervous that has been attacked by the mercury. Various method has been introduced to remove these heavy metals. The methods are liquid-liquid extraction, precipitation and membrane separation technology. The membrane separation is better compared to the other method as it has lower power consumption, smaller footprint, lower pressure drop and high efficiency. Chitosan is a well-known polymer as it is one of the most available biopolymer in nature. The membrane can be enhanced as it is combine with the suitable polymer and can be well-known as hybrid membrane. Polyvinyl alcohol is suitable to be combine with chitosan as both are extensively use to enhance the properties of chitosan in both mechanical and chemical. The membrane is improvised as it is coating with the hybrid membrane consist of polyvinyl alcohol and chitosan. Then, the hybrid membrane will be examined their characteristics by FTIR and TGA analysis. The hybrid membrane will undergo three performance testing. The performance testing are water flux, antifouling and mercury removal. Therefore, the objective of this study is to study the effect of various concentration of polyvinyl alcohol, PVA on the properties of the membrane and the performance of the hybrid membrane on mercury removal.

***Keywords*- hybrid membrane, chitosan, polyvinyl alcohol, mercury.**

I. INTRODUCTION

The heavy metals are not the good things that exist in the water and may affect the ecosystem for the long-term effect. The example of heavy metals are lead (Pb), iron (Fe), copper (Cu) and nickel (Ni). Among these heavy metals, one of the most dangerous is mercury. Effluents from manufacturing of chlorine, switch gear/batteries, fertilizers, pharmaceuticals, combustion of fossil fuels, textile industries, pulp and paper industries and agricultural chemicals are among the sources that contribute to the leakage of mercury to the water sources. The effects of the mercury to the organisms is that it can attack the central nervous system that can cause mental and motor dysfunction. This motor dysfunction can lead to paralysis, blindness and chromosome breakage (H.Bessbousse, T.Rhlalou, J-F. Verchere, L. Lebrun, 2010). Therefore, it is important to remove these heavy metals to prevent the negative effects the living organisms and also the environment.

There are various method to remove the heavy metal ions such as conventional methods and membrane separation methods. The example of conventional methods are liquid-liquid extraction, precipitation and ion exchange (S. Kounshkbangi, 2017). Among the methods, adsorption process is the best process for removal the metal ions as it is an efficient and economical method. However, there is a setback where it is difficult to regenerate the adsorbents from water and agglomeration of adsorbents in aqueous solution within an adsorption process. The other method is membrane separation technology. This technique has been compared with conventional method and the result shows membrane separation technology is better as it has lower power consumption, smaller footprint, lower pressure drop and high efficiency (Vahid Vatanpour, 2017).

Among the membrane separation technologies, membrane adsorption has appeared as a popular method to remove the heavy metal ions from the wastewater. It is popular as it has a unique advantages in removing the heavy metal ions such as high efficiency especially at low metal concentration, normal productivity, lower pressure drop, proper reusability, fast kinetics and desired removal rate (Mehdipour et al, 2015). The membrane has all of this advantages as it is so reactive with the help of functional group exist on the surface of the membrane. The functional group such as –COOH and –OH can help to adsorb the heavy metal ions by the surface complexation, chemical bonding and ion- exchange mechanisms (Salehi and Madaeni, 2014).

One of the well-known polymer is chitosan (CS). It is well known as it is second most available biopolymer in nature with many uses in the preparation of adsorptive membranes. This polymer has an excellent properties as it has high hydrophilicity, abundant reactive functional sites, biodegradability and normal chemical resistance. One other reason is that it has amine as amine groups are in advanced group for chelating heavy metal ions. (Jayakumar et al, 2011). A highly reactive and mechanically membranes are produce when chitosan combine with a suitable polymers such as cellulose acetate and polyvinyl alcohol. Polyvinyl alcohol (PVA) and chitosan is a compatible and suitable polymer as both are extensively used to enhance the properties of chitosan either in mechanical or chemical (Cheng et al, 2010).

Thus, the objective of the present work is to produce a hybrid membrane from the combination of chitosan (CS)/polyethylene glycol (PEG) and polyvinyl alcohol (PVA) with the work of TEOS as cross-linker on the PSF membrane. Then, the properties of this hybrid membrane is being studied. This work is also to evaluate the performance of the thin film on mercury removal.

