



Thin Film Composite Membrane from PSF/Chitosan/PEG: Effect of PVA Concentration on the Removal of Mercury and Antifouling Properties

Norin Zamiah Kassim Shaari, Mohamad Fazrul Basri, Raimi Ruhaizat Mohammad Yazid, Nurul Aida Sulaiman, Shahira Ramlee

Abstract: In this study, a thin film composite membrane was synthesized by coating a layer of hybrid membrane formulated from a blend of polyethylene glycol (PEG), chitosan and polyvinyl alcohol (PVA), cross linked with tetraethylorthosilicate on a polysulfone support membrane. The aim of this experiment is to study the effect of varying the PVA concentrations on the performance of the TFC membranes on the removal of mercury and to determine their antifouling behaviour. Four different concentrations of PVA were selected; 2 wt.%, 3 wt.%, 5 wt.% and 6 wt.%. Results showed that the increase concentration of PVA leads to good removal of mercury ions, and good antifouling properties which was portrayed through high FRR and RFR respectively, and low IFR. The suitable concentration of PVA was found at 3 wt. %, where it has yield TFC membrane that able to remove all the mercury ions from the solution even after 30 minutes filtration time with sufficient amount of flux as compared to other membranes. It also portrays good anti fouling behaviour due to low IFR and average value of RFR (66%). Therefore, this study concludes that the fabricated thin film composite membrane suitable to be used in membrane filtration for heavy metal removal.

Keywords : antifouling, mercury ion, polyvinyl alcohol, thin film composite

I. INTRODUCTION

With the development of big cities and major industries to cater human needs over the few recent years, population growths have caused a lot of environmental problems such as heavy metal contamination [1]. Heavy metals pollutants such

as mercury that are found in the industrial waste waters can be detrimental to all living beings due to its high toxicity [2]. The main sources of mercury are chloro-alkali plants, waste battery, oil refinery, paint production, pharmaceutical, paper/pulp, gold mining, solid waste incineration, fossil fuel combustion and chemical manufacturing [3]. The most common form of mercury ion is $HgCl_2$ in aqueous form, which can be transformed biologically or chemically into methylmercury that is the most toxic form of mercury in nature [4]. Mercury poses a severe effect on the neurological and general health of human being and living creatures [5].

Due to the active industrial activities and the unregulated bauxite mining activities, the mercury pollution in river and seawater is becoming uncontrollable in Malaysia. Among the various methods to remove mercury, micellar-enhanced ultrafiltration (MEUF) and polymer-enhanced ultrafiltration (PEUF) are gaining much attention due to their ability to remove $> 90\%$ Hg^{2+} . However these processes have significant disadvantages such as incomplete removal, high energy consumption and production of toxic sludge [4].

The simplification of this method is done by using a membrane in which the complexing polymer is integrated so that the complexation and filtration steps are performed in a single operation [5]. Recently, in order to overcome the above limitations, hybrid organic-inorganic polymer materials have been used to remove heavy metals from wastewater [6,7]. As compared to pure organic polymer and inorganic material, the use of hybrid membrane, which combines the properties of both materials, had been proven to yield better mechanical and thermal properties [8]. This is due to the introduction of hydrogen and covalent bonds in the polymer matrix during the cross-linking reaction [9].

Polysulfone is widely used in membrane fabrication due to it is stable thermally, high mechanical strength, chemical inactiveness and exceptional endurance for all sterilization techniques [10]. Apart from that, it is reasonably cheap price and good resistance to extreme pH. Chitosan are natural polysaccharide copolymers which can be discovered in a many of common natural resources such as shrimp shells and crab. It is the second richest natural copolymer after cellulose and it is a renewable resources. It has wide range of availability and versatile applications.

