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Effect of Activated Carbon in Polysufone-Polyethyleneimine-Silver Composite Membrane Towards Adsorption of Chromium (Cr), Lead (Pb), Silver (Ag) and Cadmium (Cd) in Synthetic Wastewater

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Abstract

Adsorption of heavy metal has been monopoly by activated carbon either in solid or powder form and the introduction of membrane consist of activated carbon could therefore increase the capacity of adsorption. The objective of this work was to investigate the effect of adding activated carbon in a Polysufone-Polyethyleneimine-Silver (Psf-PEI-Ag) composite membrane in terms of the heavy metal adsorption in synthetic wastewater. The membrane was developed by phase inversion at different composition of activated carbon (from 0 to 0.9%) while the other components were kept constant at 15% Psf, 0.5% Ag and 0.3% PEI. The SEM image showed a symmetrical membrane matrix with sponge-like structure. The composite membrane with 0.9wt% AC has the highest water flux and removal of heavy metal (chromium, lead, silver and cadmium). The percentage of heavy metal reduction by the composite membrane was 35% cadmium, 19% chromium, 16% silver and 2% lead. The result indicated that the introduction of activated carbon indeed plays an important role towards enhancing the adsorption of heavy metal. This work is expected to provide better understanding of activated carbon in PEI-Ag membrane and to inspire new approaches in designing membrane with higherheavy metal removal.

1. Introduction

In Malaysia, water resources can be obtained from rainfall, surface runoff, groundwater recharge, dams, aquifers and evapotranspiration. On top of that, streams and rivers also contribute 98 % of the total water used in Malaysia. Malaysia received 2,000 to 3,000 mm rainfall a year, recorded as the seventh highest in the world but most of it is lost to the surface run-off, evaporation and groundwater recharge that is often used for drinking water.

Problem arises when the heavy metals from the industry and domestic enter into the streams, lakes, rivers and groundwater. In the end, water is polluted with heavy metal residues and poses danger to the aquatic organism. Heavy metals are categorized as metallic elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. Unlike other organic contaminants, heavy metals are not biodegradable.

A major concern involving heavy metal such as chromium, cadmium, lead, zinc, and copper is the carcinogenic effect [1]. In addition, these heavy metals are usually found in the industrial wastewater and at large amount of discharge, a significant effect to the aquatic life would either be acute or chronic toxicity [2]. Therefore, it is vital to treat and process the effluent before discharged.

There are several proposed methods available for the treatment of heavy metals in wastewater including microbial system, electrochemical process, chemical precipitation, coagulation, adsorption, and membrane filtration [3]. These are divided into three categories mainly chemical, physical and biological treatment where the latter are widely known for its low economic implication and environmental friendly [4]. Despite the advantages, biological treatment would require large land area to fully utilize its performance which brings physical treatment into the main picture as an alternative.

Membrane is defined as an intervening phase separating two phases acting as a barrier to transport matter between phases. Membrane separates substances through its pore using momentum such as pressure difference, temperature difference, concentration and electric potential difference[5]. Membranes have gained an important place in chemical technology and have been utilized on broad range of applications. Among the application includes manufacturing, medical, water treatment and fuel cells [6]. For example, in wastewater treatment, membrane can successfully treat wastewater up to 98% rejection of heavy metals [7]. Membrane technology is one of the promising physical treatments that would solve the wastewater problem.

Besides the ability of membrane for wastewater treatment, activated carbon is also being widely used by various researchers in wastewater especially developed to cater the removal of heavy metal. Activated carbon is a carbonaceous material with a highly developed porous structure and large surface functional group which makes it capable of distributing toxic elements on its surface [8,9]. The adsorption process associated with activated carbon start when molecule of gases or liquids (adsorbent) attached to the surface of activated carbon (adsorbate). In theory, there are three steps associated with adsorption process starting with macro transport which refers to the movement of particle with size of more than 50 nm followed by micro transport of the particles with size less than 2 nm and finally sorption process. Sorption involved a physical attachment of organic material onto adsorbate surface. An example of industrial application utilizing adsorption process is water purification by using synthetic resin and activated charcoal as adsorbate [10].

Hence, activated carbon has been known widely as a good adsorbate and the idea of incorporating activated carbon into membrane matrix has not been fully explored. The properties of activated carbon as a highly amorphous solid with micro crystallite and graphitic lattice would increase the heavy metal adsorption performance [10]. Therefore, this study investigates the effect of activated carbon composition in polysulfone composite membrane towards heavy metal removal and flux performance.