II. METHODOLOGY

A. Preparation of polysulfone solution

First, 11 wt% polysulfone flakes were dissolved in 89 ml NMP solvent in 100 ml solution. Next, the solution was stirred above the hot plate together with magnetic stirrer for 60°C and 500rpm for 4 hours (Rajesha Kumar, Arun M. Isloor, A.F. Ismail, Suraya A. Rashid, T. Matsuura, 2013).

B. Casting of polysulfone supporting membrane

First, 2 ml of polysulfone was poured on the glass casting support. Then with the aid of doctor blade, the membrane film is form with thickness 90 micrometer (Jian Wen Wang, Yi Ming Kuo, 2007). Next, the glass plate was immersed into the container containing tap water to remove any residual solvent and the film membrane layer was removed by itself from the glass support. The membrane was transferred to other container filled with tap water for 1 night and hanged for 1 night. All steps were repeated until the solution is finished (Rajesha Kumar, Arun M. Isloor, A.F Ismail, 2014).

C. Preparation of hybrid solution

0.02 g chitosan, CS powder was dissolved in 2 wt% of acetic acid solution at room temperature and 400 rpm for magnetic stirrer. Next, 0.01 g of polyethylene glycol, PEG was added in the solution with a ratio of 2:1 CS/PEG at 80°C and 500 rpm for 4 hours Jian Wen Wang, Min Hsiung Hon, 2004). Lastly, 2 wt% of polyvinyl alcohol, PVA, 3 wt% tetraethylorthosilicate, TEOS and 1 wt% of hydrochloric acid, HCl were added to the solution at 40°C and 300 rpm for 7 hours (M.S. Sangeetha, A. Vijayalakshmi, 2016). The hybrid solution step then will be repeated by differ the PVA concentration of 3%.

D. Preparation of thin film composite membrane

4 to 5 drops of hybrid solution were coated on the PSF membrane by using glass rod. Then, the membrane that has been coated will be dried or 1 day. Next, the membranes are cured in the oven for 45°C and 1 hour (Sofiah Hamzah, Nor'aini, Marinah Mohd Ariffin, Asmadi Ali, Abdul Wahab Mohammad, 2014).

E. Characterization and performance test

For the characterization phase, the membrane and the hybrid solution were analysed with fourier transform infrared spectroscopy, FTIR and thermogravimetric analysis, TGA. Meanwhile for the performance test, the film composite membrane were undergo pure water permeability, PWP for three phases, antifouling properties and mercury removal.

F. Fourier transform infrared spectroscopy, FTIR

FTIR was used to identify the presence of functional groups and types of bondings in the integral membrane. The sample will be cut into small pieces and then place on the diamond crystal plate for analysis. The plate is needed to be clean with acetone liquid before the sample will be placed. The pressure will be set to 60-70N and the reading sample will be collected in the range of 400cm-1 to 4000 cm-1 of the spectrum wavelength (Rajesha Kumar, Arun M. Isloor, A.F Ismail, Suraya A. Rashid, T Matsuura, 2013).

G. Thermogravimetric analysis, TGA

TGA was used to investigate the thermal decomposition behavior and stability of the integral membrane the sample also need to be cut into the small pieces about 5 to 10 mg for analysis. The sample will be heated from 30ºC to 900ºC at a heating rate of 10ºC/min under nitrogen gas (A.Ghaee, M. Shariaty-Niassar, J. Barzin, A.F. Ismail, 2013).

H. Pure water permeability, PWP

This method was used to identify the amount of water that can permeate into the membrane. The apparatus was used is dead end filtration mode of membrane testing rig. Firstly, the sample membrane will be cut off into a circle shape area 19.63 cm2 and place it in the sample section. Next, 200 ml of deionized water will be poured in the stainless steel filtration cell. The operation is running in room temperature and the pressure will be set to 4 bars by using nitrogen gas. The permeate sample will be collected in a beaker. The time interval will be used is 15 minutes as it is the stability interval. All the data will be collected and the graph of permeate flux vs time will be produced. The objective of this test is to identify the permeate flux and permeability. Permeate flux is used to characterize the membrane if it is an asymmetric or composite. The permeability is used to characterize the dense film. The permeate flux, J (mL/cm2.min-1) was determined by using equation below.