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It is also regularly applied in the adsorption, chromatography and ion-exchange process predominantly for its hydrophilicity, non-toxic, biodegradability and biocompatibility [11]. It contains hydroxyl and amino groups which provides as allocation sites and good complexation which are useful for adsorbing wide range of contaminants including heavy metals [12]. However, CS also had their disadvantage which is low in mechanical stability which limits the CS usage for a large consumption. Another limitation is it is not soluble in water and in most common organic solvents (DMSO, DMF, NMP, organic alcohols, pyridine). Blending of chitosan with another organic polymer such as polyethylene glycol (PEG) is one way to enhance the solubility, where addition of PEG gives improvement to the water affinity for the blend membrane [13]. Polyvinyl alcohol (PVA) has been used in removal of hazardous metal ions from wastewater. It is particularly fascinating from an economic and biodegradability perspective, widely used in drug delivery system and also metal removal [14]. Polyvinyl alcohol is biocompatible, non-toxic and chemical resistant polymer that is substantially used in blend membranes.

Besides being the competitive method of filtration for heavy metal from wastewater, the biggest challenge of membrane filtration is fouling. Polymers used in membrane technology contain steric repulsion that gives fouling to the membrane filtration process [15]. Fouling can be in reversible or irreversible which depends on the surface of the membrane. For reversible fouling, it occurs because of the result between particles have a weak interaction and could be cleaned by physical cleaning [16]. For irreversible fouling, it was caused by strong interaction as the surface of the membrane formed a permanent fouling layer which cannot be destroyed by physical methods. Humic acid is one way of expressing the contaminated and dirty water in reality. The purpose of using humic acid solution is to observe the complex situation and understand completely on the mechanism of membrane fouling caused by humic acid or as a major component of organic matter in wastewater [17].

In this study, the hybrid membrane formulated from chitosan/PEG/PVA/TEOS supported with polysulfone membrane was examined for their performance in removal of mercury and antifouling properties at different concentration of PVA incorporated during hybrid membrane formulation.

II. METHODOLOGY

A. Materials for preparation of thin film composite

Materials used in the fabrication of thin film composite membrane include Polysulfone (PSF), Chitosan (CS), Polyvinyl Alcohol (PVA), Polyethylene Glycol (PEG), 1-Methyl-2-Pyrrolidone (NMP) and Tetraethylorthosilicate (TEOS). The polysulfone (PSF) with an average molecular weight of 22,000 by MO beads, polyethylene glycol with a molecular weight of 1400, 1-methyl-2-pyrrolidone (NMP) with purity of 99% and acetic acid with 99% purity were purchased from Merck, Malaysia. Chitosan (CS) with molecular weight of 100,000-300,000 was purchased from Acros Organics. Tetraethylorthosilicate (TEOS) with 99% purity, hydrochloric acid with 37% purity as catalyst and polyvinyl alcohol with MW 60,000 were obtained from Sigma Aldrich, Malaysia. Deionized water was also used as

solvent. All this material was employed without further purification.

B. Preparation of porous support membrane

Polysulfone as support membrane were prepared by phase inversion method. Polysulfone pellet of 13g was dissolved into 1-methyl-2-pyrrolidone which act as solvent on preparing 13wt% polysulfone polymer solution. The solution was stirred and heated at 60 °C for 4 hours until homogenous mixture was formed. The solution was kept in confined glass jar to avoid from being exposed to the air. The homogenous mixture solution was left 1 day to remove air bubbles. By using a film applicator with a gap of film thickness of 90µm, the polysulfone solution was then cast on a glass plate. The plate was then immersed in water after 30 s. The produced membrane film was then soaked overnight in the large amount of water. The film was then sun-dried for 1 day before it was heat-cured in an oven for 1 hour at 45°C.

C. Preparation of CS/PEG/PVA hybrid membrane solution

0.02g of chitosan (CS) powder was dissolved in 2 wt% acetic acid solution at room temperature and was stirred at 450 rpm for 1 hour. Then 0.01g of polyethylene glycol (PEG) was added into the solution with the weight ratio of 2:1. The solution was heated at 80°C and stirred at 450 rpm for 4 hours. 2 wt.% of polyvinyl alcohol solution was prepared separately by dissolving 2 gm PVA pellet into 98 gm distilled water followed with vigorous stirring and heated at 90°C for 4 hours. Lastly, all the 3 mixtures were added together along with 3wt% of TeOS as cross linker and 1wt.% of hydrochloric acid as catalyst, and followed with stirring and heating for 7 hours at 40°C. The same procedures were repeated with 3 wt. %, 5 wt.% and 6 wt.% of PVA solution added during preparation of hybrid solution.