2. Experimental details

2.1 *Materials*

Polysulfone (Psf, MW~ 35,000 gmol-1), Polyethyleneimine (PEI, MW~25,000 gmol-1) in liquid form, and N-Methyl-2-pyrrolidone (NMP, 99.5%) are obtained from Sigma-Aldrich (UK). Silver nitrate (AgNO3, MW~169.87 gmol-1) is obtained from Fisher Chemical (UK) and granular activated carbon (AC) is synthesized from palm kernel shell.

2.2 *Preparation of Composite Membrane*

Silver nitrate, polyethyleneimine and activated carbon were slowly added into a PSf/NMP solution and continued stirring until completely dissolved. This solution was further agitated for another 24 hours to reach homogeneous mixing. Then, the membrane solution was cast on a clean, dry, level glass plate at ambient atmosphere, 30 ˚C as follows: 5 ml of casting solution was poured onto a glass plate for gap setting of 100 µm and left for evaporation process. After 1 minute, membrane was immersed in deionized water for 1 hour at room temperature to allow membrane formation. Membrane was washed in deionized water to remove the remaining solvent and finally left to dry at room temperature for 1 day. This method was repeated for all five membranes (Table 1).

Table 1: Composite membrane composition

Type	**Psf (wt. %)**	**NMP (wt. %)**	**PEI (wt. %)**	**$AgNO_3$ (wt. %)**	**AC (wt. %)**
CM1	15.0	85.0	-	-	-
CM2	15.0	84.2	0.3	0.5	0.0
CM3	15.0	83.9	0.3	0.5	0.3
CM4	15.0	83.7	0.3	0.5	0.5
CM5	15.0	83.3	0.3	0.5	0.9

2.3 *Scanning Electron Microscopy*

Morphologies of the composite membranes with different weight of activated carbon were observed by a scanning electron microscopy (SEM, JEOL JSM-6390LA, USA). A piece of sample from the membrane was coated using a gold sputter under vacuum condition prior to SEM imaging at magnification of 20,000x . For the cross-section and surface analysis, the membrane was prepared in liquid nitrogen and placed vertically and horizontally, respectively, onto a SEM stub covered with carbon tape.

2.3 *Water flux*

Each flat sheet membrane was cut into circular form and immersed in deionized water for 5 minutes prior to a dead-end filtration test. The test was conducted by pouring 30 ml of water into a cell with membrane at the end as a filter under pressure of 2 bar for 10 minutes. The flow of filtered water is directly perpendicular to the membrane surface (Equation 1);

$$J_w = \frac{V}{A\Delta t} \tag{1}$$

where V is volume of permeated water (L), A is the effective area of membrane (m^2) and Δt is the time taken (hour) to filter.

2.3 *Adsorption Test*

Four different synthetic wastewater were prepared for adsorption test; chromium (Cr), lead (Pb), silver (Ag) and cadmium (Cd). The solutions containing Cr, Pb and Cd were prepared by dissolving 0.05 g of $K_2Cr_2O_7$, $Pb(NO_3)_2$, $Ag(NO_3)$ and $Cd(NO_3)_2.4H_2O$ correspondingly in a 500 ml deionized water. The initial concentration of metal in the synthetic wastewater solution was determined using an Atomic Absorption Spectrometer (AAS, Solar 939 Unicam, UK). Prior to experiment, all synthetic wastewater was stored in tight bottles to prevent changes of concentration through evaporation/condensation.

Heavy metal adsorption test was conducted with a dead-end filtration system where 50 ml of synthetic wastewater solution was poured into the cell. The composite membranes were cut into circles with a diameter of 44.5 mm. The test was conducted under pressure of 3 bar for a duration of 30 minutes. Final metal concentration of the permeated solution was determined by AAS. The removal efficiency is obtained from Equation 2:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

where C_0 and C_t are the initial and final concentrations of heavy metals present in the wastewater.