$$\text{Permeate Flux, } J = \frac{\Delta V}{A.\Delta t}$$

I. Anti-fouling properties

For this test, humic acid solution is produced by dissolving 1 g of humic acid in distilled water to obtain 500 ppm of NaOH solution. Then the solution is stored in a sterilized glass bottle at 5°C. Next, the dead end filtration rig will be used at 4 bar of pressure. This process will have 3 phases. First, deionize water as feed solution for 30 minutes and stabilized flux will be denote as Jo. Second, the membrane will be tested with humic acid solution for 2 hours and the permeate data will be collected for every 30 minutes. The permeate data will be collected against filtration time. The permeate flux will be denoted as Jp. Next, the membrane will be cleaned by back-washed method. The back washing method is run by immersing the membrane in 20 ml of deionized water and being stirred in a shaker at 200 rpm for 30 minutes. Last step is deionized water will be used again and permeate data will be recorded after 30 minutes of interval time. The final flux will be denoted as J1. All the data collected will be used to calculate the relative flux decay, RFD and relative flux recovery, RFR based on the equation listed below (Sofiah Hamzah, Nor'aini, Marinah Mohd Ariffin, Asmadi Ali, Abdul Wahab Mohammad, 2014).

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

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

J. Mercury removal

The same method as mention in the section H is repeated but with different solution. For this section, mercury solution with 1ppm was used on the 2% and 3% PVA hybrid membrane. The experiment was set for 4 bar nitrogen gas. The permeate sample was collected in the beaker. The time interval was 15 minutes and the graph of permeate flux was produced. Then, the analysis of mercury removal was analysed.

III. RESULTS AND DISCUSSION

A. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to identify the functional groups in the hybrid membrane. This analysis help to identify the functional groups. Hybrid solution consist of chitosan, polyethylene glycol, PEG and variable of concentration of polyvinyl alcohol, PVA consist of 2% and 3% have been analysed by the FTIR for this experiment. The graph shows the transmittance,% versus wavelength, cm^{-1}.

From the figure 3.1, there is O-H group at 3334 cm^{-1} (2% PVA) and 3361 cm^{-1} (3% PVA) because of incomplete drying process. There is also C-C extend ring exists at peak 1585 cm^{-1} for both 2% and 3% PVA while at the peak of 1014 cm^{-1} (2% and 3% PVA), there is ether gathering (C-O-C) (Rajesha Kumar, Arun M. Isloor, A.F. Ismail, T. Matsuura, 2013). Both of hybrid solution have the O=S=O group at the peak 557cm^{-1} which related to symmetric and asymmetric stretching of the sulfonated group Law Yong Ng, Choe Peng Leo, Abdul Wahab Mohammad, 2011). Lastly, from the graph we can see that all the hybrid solution that has been analysed give a quite similar pattern of transmittance peak at each wavelength and hybrid solution with 3% PVA has a longer adsorbed peak compared to 2% PVA hybrid solution.

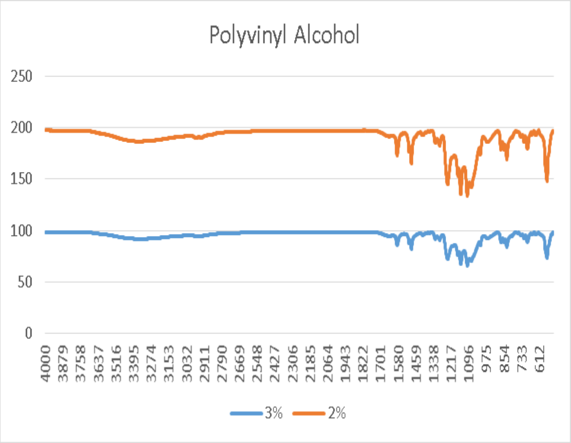
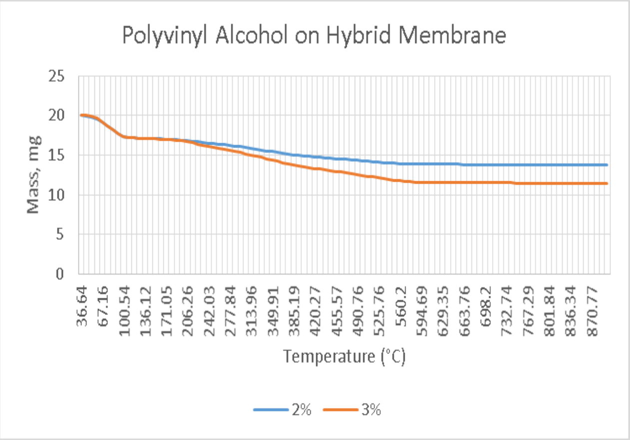