D. Preparation of thin film composite membrane

The hybrid membrane solution was coated onto polysulfone support membrane by using a glass rod. The thin film composite was left to dry for 24 hours at a room temperature. Then, it was cured at 45°C in an oven for 1 hour.

E. Performance of Thin Film Composite Membrane

Removal of mercury

The performance testing of thin film composite membrane was carried out by using a dead end mode of filtration rig. Firstly, the sample of membrane was cut into a circle shape with the surface area of 19.63 cm². During the experiment, the 300 mL of feed solution was placed in a stainless steel filtration cell. 1 ppm mercury solution was used as the feed solution. 1 ppm mercury solution was prepared from the dilution process of 100 ppm pure solution.

The operation was conducted at room temperature with an applied pressure at ± 4 bar by using a nitrogen gas. The permeate sample was collected in a beaker for volume measurement. The permeate flux (J) was calculated by using (1).

$$J = \frac{\Delta V}{A \cdot \Delta t} \quad (1)$$

Where ΔV is the volume collected, A is cross sectional area of the membrane, and Δt is the filtration time.

Antifouling analysis

Prior to the antifouling analysis, humic acid solution was prepared by dissolving 10 g of humic acid in 500 ppm NaOH solution in the 1L volumetric flask. The solution was then stored in a glass bottle and was kept in the refrigerator to cool and maintain at 5°C.

Then, the same procedures as described for the removal of mercury were used for the filtration process, where it was divided into three stages. Firstly, deionized water was used as feed solution for a 30 minutes filtration process and the stabilized flux was recorded and denoted as J_o . Secondly, the deionized water was replaced with the humic acid solution and the filtration was continued for 2 hours, where the final flux was denoted as J_p . Then the back-washing method was conducted by immersing the membrane in 20 mL of deionized water in a shaker at 200 rpm for 30 minutes. The membrane was then used again for water filtration and the flux was recorded again after 30 minutes, where the final flux is denoted as J_1 . The fouling resistance of the membrane was evaluated through determination of flux recovery ratio (FRR) as shown by (2) [18]. The flux losses as a result of reversible and irreversible fouling were calculated based on reversible fouling ratio (RFR) and irreversible fouling ratio (IFR) through (3) and (4) [18] respectively.

$$FRR (\%) = \left[\frac{J_1}{J_o} \right] \times 100 \tag{2}$$

$$RFR(\%) = \left(\frac{J_1 - J_p}{J_o} \right) \times 100 \tag{3}$$

$$IFR (\%) = \left[\frac{J_o - J_1}{J_o} \right] \times 100 \tag{4}$$

III. RESULTS AND DISCUSSION

Based on Fig. 1, there was a rapid decrease in the flux after 30 minutes of filtration of the mercury feed solution. After 30 minutes, the flux becomes consistent regardless the concentration of PVA incorporated in the hybrid membrane formulation. However, membrane from 3 wt.% PVA showed the highest flux throughout the 75 minutes filtration as compared to other membranes.

The rapid decline in the flux was attributed to the adsorption and deposition of the solute (mercury) molecules on the membrane or inside the pore surface of the membrane [19]. After 30 minutes, perhaps cakes layer of solutes were formed on the membrane surface where the flux remains consistent as no solute were able to go through the membrane [20]. This situation was represented by the result as shown in Table-I, where after 30 minutes of filtration time, membranes with 3 to 6 wt.% PVA resulted in fully removal of mercury ion from the feed solution.