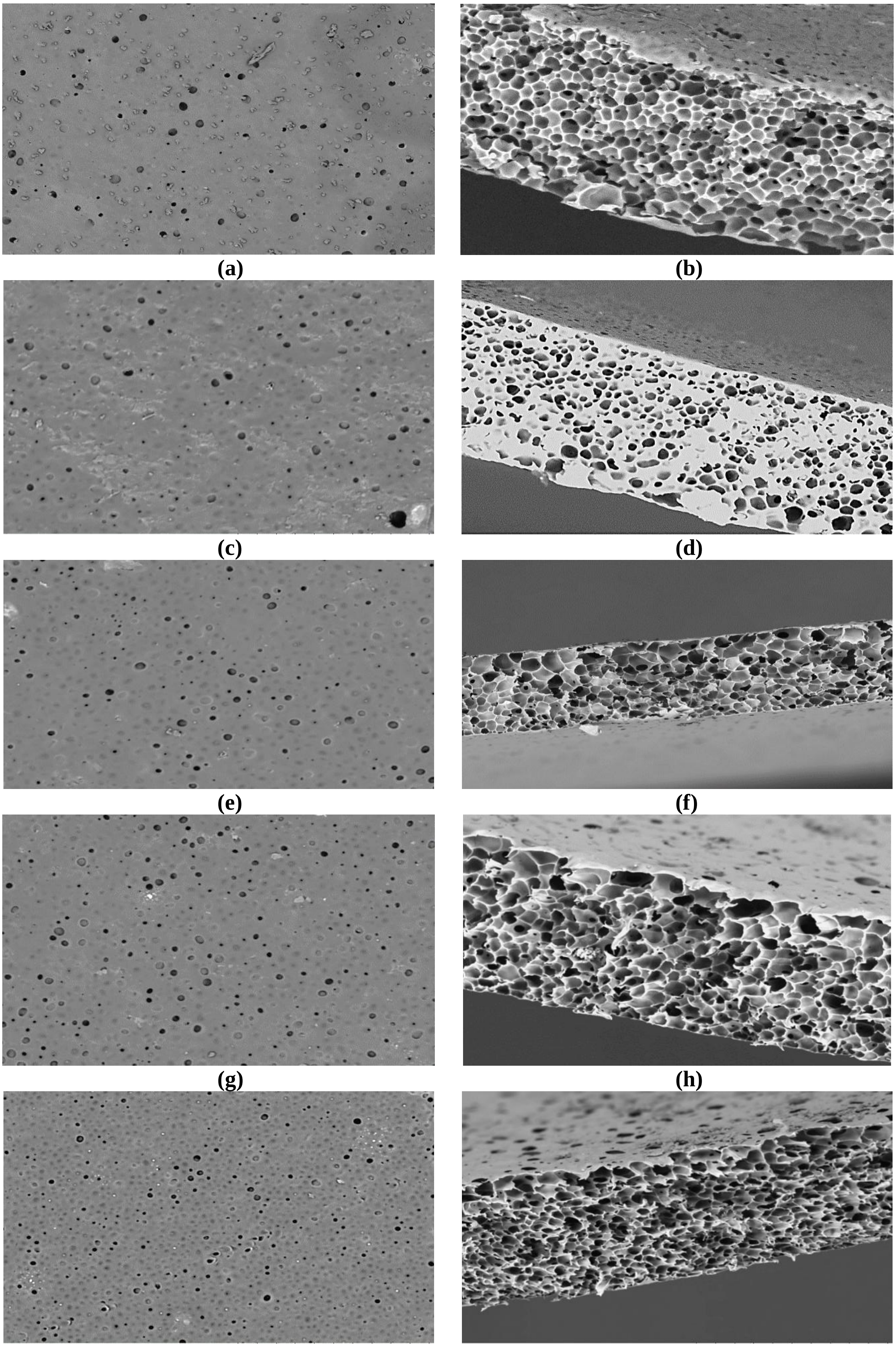
The silver leached out from the membranes was also investigated. Membranes were cut into a 1 cm × 1 cm pieces and subsequently immersed in a 10 ml of sodium chloride solution. After 1 to 2 days of being in contact with sodium chloride solution, the membranes were removed and the aqueous solutions were analyzed using AAS.

3. Results and Discussion

3.1 *Membrane Morphology*

Membrane structure has two forms: symmetric or asymmetric. Symmetrical membrane is a membrane with a uniform structure while asymmetrical membrane has a gradient structure[5]. Besides that, symmetrical membrane has cylindrical, sponge-like and dense-film structure. For asymmetrical structure, it can be further categorized into integral-asymmetric and thin-film composite[11]. Figure 1 shows the SEM images of the surface and cross-section of the membranes with different composition. CM1 is a control membrane with PSf/NMP only. CM2, CM3, CM4 and CM5 are composite membranes with 0%, 0.3%, 0.5% and 0.9% weight fraction of activated carbon, respectively.