Figure 3.1: Result of FTIR

B. Thermogravimetric analysis (TGA)



From the figure 3.2, it shows two different line that represent 2% and 3% of PVA. At the early stage, it shows a huge decrease until it reach 17mg. After that, both of the curve shows a quite similar curve. Both of the hybrid solution has low thermal stability until it reach 188 °C. Then, the graph started to shows the difference. The 2% and 3% curve started to shows a decline but the 2% PVA in hybrid solution show a greater thermal strength compared to 3% PVA hybrid solution. This outcomes were the same as desire as the increment in temperature will weaken the intermolecular chains between the polymer atoms causes a decrease of its mechanical and chemical strength (Haitao Huang Jiayu Yu, Hanxiang Guo, Yibo ShenFan Yang, Han Wang, Rong Liu, Yang Liu, 2018).

C. Pure Water Permeability (PWP)

The figure 3.3 referring to the average water flux with different concentration of PVA. As the time increase, the flux will be decrease. Both hybrid membrane have their own trend. For the 2% PVA hybrid membrane, there is slightly increase in its average water flux when the time reach 1 hour. For the 3%PVA hybrid membrane, it is continuous decrease as the time increase

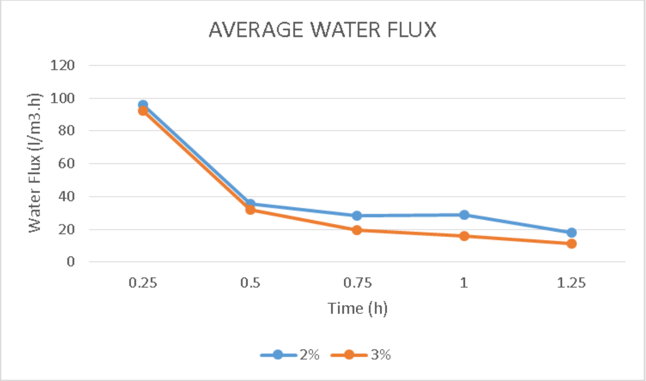


Figure 3.3: The result of PWP

The particles can clogged the membrane pores if they are in smaller size compare to the pore size of the membrane. The clogged activity will reduce the water flux. It can be related to the graph above as all the sample shown a decreasing trend as the time increase. The past research has shown that membrane which had small uniform round shape and hollow pore arrangement can decrease the fouling because of difficulties of particles to go inside the membrane which had sponge like microstructure led to membrane fouling due to porous network of the membrane(Harish Ravishankar, Felicity Roddick, Dimuth Navaratn. Veeriah Jeegatheesan, 2018).

D. Antifouling properties

Table above shown a different trend when the water is replaced with the humic acid. This is because the initial adsorption and deposition of solutes molecules from humic acid solution inside the membrane pores and on the membrane pores (Dong Yan hang, Qi Hao, Jie Liu, Yu Sheng Shi, Jun Zhu Li Su, Yan Wang, 2018). The antifouling property of the membrane is determine by performing the relative flux recovery (RFR) and relative flux decay (RFD). A good membrane must have high value of RFR and low value of RFD. This indicate the membrane is high efficiency and good fouling resistant (Zhen Lin, Chuan Hu, Xiaodong Wu, Weizheng Zhong, Mengmeng Chen, Qiugen Zhang, Aimei Zhu, Qinglin Liu, 2018).

Table 3.1: Result of the antifouling properties

Average flux	Time (hour)					
	0.5	0.5	1.0	1.5	2.0	0.5
PVA concentration	Deionized water (J_o)	Humic Acid solution (J_p)				Deionozed water (J_1)
2% PVA	56.3	17.4	13.6	11.8	9.0	44.3
3% PVA	54.6	6.4	6.3	6.3	6.0	41.8