However, different situation was observed for membrane with 2% PVA. After an hour of filtration, there was 4.86% mercury left in the solution. Only after 90 minutes filtration, the mercury is fully removed. It shows that the membrane with > 2 wt.% PVA was able to remove the mercury ions from the

solution even after 30 minutes filtration time. Furthermore, as shown in Fig. 1, the membrane resulted in the lowest flux.

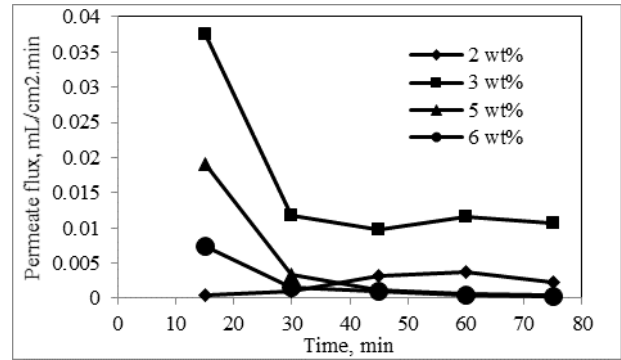


Fig. 1. Permeate flux from filtration of mercury solution

Table -I: Percentage mercury removal at different PVA concentrations

PVA Concentration	Time (min)	Percentage removal (%)
2 wt.%	30	88
	60	95.14
	90	100
3 wt.%	30	100
	60	
	90	
5 wt.%	30	100
	60	
	90	
6 wt.%	30	100
	60	
	90	

Fig. 2 shows the flux changes over three hours filtration time during antifouling analysis. Although there was a high flux produced from filtration of pure water in the first 30 minutes by membranes from 2 wt.% and 3 wt.% PVA respectively, a drastic flux declining rate was observed for 3 wt.% PVA when humic acid was used as the feed solution. However, the fluxes are higher than membrane with 5 wt.% and 6 wt.% PVA respectively. As shown in Table-II, after backwashing process, 76-79% and 82-90% flux was recovered for 2-3 wt.% and 5-6 wt.% PVA respectively. High level of efficiency of the hydraulic cleaning and good fouling resistant ability are represented by higher value of RFR and lower value of IFR, otherwise its vice versa [20]. Based on the table, the increase concentration of PVA resulted in the increase in RFR and a decrease in IFR. Besides the reversible fouling occurs on the membrane surface where the backwashing process was able to remove the accumulated solute on the membrane's surface, the presence of excess hydroxyl groups from PVA incorporated in the membrane formulation has enhanced the antifouling property of these membranes. The adsorption of humic acid (HA), which was represented by FRR and RFR, becoming low for the composite membrane as the hydrophilicity of the membrane increases, where the hydration layer is formed on the membrane with hydrophilic properties and act as a barrier to avoid HA adsorption [21].

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In this study, this is considered as steric stabilization effect, where the hydration layer emerged from the strong hydrogen bonding between the water molecules and the oxygen atoms in PEG and PVA respectively [22,23]. This phenomenon will prevent the adsorption of foulant material. Based on Table 2, all membranes portrayed good antifouling as low percentages of IFR were recorded. It shows that although pore blocking and cake formation, which are reversible fouling occurred on the membrane but only little pore constriction, which is irreversible had occurred [24]. Membrane with 3 wt.% PVA was found to yield good removal of mercury ion without jeopardizing the flux. The antifouling properties of the membrane are considered tolerated because it has low IFR despite low FRR.