The cross sectional area of the membranes was induced by the phase inversion showing a symmetrical structure with a lot of micro void appearance across the membrane matrix. According to Pinnau and Freeman (2000), cross-section of a typical polysulfone membrane prepared via phase inversion are usually symmetric in structure along with formation of micro void within the matrix. On top of that, increased AC content to 0.9 wt. % (CM5) showed a clear formation of sponge structure as shown in Figure 1 (i) and (j) which is aligned with a stipulation stating that the increase amount of activated carbon causes pores to broaden/enlarged, thus increasing the membrane structure porosity [12].



(a) **(b)**

(c) **(d)**

(e) **(f)**

(g) **(h)**

(i) **(j)**

Figure 1:SEM images of top surface and cross section of composite membrane CM1(a,b), CM2(c,d), CM3(e,f), CM4(g,h) and CM5(i,j)

3.2 *Water flux*

Water flux and rejection are the two most important parameters for membrane applications [13]. The water flux testing provided an indication of the membrane hydraulic performance. The results are shown in Table 2.

Table 2: Membrane hydraulic performance

Membrane	Activated carbon (wt%)	Water flux ($L/m^2.hr$)
CM1 (Control)	-	5.54
CM2	0	9.94
CM3	0.3	11.15
CM4	0.5	22.25
CM5	0.9	49.33

It is evident that the water flux increased as the AC was incorporated into the membranes. This result is attributed to the increase of membrane hydrophilicity and possibly by the increase in porosity [14]. Hydrophilicity refers to the affinity of the membrane material for water or ability of the membrane to become wetted with water [15].

CM5 has the highest water flux with a difference of 43.79 L/m^2.hr compared to the control which is a significant increase of 88% water flux performance. Based on Figure 1, the large difference of water flux was expected because CM1 has a dense structure with a distinct honeycomb pattern unlike CM5 that has a porous structure. Also, the addition of silver nitrate has contributed to the increase in water flux for CM2 from 5.54 L/m^2 .hr (CM1) to 9.94 L/m^2 .hr (CM2).

Andrade et al. (2015) studied the water flux performance of polysulfone membranes modified with silver nanoparticles prepared by phase inversion method. In the event of silver nitrate addition, a significant increase of water flux was observed with an increase composition of silver in the membrane.

In a different study by Hwang et al. (2013), water flux of composite membrane increased as the AC particle content increased. Authors proposed that the addition of AC particles may affect the pore size, pore distribution, and filtration flux. All these findings are in agreement with the results observed in this study.

3.3*Removal of heavy metal*

Figure 2 shows the trends of heavy metals rejection using different membranes. In general, the trends of rejection show a sudden drop from CM2 to CM3 except for chromium that was already dropped at CM2. Rejection of heavy metal were consistent for CM1 (between 97 to 98%) most likely caused by the small pore size and dense structure that increased the ability of CM1 to entrap or filter heavy metal. However the trade-off of having a high rejection was the low water flux at 5.54 L/m^2.hr.

In general, the addition of activated carbon had reduced the ability of the membrane to filter heavy metal. CM5 having 0.9wt% activated carbon which has the highest water flux can only remove 19% of chromium although the rejection value was the highest among the membranes with activated carbon. The removal of cadmium and silver also showed that CM5 was capable of rejecting the heavy metals at high water flux but the low lead removal showed that at high water flux almost all lead has penetrated CM5.

Chromium rejection showed an increase from approximately 13% (CM2) to 19% (CM5) although the gradient was not apparent but the increase of rejection might as well contribute by activated carbon inside the membrane matrix that absorb the heavy metal. In recent review article, activated carbon has been regarded as adsorbent with highest adsorption capacity for the removal of chromium through adsorption[16].

All heavy metal results showed approximately 20% rejection for CM3 while cadmium has more than the average rejection at 35%. The result might as well be explained by ionic radii of the metal ions. The decrease in ionic radii is as follows: Cr^{3+} (130 pm) > Ag^{+} (126 pm) > Pb^{2+} (120 pm) > Cd^{2+} (97 pm). The rejection of cadmium was the highest among other metals for CM3 because of the small ionic radii that allowed it to enter the activated carbon's pore. Activated carbon has surface area in the range between 1000 to 3000 m^2/g depending on the type of activation where the higher surface area always contributed by the small pores and dense quantity of pores [17–19]. After the addition of activated carbon, the rejection of cadmium, silver and chromium showed a consistent trend within 15 to 19 % for chromium and silver while cadmium showed steady rejection at approximately 35% for CM3 to CM5. The high rejection of chromium was in correlation with several study [16,20,21] which investigate the adsorption capacity of adsorbent on different concentration of chromium. Based on this study, chromium adsorption was controlled by intra-particle diffusion model as well as pseudo-second order equation. In theory, pseudo-second order model were in place due to chemisorption. Chemisorption being the rate-limiting step in pseudo-second order has initiate the exchange of electron between adsorbent and adsorbate [22,23]. In addition to chemisorption, there are several factor that affect coefficient of adsorption kinetic for instances concentration of heavy metal, acidity of the solution, and physicochemical properties of the adsorbent and adsorbate [24].