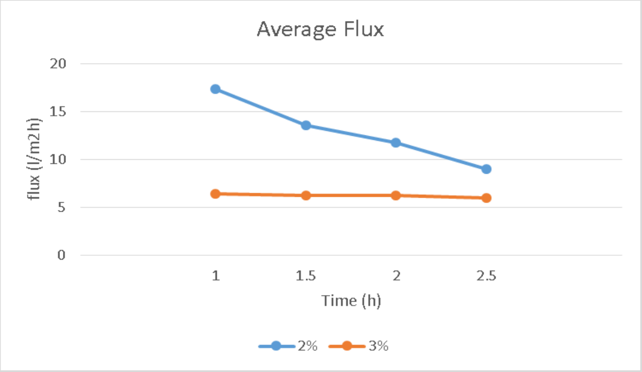


Figure 3.4: Graph of the analysis from the antifouling properties

From the table RFR and RFD, it shown that 3%PVA hybrid membrane is better than 2% PVA hybrid membrane. In the other hand, as mention above, 2% hybrid membrane shown that it is not a good membrane as it has a low value of RFR and high value of RFD.

Table 3.2: RFR data

PVA concentration	RFR
2%	7.99
3%	54.2

Table 3.3: RFD data

PVA concentration	RFD
2%	78.7
3%	76.6

E. Mercury Removal

The figure 3.5 shows that the flux is decreasing when the time increased. But there is a moment for 3% PVA hybrid membrane have increase the flux slightly at 1 hour. But there is a different case for 2%PVA hybrid membrane as it is start to increase starting at 0.75 hour and then start to decrease at 1.25 hour. Compared between these two membranes, 3% PVA membrane give a better result as it should be the flux decrease when the time increase.

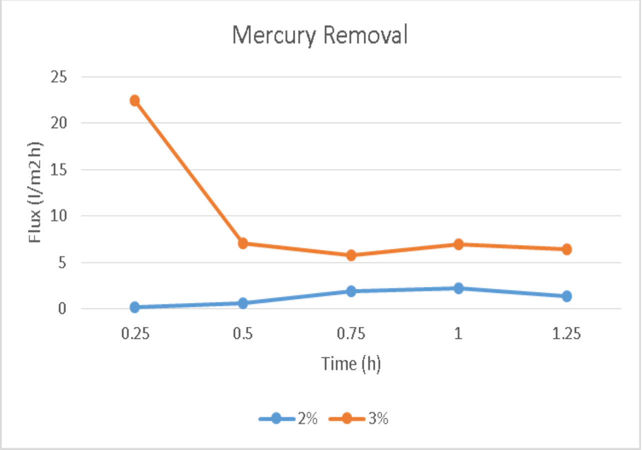


Figure 3.5: Mercury Removal analysis

Next, the membrane flux depends on the size of the pore and surface hydrophilicity membrane. The presence of chitosan, polyethylene glycol and polyvinyl alcohol on the surface of the membrane increase the surface hydrophilicity. The hybrid membrane attached on the surface of the membrane, increase the surface hydrophilicity while a part of it was leached out into the non-solvent which make the pore to become larger. The increasing concentration of the hybrid membrane (PVA, PEG, CS) will increase the water permeability. This is because pore sizes and hydrophilicity has been increased (Rajesha Kumar, Arun M. Isloor, A.F. Ismail, T. Matsuura, 2013). Thus, to increase the hydrophilicity and high pure wate permeability, the membrane needed to be low concentration of PSF and high concentration of hybrid solution (CS, PEG, PVA) (Rajesha Kumar, Arun M. Isloor, Ahmad Fauzi Ismail, T. Matsuura, 2013).

IV. CONCLUSION

The manufacture of thin fil composite membrane were successful by using phase inversion method for support membrane (PSF membrane and hybrid solution by organic blend of chitosan/polyethylene glycol/polyvinyl alcohol with TEOS as a cross-linker. Based on the experiment, polyvinyl alcohol gives a great impact on the hybrid solution and hybrid membrane. It give a boost to the characterization and performance. The hybrid membrane with 3% PVA concentration have a better flux rate, good antifouling properties and high value of RFR by referring to the results of the experiment. This is due to the hybrid solution give the membrane to become high hydrophilicity, porosity and pore size reduce the clogging and accumulation of solutes inside the membranes pores on the membrane surfaces. All this properties made the membrane to get a high flux ration and antifouling properties. In conclusion, hybrid membrane with higher concentration of polyvinyl alcohol will increase all the ptential of the membrane. It is also can become a candidate as antifouling membrane in membrane applications.

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