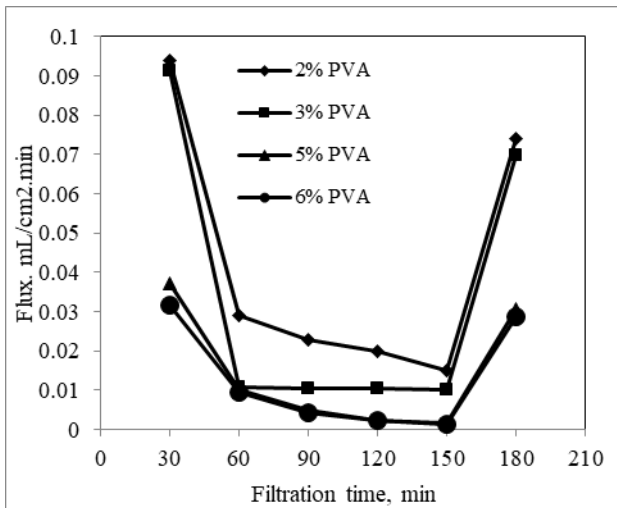


Fig. 2. Flux changes over 3 hour filtration during antifouling analysis

Table -II: The antifouling properties for membranes with different PVA concentration

PVA concentration, wt. %	FRR (%)	RFR (%)	IFR (%)
2	78.7	62.70	21.31
3	76.6	65.57	23.44
5	82.8	78.37	17.16
6	90.4	86.23	9.62

IV. CONCLUSION

Findings from this study shows that by increasing the concentration of PVA, better removal of mercury ions was observed. However, they suffer with low permeate flux. In term of antifouling analysis, membrane with 6 wt.% PVA has the best antifouling behaviour, which was depicted through the highest FRR and the lowest IFR.