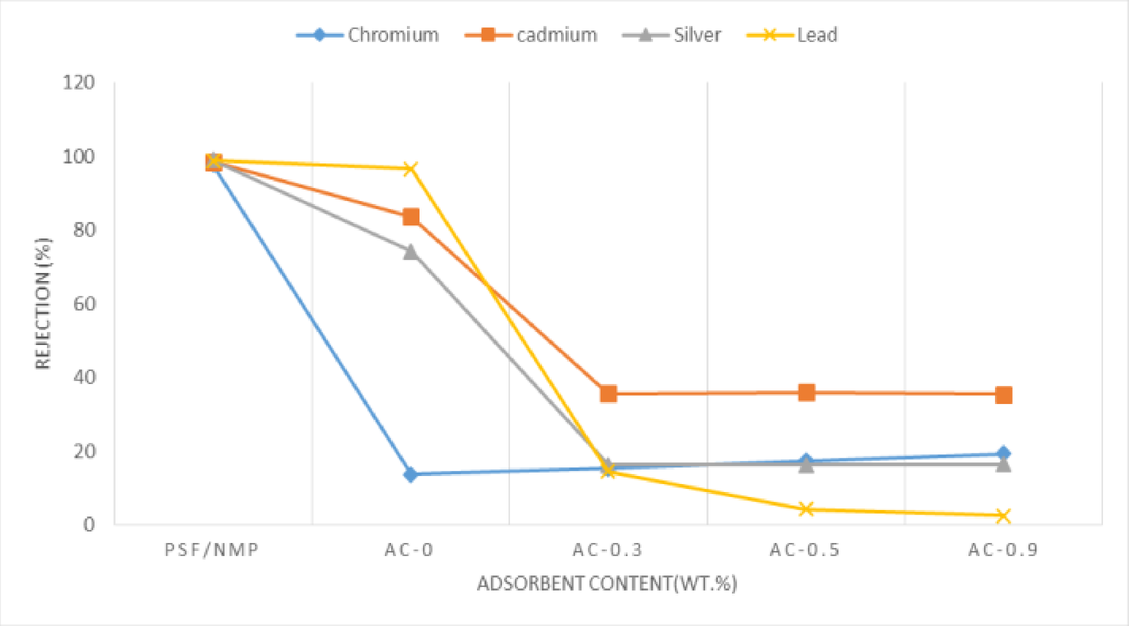


Figure 2: Heavy metal rejection for different membrane composition

On the other hand, the increase of activated carbon composition reduced the ability of membrane to remove lead where the reduced performance can be observed in Figure 3 from 14% (CM3) rejection and eventually dropped to 2% (CM5). Therefore, the addition of 0.3wt% activated carbon was the optimum composition for all type of heavy metal removal in this study where further increase of composition would either reduce or provide insignificant improvement to heavy metal rejection.

Conclusions

With the addition of activated carbon, the membrane morphology was modified. The dense structure of polysulfone membrane (CM1) was changed to a more porous structure with a lot of macrovoid formation by the addition of activated carbon especially 0.9 wt% (CM5). The improved porosity of CM3 to CM5 were proved by the increasing water flux. Water flux values for CM3, CM4 and CM5 were 55%, 77% and 88% higher than CM1 while the cadmium rejection by CM3, CM4, CM5 were 63%, 62% and 63% lower than that of CM1, respectively. This is because the composite membrane (CM) with the added activated carbon possessed higher porosity that increased the possibility of the heavy metal ions to pass through during filtration. However, the high flux has reduced the time for the heavy metal to be adsorbed onto activated carbon impregnated in the membrane matrix. This finding implicate the possibility of embedding activated carbon into composite membrane to serve as heavy metal adsorbent. From this point forward, an optimization study to fine-tune the membrane porosity against activated carbon content/composition is suggested to ensure the developed composite membrane (CM) can operate efficiently by means of filtration application with adsorption capability.

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