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REFERENCES

- B.F. Medhat, M. Pakizeh, "Preparation and characterization of a nanoclay/PVA/PSf nanocomposite membrane for removal of pharmaceuticals from water," *Applied Clay Science*, vol. 162, 2018, pp 326-338.
- M.A. Abu-Saied, R. Wycisk, M.M. Abbassy, G.A. El-Naim, F. El-Demerdash, M.E. Youssef, H. Bassuony, P.N. Pintauro, "Sulfated chitosan/PVA absorbent membrane for removal of copper and nickel ions from aqueous solutions—Fabrication and sorption studies," *Carbohydrate Polymers*, vol. 165, 2017, pp 149-158.
- S. Nasirmoghaddam, S. Zeinali, S. Sabbaghi, "Chitosan coated magnetic nanoparticles as nano-adsorbent for efficient removal of mercury contents from industrial aqueous and oily samples," *Journal of Industrial and Engineering Chemistry*, vol. 27, 2015, pp 79-87.
- Y. Huang et al., "Removal of mercury (II) from wastewater by polyvinylamine-enhanced ultrafiltration," *Separation and Purification Technology*, vol. 154, 2015, pp 1-10.
- C.Y. Wu, H. Mouri, H., S.S. Chen, D.Z. Zhang, M. Koga, J. Kobayashi, "Removal of trace-amount mercury from wastewater by forward osmosis," *Journal of Water Process Engineering*, vol. 14, 2016, pp 108-116.
- B. Samiey, C.H. Cheng, J.W. Cheng, "Organic-inorganic hybrid polymers as adsorbents for removal of heavy metal ions from solutions: A Review," *Materials*, vol. 7, 2014, pp 673-726.
- N.A. Sulaiman, N.Z.K. Shaari, N.A. Rahman, "Removal Of Cu (II) and Fe (II) Ions through Thin Film Composite with Hybrid Membrane," *J. Eng. Sci. Technol., Special issue on SOMCHE 2015*, 2016, pp 36-49.
- Y. Huang et al., "Batch process of polymer-enhanced ultrafiltration to recover mercury (II) from wastewater. *Journal of Membrane Science*, vol. 514, 2016, pp 229-240.
- U.D. Meltem, L.B. Paul, S.G. Patricia, N. Cristina, X. Hui, S. Seth, "Achieving very low mercury levels in refinery wastewater by membrane filtration. *Journal of Hazardous Material*, vol. 215-216, 2012, pp 98-107.
- X. Chen, B. Tang, J. Luo, Y. Wan, "Towards high-performance polysulfone membrane: The role of PSF-b-PEG copolymer additive," *Microporous and Mesoporous Materials*, vol. 241, 2017, pp 355-365.
- E. Salehi, S.S. Madaeni, "Influence of poly(ethylene glycol) as pore-generator on morphology and performance of chitosan/poly(vinyl alcohol) membrane adsorbents," *Applied Surface Science*, vol. 288, 2014, pp 537-541.
- F.Y. Zheng, R. Li, J. Hu, J. Zhang, X. Han, X. Wang, Y. Zhang, "Chitin and waste shrimp shells liquefaction and liquefied products/polyvinyl alcohol blend membranes," *Carbohydrate Polymers*, vol. 205, 2019, pp 550-558.
- J.W. Wang, M.H. Hon, "Biodegradation behavior and cytotoxicity of composite membrane composed of B-dicalcium pyrophosphate and glucose mediated (polyethylene glycol.chitosan)," *Journal in science: materials in medicine*, vol. 15, 2014, pp 129-136.
- J.Y. Yoon, H. Zhang, Y.K. Kim, D. Harbottle, J.W. Lee, "A high-strength polyvinyl alcohol hydrogel membrane crosslinked by sulfosuccinic acid for strontium removal via filtration," *Journal of Environmental Chemical Engineering*, vol. 7, 2019, 102824.
- M.X. Cheng, N.M. Fan, Q. Miao, D. Kai, D. Yuan, K.G. Yong, "Quantitative fabrication, performance optimization and comparison of PEG and zwitterionic polymer antifouling coatings," *Acta Biomaterialia*, vol. 59, 2017, pp 129-138.
- K. Ambreen, A.S. Tauqir, K. Yaqoob, L. Shenghai, A.N.N. Syed, C. Zhaoliang, "Fabrication and characterization of polysulfone/modified nanocarbon black composite antifouling ultrafiltration membranes," *Journal of membrane Science*, vol. 554, 2018, pp 71-82.
- Y. Wei, L.Z. Andrew, "Humic Acid Fouling during Ultrafiltration," *Environmental Science and Technology*, vol. 34, 2000, pp 5043-5050.
- E. Habib, Y. Reza, S. Mahdi, R. Mahyar, "Synthesis, characterization, and anti-fouling properties of cellulose acetate/polyethylene glycol-grafted nanodiamond nanocomposite membranes for humic acid removal from contaminated water," *Iranian Polymer Journal*, vol. 27, 2018, pp 381-393.
- D.Y. Zhang, Q. Hao, J. Liu, Y.S. Shi, J. Zhu, L. Su, Y. Wang, "Antifouling polyimide membrane with grafted silver nanoparticles and zwitterion," *Separation and Purification Technology*, vol. 192, 2018, pp 230-239.
- H. Huang, J. Yu, H. Guo, Y. Shen, F. Yang, H. Wang, R. Liu, Y. Liu, "Improved antifouling performance of ultrafiltration membrane via preparing novel zwitterionic polyimide," *Applied Surface Science*, vol. 427, 2018, pp 38-47.

21. X. Zhaozan, L. Jiayou, T. Hai, L. Nanwen, "Antifouling polysulfone ultrafiltration membranes with pendent sulfonamide groups," Journal membrane of Science, vol. 548, 2018, pp 481 - 489.
22. K. Abe, K. Higashi, K. Watabe, A. Kobayashi, W. Limwikrant, K. Yamamoto, K. Moribe, " Effects of the PEG molecular weight of a PEG-lipid and cholesterol on PEG chain flexibility on liposome surfaces," Colloids Surf A, vol. 474, 2015, pp 63–70.
23. A. Akbari, R. Yegani, B. Pourabbas, "Synthesis of poly (ethylene glycol)(PEG) grafted silica nanoparticles with a minimum adhesion of proteins via one-pot one-step method," Colloids Surf A, vol. 484, 2015, pp 206–215.
24. E.M.V. Hoek, A.K. Ghosh, X. Huang, M. Liang, J.I. Zink, "Physical-chemical properties, separation performance, and fouling resistance of mixed-matrix ultrafiltration membranes," Desalination, vol. 283, 2011, pp 89-99.

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